DOE F 241.3
(2-01) p.1 of 2

UNITED STATES DEPARTMENT OF ENERGY (DOE)
Announcement of Scientific and Technical Information (STI)
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OMB CONTROL NO. 1910-1400

PART I: STI PRODUCT DESCRIPTION
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B. Recipient/Contractor
Missouri University of Science and Technology, 215 ME Annex, 1870
Miner Circle, Rolla, MO 65409-1330

C. STI Product Title
Geological Sequestration of CO2 by Hydrous Carbonate Formation with Reclaimed Slag

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E. STI Product Issue Date/Date of Publication
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F. STI Product Type (*Select only one*)
☒ 1. TECHNICAL REPORT
☒ *Final* ☐ *Other (specify)*

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☐ 3. JOURNAL ARTICLE
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G. STI Product Reporting Period
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H. Sponsoring DOE Program Office
Office of Industrial Technologies (OIT)(EE20)

I. Subject Categories *(list primary one first)*
32 Energy Conservation, Consumption and Utilization
Keywords: CO2 Sequestration, Reclaimed Slag

J. Description/Abstract

The concept of this project is to develop a process that improves the kinetics of the hydrous carbonate formation reaction enabling steelmakers to directly remove CO_2 from their furnace exhaust gas. It is proposed to bring the furnace exhaust stream containing CO_2 in contact with reclaimed steelmaking slag in a reactor that has an environment near the unit activity of water resulting in the production of carbonates. The CO_2 emissions from the plant would be reduced by the amount sequestered in the formation of carbonates. The main raw materials for the process are furnace exhaust gases and specially prepared slag.

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L. Recipient/Contract Point of Contact *Contact for additional information (contact or organization name To be included in published citations and who would Receive any external questions about the content of the STI Product or the research contained herein)*
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UNITED STATES DEPARTMENT OF ENERGY (DOE)
Announcement of Scientific and Technical Information (STI)
(For Use By Financial Assistance Recipients and Non-M&O/M&I Contractors)

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☐ 1. THIS DELIVERABLE COMPLETES ALL REQUIRED DELIVERABLES FOR THIS AWARD
☐ 2. THIS DELIVERABLE FULFILLS A TECHNICAL INFORMATION REPORTING REQUIREMENT, BUT SHOULD NOT BE DISSEMINATED BEYOND DOE.

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REPORT DOCUMENTATION PAGE

Title and Subtitle:

AISI/DOE Technology Roadmap Program for the Steel Industry
TRP 9955: Geological Sequestration of CO2 by Hydrous Carbonate Formation
With Reclaimed Slag

Authors:

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Performing Organization

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Abstract

The objective of this project is to develop and demonstrate a process for sequestering CO_2 from steel making in either a BOF or an EAF by forming carbonates with the alkaline earth component of used slag for beneficial reuse in other applications.

Background: It is well known that hydrous carbonates can form readily at the surfaces of alkaline earth, rare earth and manganese oxide in the presence of water and ambient CO_2 activity such as in aqueous suspensions (Richards 1990, 1992).

The concept of this project is to develop a process that improves the kinetics of the hydrous carbonate formation reaction enabling steelmakers to directly remove CO_2 from their furnace exhaust gas. It is proposed to bring the furnace exhaust stream containing CO_2 in contact with reclaimed steelmaking slag in a reactor that has an environment near the unit activity of water resulting in the production of carbonates. The CO_2 emissions from the plant would be reduced by the amount sequestered in the formation of carbonates. The main raw materials for the process are furnace exhaust gases and specially prepared slag.

DOCUMENT AVAILABILITY

Acknowledgement: "This report is based upon work supported by the U.S. Department of Energy under Cooperative Agreement No. DE-FC36-97ID13554."

American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report

TRP # 9955

Award Number: DE-FC36-97ID13554

Project Period: 3/2005 - 12/2007

Recipient: Missouri University of Science and Technology (MST)
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Other Partners: ArcelorMittal - Dofasco, TerniumHylsa, Ipsco, Praxair, US Steel, Gallatin Steel, ArcelorMittal, Nucor, Timken

January 2008

CONTENT

1. Project Summary

The objective of this project is to develop and demonstrate a process for sequestering CO_2 from steel making in either a BOF or an EAF by forming carbonates with the alkaline earth component of used slag for beneficial reuse in other applications.

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A number of tasks were identified during the initial kick-off meeting and each was completed. Scientific and practical results of the work are presented in Attachments and included; Literature Review, 5 published articles, and 3 submitted for publication articles, as well as one Industrial Reactor Modeling Report.

2. Project Plan

Detailed Work Plan for CO_2 Sequestration Project is given in Table 1.

Number	Task/Subtask Description	Start Date	Completion Date	Inter-relationship
1.0	Kick-off Meeting		3/17/05	Before 2.0
2.0	Survey of Plant Application	3/17/05		
2.1	• -Written survey review by participants and AISI		4/21/05	Before 2.2
2.2	• - Survey sent out to plants	4/30/05	4/30/05	Before 2.3 starts
2.3	• - Plant visits	5/30/05	6/30/05	Before 2.4 completes
2.4	• - Survey summary	6/30/05	7/15/05	Before 4.0
3.0	Literature Survey – Written Summary	3/17/05	7/30/05	
4.0	Bench Evaluation of Kinetics	6/30/05	6/30/06	Must complete before task 5 ends
4.1	• - Procedure development	6/15/05	7/30/05	
4.2	• - Characterization of slags	6/15/05	12/31/05	
4.3	• - Development of kinetic models (in existing codes such as Fluent, Metsim)	6/15/05	6/30/06	
4.4	• - Experimental studies	7/30/05	6/30/06	
5.0	Model Evaluation of Production System	5/30/06	8/30/06	Before 6.0
6.0	Build Bench Pre-pilot Model of Selected System	8/30/06	10/30/06	Before 7.0
7.0	Test Runs on Bench Model of Selected System	10/30/06	1/30/07	Before 8.0
8.0	Final Report	1/30/06	2/30/07	
9.0	Oversight and coordination by industrial sponsors		2/30/06	

Table 1 - Project Plan

3. Progress Toward Achieving Specified Tasks

Task 1 - Kickoff meeting with potential industrial sponsors

A number of tasks were identified during the initial kick-off meeting for the program and are included in the following paragraphs. Descriptions of the Tasks and the results are given below. This meeting served to build the components of the industrial site survey and get input on any reshaping of Task 3, Literature Survey, based on plant situations in which the sequestration process could be applied.

Task 2 - Industrial site application survey

This provides a basis on practical knowledge on application parameters such as:

- Slag compositions and temperatures at which the slag could be delivered to the process
- The gas temperatures and compositions available to input to the process
- The logistics of delivering the input streams to the process
- Reactor site situation and plant engineering restrictions surrounding potential sites

Data collection included generation and distribution of a participant survey (Attachment A). The survey focused on slag handling practices and CO_2 sources. An initial survey was distributed on June 10, 2005, and re-distributed on June 29, 2005 in a more focused format. Additionally representatives from UMR visited Nucor, Gallatin, ArcelorMittal, USS, and Ipsco plants in the mid-west U.S. to gather first-hand data on slag handling and CO_2 sources, as well as samples of steel making slag. Slag samples were obtained from four of the plant and returned to UMR for analysis and testing. Further data collection focused on a literature search to obtain published work to support the test program.

Task 3 - Literature survey

The literature search has yielded 87 relevant publications and 17 relevant patents (U.S. and worldwide). The Literature Review (Attachment B) contained information about:
- Methodology of research
- Slag production, handling, and uses
- Slag Characterization (physical and chemical properties, mineralogy, thermodynamic of stabilization)
- CO_2 capture and geological sequestration
- Offgas emission in steelmaking
- Carbonate formation in steelmaking slag
- Intellectual capital for geological sequestration
- Bibliography

Task 4 - Bench evaluation of kinetics

This task included subtasks:
4.1 Procedure development. Two types of experimental procedure for kinetics studies were performed.

Gas-solid reactions. The first stage of equipment set-up was focused on the construction of a large scale thermogravimetric analysis (TGA) device. This includes a vertical tube furnace (2" diameter, 1000°C capability) over which a balance is mounted. The balance can hold samples of 410 g net weight (0.001 mg accuracy). A gas distribution system has been set-up to introduce dry and wet gases (Ar, N_2, CO_2, and air) at the bottom of the furnace flowing upward through the suspended samples. A basic data acquisition system has been set-up to collect time, temperature, and weight measurements.

Gas-solid-liquid reactions. A bench scale system was built to study slurry process kinetics with pH monitoring. Three synthetic slags were produced and used in addition to participant slags in bench testing of wet processes. The preliminary results of reaction carbonization in water solution were obtained:

- steel making slags have potential of CO_2 sequestration by mineral carbonization of calcium and magnesium phases
- the maximum possible degree of calcium carbonization ranged from zero to 60% and significantly depended upon slag composition, structure and history of formation (thermal history and formulation sequence)
- correlations between slag composition and the possible degree of carbonization were obtained.

4.2 Characterization of slags. The characterization of slag obtained from industry and 3 types of synthetic slags included:

a. Physical Properties of Aggregate
    i. Particle Size
    ii. Density/Porosity
    iii. Specific surface (BET method)
b. Chemical/Phase Make-up
    i. X-ray Powder Diffraction
    ii. Chemical Analysis
    iii. Light Microscopy
    iv. Scanning Electron Microscopy

Data was used for thermodynamic calculation, kinetics of selective reactions study, and metal liberation. In addition, samples from dicalcium silicate were made and characterized.

4.3.- 4.4. Experimental Study and Development of Kinetic Models. Kinetics of two types of CO_2 sequestration processes by steelmaking slag (slag-gas and slag-gas-water) was experimentally and theoretically studied.

TGA method was used for "dry" process study. It was shown, that gas humidification accelerated reaction kinetics. Modeled materials (lime, mechanical mixture CaO-SiO_2 and dicalcium silicate) were tested at different temperature with using unidirectional reaction pass.

Slurry process was studied using EAF and LMF slag of different particle size. Kinetics of two processes was identified. The first one included calcium leaching from slag and the second one included direct carbonization of slag particles. Slag-water slurries were reacted with CO_2 in laboratory flask tests showing that the degree of carbonization (formation of carbonate) is time and particle size dependent.

The modified shrinking core model was used for description of experimentally measured kinetics with taking into account changing density and diffusivity of product layer of carbonized slag particles. The model fit well to experimental data and was used for industrial process design.

The results were published in the following papers:

- "Sequestration of CO_2 from Steelmaking Offgas by Carbonate Formation with Slag." by C. Hank Rawlins, Von L. Richards, Kent D. Peaslee, and Simon N. Lekakh, Proceedings of AISTech 2006 (Attachment C1).
- "Steelmaking Slag as a Permanent Sequestration Sink for Carbon Dioxide" by C.H. Rawlins, Von L. Richards, K.D. Peaslee, and S.N. Lekakh, p25-28 of the October 2006 of Steel Times International. (Attachment C2).

Task 5 - Model evaluation of potential production systems

The proposed concept for an industrial system consisted of two reactors interconnected with a solution exchange loop which could be incorporated into existing industrial streams of slag and off gas. This system was modeled and experimentally verified. Fundamental kinetic data of carbonate sequestration by steel making slag in aqueous solution from previous tasks was adapted for a computational model. The aqueous phase contacts with the slag in Reactor 1 where it could leach calcium ions. When the aqueous phase contacts the offgas in Reactor 2 it will dissolve CO_2 and there will be a number of the possible scenarios for $CaCO_3$ precipitation. The carbon sequestration process was modeled using the METSIM software under different possible scenarios. Two of the more important scenarios are listed below:

- Scenario 1: Fresh water is supplied to leach the slag in Reactor 1; water enriched with calcium ions is pumped to Reactor 2, where calcium carbonate would be formed and precipitated; and then the water (containing some residual dissolved CO_2) would be discarded or recirculated after deep de-gassing;
- Scenario 2: The water to Reactor 1 would be recirculated from Reactor 2 without de-gassing and the possible reactions depend on the reaction kinetics as well as process parameters.

The block diagram of METSIM model consisted of two blocks, which represented Reactor 1 and Reactor 2 connected by streams. The model allowed the different scenarios to be studied. The model was verified by using experimental data for carbonization kinetics and Ca leaching reactions.

The results were published:
- Rawlins, C.H, Richards, V.L., Peaslee, K.D., and Lekakh, S.N., "Experimental Study of CO2 Sequestration by Steelmaking Slag," TMS2007 Materials Process Fundamentals, Edited by P. Anyalebechi, TMS, Mar. 2007, pp. 193-202. (Attachment C3)

- Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., "The Use of Steelmaking Slag for Mineralogical Sequestration of Carbon Dioxide-Aqueous Processing," AISTech 2007, Vol. II, May 2007. (Attachment C4)

Task 6 - Build bench pre-pilot model of selected system

For experimental verification of the different scenarios a lab scale apparatus consisting of two connected reactors was tested, with recirculation of the aqueous phase with and without partial degassing by argon bubbling. Reactor 1 contained up to 2 kg of slag mechanically stirred with 20 liters of aqueous solution. The aqueous liquor was pumped at varying rates to Reactor 2, which had a two-liter volume. A bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles and to allow intimate mixing between the gas and alkaline solution. A multi-channel pH meter was used to measure the pH level in both reactors. At the completion of each test, a sample of the slurry mixture from Reactor 1 was filtered, dried, and analyzed for carbonization.

Task 7 - Evaluation runs on bench scale system

The experiments were done by using a two stage slurry reactor where slag reacted with aqueous solution and a gas bubbling reactor where CO_2 gas reacted with aqueous solution. The system also included a pump which exchanged solutions between the two stages and a pH monitoring device. Two groups of parameters were studied. The first group included the main process parameters, in particular, the ratio between volume of slag and aqueous solution, rate of CO_2 bubbling as well as the rate of solution exchange. These parameters were studied using pure lime because this material has well known reaction kinetic parameters. The second group of parameters was slag composition and particle size. These experiments were done under constant values of first group parameters.

The obtained experimental data was compared to METSIM modeled results and was used for process parameter optimization. The industrial system applicable for 1,000,000 ton steel annual production was investigated. Data is presented in Attachment F "Industrial Reactor Modeling"

The results were also published in the article:
- Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., "Mineralogical Sequestration of Carbon Dioxide through Aqueous Processing of Steelmaking Slag," MS&T'07 Energy Materials and Technologies II, Sep. 2007, pp. 225-237. (Attachment C5)

Task 8 - Final report

The achieved result presented in the final report

Task 9 - Coordination for industrial oversight by sponsors – once per year

- The program, task plan, and results were annually reviewed by industrial sponsors:
    - 7th AISI/DOE Industry Briefing Session on September 21, 2005
    - 8th AISI / DOE TRP Industry Briefing Session on October 10-11, 2006
    - 9th AISI/DOE Industry Briefing Session on October 10, 2007

- The results were presented and discussed in conferences:
    - AISTech (2006)
    - TMS (2007)
    - AISTech (2007)
    - MS&T'07 (2007)

- The results were revealed in reports:
    - Industrial Survey
    - Literature review
    - Industrial Reactor Modeling Report

- The results were published/submitted for publication in articles:

Published:

1. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N., “Sequestration of CO2 from Steelmaking Offgas by Carbonate Formation with Slag,” AISTech 2006 Proceedings, Vol. II, May 2006, pp. 1133-1144.
2. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N., “Sequestration of CO2 from Steelmaking Offgas by Carbonate Formation with Slag,” AISTech 2006 Proceedings, Vol. II, May 2006, pp. 1133-1144.
3. Rawlins, C.H, Richards, V.L., Peaslee, K.D., and Lekakh, S.N., “Experimental Study of CO2 Sequestration by Steelmaking Slag,” TMS2007 Materials Process Fundamentals, Edited by P. Anyalebechi, TMS, Mar. 2007, pp. 193-202.
4. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., “The Use of Steelmaking Slag for Mineralogical Sequestration of Carbon Dioxide-Aqueous Processing,” AISTech 2007, Vol. II, May 2007.
5. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., “Mineralogical Sequestration of Carbon Dioxide through Aqueous Processing of Steelmaking Slag,” MS&T’07 Energy Materials and Technologies II, Sep. 2007, pp. 225-237.

Articles accepted for publication

1. Lekakh, S.N., Rawlins, C.H., Robertson, D.R., Richards, V.L., and Peaslee, K.D., “Aqueous Leaching and Carbonization of Steelmaking Slag for Geological Sequestration of Carbon Dioxide,” Metallurgical and Materials Transactions B, accepted for publication October 2007.
2. Richards, V.L., Rawlins, C.H., Lekakh, S.N., and Peaslee, K.D., “Sequestration of Carbon Dioxide by Steelmaking Slag: Process Phenomena and Reactor Study,” submitted for TMS 2008 CO_2 Reduction Metallurgy Symposium, Ed. by N. R. Neelameggham, Mar. 2008.

Articles submitted for publication

1. Lekakh, S.N., Robertson, D.G.C., Rawlins, C.H., Richards, V.L., and Peaslee, K.D., “Two-Stage Reactor for Geological Sequestration of Carbon Dioxide Using Steelmaking Slag,” Metallurgical and Materials Transactions B, submitted for publication October 2007.
2. *Peaslee, K.D., Richards, V.L., Rawlins, C.H., and Lekakh, S.N., "*Carbon Dioxide Sequestration with Steelmaking Slag: Process Feasibility and Reactor Design", AISTech 2008

4. Result of Work
(Summary of Reports and Publication)

4.1 Literature Review "CO_2 SEQUESTRATION BREAKTHROUGH PROGRAM PHASE I: GEOLOGICAL SEQUESTRATION OF CO2 BY HYDROUS CARBONATE FORMATION WITH RECLAIMED SLAG" by Rawlins, C.H.

The objective of this project is to develop and demonstrate a process for sequestering CO_2 generated from steel production (BOF/EAF) by forming carbonates with the alkaline earth components in slag, generating a higher value slag co-product. The net project result will be the design of a reactor to treat steelmaking exhaust gas rich in CO_2 with raw or minimally processed slag. To achieve this result, the core research focus is to improve the process kinetics of the hydrous carbonate formation reaction, enabling direct removal of CO_2 from steelmaking exhaust. The net plant CO_2 emissions will be reduced by the amount sequestered in the carbonate formation, and the resulting slag product increases in value due to immediate stabilization allowing direct use in a wider range of construction or other applications. In addition, the reaction will produce low-grade sensible heat that can be recuperated for in-plant services.

Project research will proceed in the stepwise manner detailed in AISI project contract TRP9955: "CO_2 Sequestration Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag." Key tasks include industrial site application survey and visit, literature search, slag characterization, bench evaluation of kinetic factors, and bench scale prototype reactor design. This document serves as the literature search review, and will cover published information pertaining to slag production and characterization, carbonate mineral sequestration, CO_2 capture in slag, and intellectual capital (research knowledge base and patents). The results of the literature review will be used to define the thermodynamic and kinetic test boundary parameters, compare thermodynamic, kinetic, and characterization results, and as idea feedstock for CO2/slag reactor design.

4.2 Published Articles

1. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N., "Steelmaking Slag as a Permanent Sequestration Sink for Carbon Dioxide," Steel Times International, Vol. 30, No. 7, October 2006, pp. 25-28.

This research has demonstrated that a new process to react steelmaking slag with the off-gas from steelmaking has the potential of capturing 6-11% of the CO_2 emissions from integrated mills and 35-45% from scrap-based steelmakers. In addition to the positive environmental impact of this new technology, the resulting slag product will have better properties, increasing its sustainable value through the rapid conversion of CaO and MgO to carbonates. This will open up new markets for slag products and eliminate the current storage time and space requirements.

2. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N., "Sequestration of CO2 from Steelmaking Offgas by Carbonate Formation with Slag," AISTech 2006 Proceedings, Vol. II, May 2006, pp. 1133-1144.

The alkaline earth-containing phases in steelmaking slag can form carbonates thus sequestering carbon dioxide from the surrounding atmosphere. Work has been undertaken to improve the carbonate formation kinetics, enabling steelmakers to directly remove CO_2 from furnace offgas with slag, which in turn reduces the slag stabilization time. A study of basic oxygen furnace (BOF) and electric arc furnace (EAF) slags is reported in conjunction with their carbonate formation thermodynamics and capacities, yielding an overall slag CO_2 capture potential. Preliminary results are presented from bench-top "wet" and "dry" slag carbonation tests on industrial slags using a slurry reactor and large-scale thermogravimetric analysis (TGA).

The results of bench-scale CO_2 sequestration tests by steelmaking slags is presented in this paper. In the "dry" process, the rate of reaction of solid lime or slag increases proportional to the reactor temperature. However, an upper boundary condition exists, defined by a thermodynamic phase stability diagram that must be identified for each phase in the slag. Tests results showed that the addition of water vapor (humidification) to the CO_2 gas significantly accelerated the carbonation reaction of pure lime. The mechanism of this catalytic effect is possibly defined by the formation of intermediate calcium hydrate gel on the solid particle surface. A "wet" process, which includes the interaction between three phases (water-solid slag-CO_2 gas), has a much higher carbonation reaction rate when compared to "dry" process. The percent of carbonation statistically correlated to the CaO contents of industrial slags. This data will be used to determine the design parameters for a lab-scale reactor for CO_2 sequestration by steelmaking slags.

3. Rawlins, C.H, Richards, V.L., Peaslee, K.D., and Lekakh, S.N., "Experimental Study of CO_2 Sequestration by Steelmaking Slag," TMS2007 Materials Process Fundamentals, Edited by P. Anyalebechi, TMS, Mar. 2007, pp. 193-202.

Steelmaking processes intensively use carbon-containing materials and generate a significant amount of carbon dioxide emissions. The U.S. steel industry produces ~1.75 tons CO_2 for every ton of steel shipped. At the same time, steelmaking processes use calcium and magnesium oxide containing minerals for slag formation, which are excellent CO_2 capture agents. The goal of this investigation was to experimentally study carbon dioxide sequestration by steelmaking slag with simultaneous acceleration of the slag stabilization processes in preparation for re-use as a construction material. Thermogravimetric methods and a slurry reactor were used to study reaction kinetics. The degree of slag carbonization was evaluated for industrial and synthetic slags in dry and wet and processes.

In the packed bed process, the rate of reaction of solid lime or slag increases proportional to the reactor temperature. However, an upper boundary condition exists, defined by a thermodynamic phase stability diagram that must be identified for each phase in the slag. Tests results showed that the addition of water vapor (humidification) to the CO_2 gas significantly accelerated the carbonation reaction of pure lime. The mechanism of this catalytic effect is possibly defined by the formation of intermediate calcium hydrate gel on the solid particle surface. A slurry process, which includes the interaction between three phases (water-solid slag-CO_2 gas), has a much higher carbonation reaction rate when compared to packed bed process.

4. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., “The Use of Steelmaking Slag for Mineralogical Sequestration of Carbon Dioxide-Aqueous Processing,” AISTech 2007, Vol. II, May 2007.

Carbon dioxide is generated directly from the furnaces used in iron and steel production, or indirectly from supply systems such as coal-burning power plants providing electric power to the plant. Steelmaking CO_2 emissions vary by geographic region and the production method. For example, integrated steel mills generate more CO_2 per ton of steel than mini-mills generate due to the use of coke and iron-making pre-processes. In 2000, U.S. integrated mills emitted 33.5 million tons of CO_2 in carbon equivalent (CE) units, of which 64% was generated through the production and use of coke. During the same year, U.S. mini-mills generated 13.7 million tons of CO_2 CE, where 80% was generated from the supply power plants. On average, in 2000 the U.S. steel industry produced 0.42 tons of CO_2 CE per ton of steel shipped. Table I compares the rates of CO_2 emissions in the U.S. with several European countries and Japan. Most countries are approaching the theoretical production limit of 0.40 tons of CO_2 CE per ton of steel shipped, indicating that emission reductions from technological changes in production methods will have less of an impact in the future.

The aim of this project is to develop a functional sequestration technology using steelmaking slag to permanently capture carbon dioxide produced and currently emitted by steelmaking operations. A parallel benefit of slag-based CO_2 sequestration is chemical stabilization of slag minerals, thus rendering the slag immune to end-use swelling or leaching and eliminating the need for stockpile aging prior to commercial use. The potential of steelmaking slag to react with CO_2 to form permanent carbonate minerals is derived from slag’s high concentration of alkaline earth metal oxides. The two most important oxides are CaO (lime) and MgO (magnesia), which range from 30-50% and 10-12% of the slag mass, respectively. Both lime and magnesia readily form hydroxides or carbonate compounds under atmospheric conditions, with the carbonate compounds forming the most thermodynamically stable phase.

Previous work has shown that the slag produced during steelmaking has the potential of sequestering 5.0-10% of the BF-BOF CO_2 emissions and 28-34% of EAF carbon dioxide emissions. In addition, the estimated 15-20 kg of LMF slag produced per ton of steel has the potential of capturing an additional 1.0-1.3% of BOF and 7.8-10.4% of EAF CO_2 emissions. Thus, the total sequestration potential for steelmaking slag is 6-11% of the CO_2 emitted from integrated mills and 35-45% emitted from scrap-based steelmakers. A furnace offgas CO_2 capture and sequestration system will most likely be installed after the baghouse to prevent contamination of the slag with baghouse dust. At this point offgas conditions at this point have been estimated to be 90-150°C, with a peak CO_2 concentration of 10-11 vol.% and an average of 4-5 vol.%.

Two different designs are being tested for a slag-offgas reactor. The first design is a dry process using a plug flow or rotary reactor as detailed previously. The second design is the focus of the current study and includes a wet process whereby slag is mixed with water to form a slurry through which offgas is bubbled. A two-stage system allows for aqueous dissolution of the alkaline oxides in the first stage, followed by a reaction of the resultant aqueous liquor with CO_2 in a separate vessel or location. Compared with a dry system, wet processing has a much higher CO_2 reaction rate, thus allowing for a smaller reactor vessel. In addition, catalytic agents such as carbonic anhydrase may be added to form an aqueous biomimetic process that has been shown to provide more tan two orders of magnitude increase in mineral carbonate formation in experiments for wet industrial CO_2 scrubbers.

Sequestration of carbon dioxide by steelmaking slag was studied for a three-phase system of industrial slag, water, and CO_2 gas. Slag-water slurries were reacted with CO_2 in laboratory flask tests showing that the degree of carbonization (formation of carbonate) is time- and particle size-dependent. The rate of carbonization fits well to the shrinking core model, showing that diffusion through the carbonate product layer is the rate limiting step with the reaction rate proportional to $(\text{time})^{0.5}$. Testing in a two-stage wet reactor showed that degree of carbonization is proportional to slag alkaline content and particle surface area (i.e., reduction in particle size). The testing of a bench-scale reactor prototype revealed the main process control parameters and will be used for industrial process scale-up.

5. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., "Mineralogical Sequestration of Carbon Dioxide through Aqueous Processing of Steelmaking Slag," MS&T'07 Energy Materials and Technologies II, Sep. 2007, pp. 225-237.
Sequestration of carbon dioxide by steelmaking slag was studied for a three-phase system of industrial slag, water, and CO_2 gas. Slag-water slurries were reacted with CO2 in laboratory batch tests showing that the degree of carbonization (formation of carbonate) is time and particle size-dependent. The rate of carbonization fits well to the shrinking core model, showing that diffusion through the carbonate product layer is the rate limiting step with the reaction rate proportional to the square root of time.

The calcium carbonate product layer consists of overlapping plates that increase in density with time. Testing in a two-stage wet reactor showed that degree of carbonization is dependent upon the slag alkaline content and particle surface area (i.e., reduction in particle size). Testing in a two-stage wet reactor showed that degree of carbonization is proportional to slag alkaline content and particle surface area (i.e., reduction in particle size).The testing of a bench-scale reactor prototype allows the study of leaching and carbonation independently for scale-up to an industrial process model.

4.3 Articles Accepted for Publication

1. Lekakh, S.N., Rawlins, C.H., Robertson, D.R., Richards, V.L., and Peaslee, K.D., "Aqueous Leaching and Carbonization of Steelmaking Slag for Geological Sequestration of Carbon Dioxide," Metallurgical and Materials Transactions B, accepted for publication October 2007.

Sequestration of carbon dioxide by steelmaking slag was studied in an atmospheric three-phase system containing industrial slag particles, water, and CO_2 gas. Batch-type reactors were used measure the rate of aqueous alkaline leaching and slag particle carbonization independently. Four sizes of slag particles were tested for Ca leaching rate in deionized water at a constant 7.5 pH in an argon atmosphere, and for carbonate conversion with CO_2 bubbled through an aqueous suspension. Conversion data (fraction of Ca leached or converted to carbonate) were evaluated to determine the rate-limiting step based on the shrinking core model. For Ca-leaching, the chemical reaction is the controlling mechanism during the initial period of time, which then switches to diffusion through the developed porous layer as the rate limiting step. Carbonate conversion proceeded much slower than leaching conversion and was found to be limited by diffusion through the product calcium carbonate layer. The calculated value of diffusivity was found to be 5×10^{-9} cm^2/sec, which decreased by an order of magnitude with increasing carbonization conversion as a result of changing density of the product layer. The experimental data fit the shrinking core model well after correction for the particle specific surface area.

The reaction rates of aqueous Ca-leaching and direct carbonization were quantified independently to yield the reaction parameters and rate-limiting mechanisms as listed below.

- The specific surface area of slag particles is increased by leaching or carbonization. Selective dissolution of the Ca-bearing phase results in increased surface porosity, while carbonization produces overlapping plates of $CaCO_3$ product layer that created a highly irregular surface.
- Both Ca-leaching and carbonization were analyzed using the shrinking core model. The experimental data for both processes fit this model well, after correction for effective particle size, which is based on the measured specific surface area.
- Analysis of Ca-leaching shows a linear proportionality to particle size during the initial stage (to 0.30 conversion) supporting a chemical reaction controlled model (CaO dissolution). The later stage of leaching is controlled by diffusion of the Ca^{2+} ions through the resulting porous surface layer, as shown by square-root proportionality of reaction time to particle size.
- Increasing the leachate temperature from 20 to 60°C (at atmospheric pressure) enhanced the Ca-leaching rate during the initial period time, however the terminal amount of Ca leached after 24 hours did not differ greatly (47% vs. 50%).
- Carbonate conversion is heavily dependent on particle size and the reaction is limited by product layer diffusion. The calculated value of diffusivity decreased by an order of magnitude from the initial value of $5x10^{-9}$ cm^2/sec, as a result of changing density of product layer.
- Carbonate conversion proceeded slower than leaching conversion however both processes are inhibited by the calcium carbonate product layer.

2. Richards,V.L., Rawlins, C.H., Lekakh, S.N., and Peaslee, K.D., "Sequestration of Carbon Dioxide by Steelmaking Slag: Process Phenomena and Reactor Study," submitted for TMS 2008 CO_2 Reduction Metallurgy Symposium, Ed. by N. R. Neelameggham, Mar. 2008.

Steel-making processes generate carbon dioxide air emissions and a slag co-product. The aim of this project was to develop a functional sequestration system using steelmaking slag to permanently capture carbon dioxide emitted in steelmaking offgas. A possible parallel benefit of this process would be rapid chemical stabilization of the slag minerals with reducing swelling or leaching.

This paper summarizes the original results of the project, including mineralogical and structural features of carbon sequestration with steel making slag, mathematical modeling of reaction phenomena using a modified shrinking core model, METSIM modeling of several possible industrial applications, a thermo-gravimetrical study of the reaction between slags and different gases, and design and testing for a lab scale apparatus consisted of two reactors.

- Carbon dioxide sequestration with steelmaking slag was studied in a two-phase (gas-solid) and three-phase (gas-liquid-solid) systems containing industrial CO_2 gas, water, and slag, at ambient temperature and pressure. The reaction rates of aqueous Ca-leaching and direct carbonization were quantified independently to yield the reaction parameters and rate-limiting mechanisms as listed below.

- The reaction kinetics was described with modified shrinking core model. The model reflected the morphology of product layer formation. The obtained experimental data and kinetic parameters were used for modeling an industrial prototype reactor.

- The concept of apparatus consisted of two interconnected reactors was proposed for industrial application of carbon dioxide sequestration by steel making slag. The design allows incorporating the sequestration system into existing streams of slag and off-gasses containing CO_2. METSIM process simulator was used to model of carbon dioxide sequestration using steelmaking slag.

- A comparison of several scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles and accelerating the reaction kinetics. In addition, this scenario could produce pure calcium carbonate. However, the water requirement in a continuous system is much higher than a recirculated system.

- To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor without a degassing step. The dissolved carbonic acid results in the formation of a calcium carbonate layer on the slag particles, which inhibits leaching of calcium ions. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly assisted the amount of calcium that could be carbonized. The developed METSIM model can be used for the design of an optimized CO_2 sequestration reactor system based on different slag fractions and compositions.

4.4 Articles Submitted for Publication

1. Lekakh, S.N., Robertson, D.G.C., Rawlins, C.H., Richards, V.L., and Peaslee, K.D., "Two-Stage Reactor for Geological Sequestration of Carbon Dioxide Using Steelmaking **Slag," Metallurgical and Materials Transactions B, submitted for publication October 2007.**

Hydrous carbonate sequestration of CO_2 using steelmaking slag was studied using a METSIM process model for analysis of experimental data and determination of reactor design parameters. A two-stage system with water/slag contact in Reactor 1 and alkaline-leachate/CO_2 contact in Reactor 2 was analyzed for several possible operating scenarios including batch versus continuous processing and fresh water versus recirculation. The METSIM leaching and carbonization models were verified with results obtained from previous slag sequestration experiments. Fresh water additions to Reactor 1 allowed the highest leaching efficiency and resulted in excellent carbonization in Reactor 2, however, a continuous system has a high water demand. Recirculation of the spent leachate minimizes the fresh water addition but produces a calcium carbonate product layer on the slag particles in Reactor 1 which inhibits the leaching process. Increasing the slag surface area, slag/solution ratio, or reactor residence time partially overcomes product layer blinding. The optimal residence time was defined for different process parameters and slag particle size. It was shown that the METSIM model is a useful tool for designing and optimizing CO_2 sequestration reactor systems based on different slag fractions and compositions.

2. Peaslee, K.D., Richards, V.L., Rawlins, C.H., and Lekakh, S.N., "**Carbon Dioxide Sequestration with Steelmaking Slag: Process Feasibility and Reactor Design", AISTech 2008**

The goal of this research is to develop a functional sequestration process using steelmaking slag to permanently capture carbon dioxide emitted from steelmaking offgas. A parallel benefit of this process is rapid chemical stabilization of the slag minerals with reducing swelling or leaching potential. This paper summarizes the results of the project, including mineralogical features of carbonate formation in steelmaking slag, study of the reaction mechanisms, thermogravimetrical analysis of the reaction between solid-state slag and different gases, design and testing of a two-stage lab scale reactor system, METSIM modeling of several possible reactor designs, and exploration of the economic feasibility of the process based on process operating costs, metals recovery and credit for CO_2 sequestration.

4.5 Report "Carbon Dioxide Sequestration by Steel Making Slag - Industrial Process Modeling"

METSIM process simulation software was used to model several reactor scenarios for hydrous carbonate sequestration of CO_2 using steelmaking slag. A two-stage reactor design was modeled. The process allowed introducing water and slag into the first reactor and carbon dioxide into the second reactor, with the possibility of recirculation of solution. A comparison of the scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles, which could reduce the leaching efficiency. However, the water requirement in a continuous system is much higher than a recirculated system.

To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor. The drawback to this system is that the residual absorbed CO_2 in the recirculated water results in the direct formation of a calcium carbonate later on the slag particles, which inhibits leaching of calcium ions. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly assisted the amount of calcium that could be carbonized.

It was shown that the METSIM model is a useful tool for designing and optimizing CO_2 sequestration reactor systems based on different slag fractions and compositions. The industrial carbon dioxide sequestration process by steel making slag was modeled for one industrial case (1 million tons of EAF steel production) with different process parameters and slag conditions.

5. Attachments

A. Survey (13 pages)

B. Literature Review (103 pages)

C. Published Articles (88 pages)

C1. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N“ Steelmaking Slag as a Permanent Sequestration Sink for Carbon Dioxide,” Steel Times International, Vol. 30, No. 7, October 2006, pp. 25-28.

C2. Rawlins, C.H., Richards, V.L., Peaslee, K.D., and Lekakh, S.N., “Sequestration of CO_2 from Steelmaking Offgas by Carbonate Formation with Slag,” AISTech 2006 Proceedings, Vol. II, May 2006, pp. 1133-1144.

C3. Rawlins, C.H, Richards, V.L., Peaslee, K.D., and Lekakh, S.N., “Experimental Study of CO_2 Sequestration by Steelmaking Slag,” TMS2007 Materials Process Fundamentals, Edited by P. Anyalebechi, TMS, Mar. 2007, pp. 193-202.

C4. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., “The Use of Steelmaking Slag for Mineralogical Sequestration of Carbon Dioxide-Aqueous Processing,” AISTech 2007, Vol. II, May 2007.

C5. Rawlins, C.H., Lekakh, S.N., Richards, V.L., and Peaslee, K.D., “Mineralogical Sequestration of Carbon Dioxide through Aqueous Processing of Steelmaking Slag,” MS&T’07 Energy Materials and Technologies II, Sep. 2007, pp. 225-237.

D. Articles Accepted for Publication (28 pages)

D1. Lekakh, S.N., Rawlins, C.H., Robertson, D.R., Richards, V.L., and Peaslee, K.D., “Aqueous Leaching and Carbonization of Steelmaking Slag for Geological Sequestration of Carbon Dioxide,” Metallurgical and Materials Transactions B, accepted for publication October 2007.

D2. Richards,V.L., Rawlins, C.H., Lekakh, S.N., and Peaslee, K.D., “Sequestration of Carbon Dioxide by Steelmaking Slag: Process Phenomena and Reactor Study,” submitted for TMS 2008 CO_2 Reduction Metallurgy Symposium, Ed. by N. R. Neelameggham, Mar. 2008.

E. Articles Submitted for Publication (36 pages)

E1. Lekakh, S.N., Robertson, D.G.C., Rawlins, C.H., Richards, V.L., and Peaslee, K.D., “Two-Stage Reactor for Geological Sequestration of Carbon Dioxide Using Steelmaking Slag,” Metallurgical and Materials Transactions B, submitted for publication October 2007.

*E2. Peaslee, K.D., Richards, V.L., Rawlins, C.H., and Lekakh, S.N., "*Carbon Dioxide Sequestration with Steelmaking Slag: Process Feasibility and Reactor Design", AISTech 2008

F. Industrial Reactor Modeling Report (18 pages)

American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report - Attachment A

Industry Survey Report

January 2008

CO_2 SEQUESTRATION BREAKTHROUGH PROGRAM PHASE I: GEOLOGICAL SEQUESTRATION OF CO_2 BY HYDROUS CARBONATE FORMATION WITH RECLAIMED SLAG

AISI PROJECT TRP9955

INDUSTRIAL APPLICATION SURVEY RESULTS

by

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March 2006

1. INTRODUCTION

1.1 PURPOSE OF SURVEY

Task 2.0 of this project comprises of a written survey of applicable plant processes by the project participants. The purpose of the survey is to provide a basis of practical knowledge on application parameters such as:

- Composition and temperature at which the slag could be delivered to the process
- Gas temperature and composition available as input to the process
- The logistics of delivering the input streams to the process
- Reactor site situation and plant engineering restrictions surrounding potential sites
- Ensure that any process developed has applicability in a plant situation

A written survey was generated at UMR and sent to the industrial oversight committee for review before implementation, to insure that the correct topics are adequately covered. All survey data was returned to UMR for analysis.

1.2 SURVEY FORM

A copy of the completed survey form is included with this report for reference. The file is entitled “AISI_IndustrialSlagSurvey.doc”.

1.3 DESIGNATION OF SURVEY PARTICIPANTS

All data supplied by the industrial participants is kept anonymous in this report by use of a reference code. Table 1 details the reference code and the corresponding information supplied by the participant.

Reference Code for Project Participants

Company	Plant Location	Completed Survey	Slag Sample Type and Age	Other Information Supplied
A	1	Yes	α-EAF, <24 hrs β-EAF, 1 week γ-LMF, 1 week	
B	1	No	α-BOF, 2-3 days	Slag production rate data supplied by 3rd party
C	1	No	α-BOF, 1 week	
D	1	Yes	α-EAF, 1-2 days β-EAF, at pour	One month slag chemistry, Process flow diagram
E	1	Yes	α-EAF, 2-3 days	
E	2	No	α-EAF, 2-3 days	
E	3	No	---	CO_2 emissions data
F	1	Yes	---	

2. PLANT VISITS

2.1 PURPOSE OF PLANT VISITS

During the first week of June 2005, representatives from UMR visited six steelmaking plants located throughout the Midwestern U.S. The purpose of these visits was to gather data in conjunction with the written industrial survey, and introduce the individual participant sites to the project. Slag samples were obtained at most of the sites, along with data from the slag and offgas handling facilities. The plant visit reports highlight details at each installation that are important for the design of a slag handling system.

2.2 PLANT VISIT REPORTS

2.2.1 Plant A1 (EAF)

- Vendor takes possession of the slag after dumping into the slag pot ladle. The slag is dumped into pits, spray quenched, ran through a magnetic separator, and screened. The non-magnetic fraction is crushed and screened again. The final non-magnetic products are <1/8”, 1/8”x3/8”, and 3/8”x5/8”.
- The fine non-magnetic product is sold for local asphalt use. The other non-magnetic products are mainly sold to a neighboring state for construction. That states law requires the slag to be aged at least 90 days after crushing before use.
- LMF slag is processed separately from EAF slag.
- The baghouse is operated at negative pressure (-20 IWC). The discharge gas is 180-200°F. No spray is introduced into the exhaust gas, but a gas-gas exchanger is used for cooling. Total discharge flow rate is 980,000 ACFM.
- Total carbon put into the melt (injection and charge) is ~30 lbs/ton.
- Obtained a sample of fresh (<24 hours old), unprocessed EAF slag, along with samples of processed EAF (non-mag, 0-1”, <1 week old) and LMF slag.

2.2.2 Plant B1 (BOF)

- Exhaust fans are operated on the clean side of air cleaning. Air is introduced to the dirty side of air cleaning to combust the CO. A scrubbing system is used to remove particulates (to a sludge pond), and the exhaust gas is discharged from the stack. Monitored components of the exhaust gas are O_2, CO, and CO_2. BOF exhaust is 10:1 ratio of CO:CO_2.
- The slag products are 0x3/8”, 3/8”x3”, and >3”. A sample of the 0”x3/8” (with addition of 1” particles) was obtained.
- Slag discharge is a concern as the Mn content is monitored by EPA toxicity release limits. BOF and LMF slag are combined, hot metal desulfurization and BF slag are combined, and EAF kept separately. Processing time for the slag is 3-4 days.

2.2.3 Plant C1 (BOF)

- Slag is managed by the vendor upon dumping into pots. The slag in the pots is dumped into pits, spray cooled, magnetically separated, and sized. Approximate turnaround time for the slag is 24-48 hours.

- The slag is separated into A, B, and C metallic and A, B, and C non-metallic. The A&B metallic goes back into steel production, while the C metallic goes into BF feed or sinter. The A&B non-metallic goes into BF feed or sinter, while the C non-metallic has no marketable use yet. C non-metallic is 0”x3/8”.
- Exhaust gas is combusted, spray quenched (cooling and 1st stage particulate removal), scrubbed (2nd stage particulate removal), cooled, and then exits through the fans and stack.
- The gas temperature after the fans is 150°F, at a 360,000 ACFM flow rate
- Each heat is 230 tons and produces about 45,000 pounds of slag per heat.
- A sample of grade C non-magnetic slag was obtained.

2.2.4 Plant D1 (EAF)

- The steel is primarily Al killed, however some Si is used in the LMF. Burnt lime is used as the fluxing agent. Each heat is 180 short tons (liquid), with 15 tons slag produced at the EAF and 3 tons slag at the LMF.
- The primary furnace requires dumping the pot every heat, but the LMF requires dumping the pot every three heats. A vendor takes the slag once it is dumped into the pots. The molten slag is removed from the melt shop and transported to a separate enclosed building where it is dumped onto a pad. The slag pad is enclosed to control dust.
- The slag is spray quenched, magnetically separated, and the non-mag fraction screened at three sizes: <1”, 1”x3”, and >3”. Approximately 90% of the slag product goes to asphalt production, with the remainder for straight aggregate use. Total processing time of the slag is less than one week. Demand for the slag is 100%. A slag bucket sample was taken from the <1” pile, and a sample of “raw” slag was taken from the pour (cooled and placed into a can). No falling slag is present. Data on slag composition for May 2005 was provided.
- Gas from the melt shop is collected both directly from the furnace (one per furnace) and overhead canopy (two ports). A combustion gap is located at the direct furnace takeoff, and the gas is naturally cooled. At the furnace CO, O_2, and SO_2 are monitored, while at the baghouse CO and NO_x are monitored. No CO_2 monitoring is done. The gas is removed with dirty fans, processed at the baghouse, and baghouse discharged with no stack. Gas parameters are ~40-50 PPM CO average (at baghouse), with 1.3 million ACFM flow. Gas temperature at the baghouse ranges from 125-180°F in winter and 150-250°F in summer. A process flow diagram of the exhaust gas system was provided, along with a PLC strip chart printout.

2.2.5 Plant E1 (EAF)

- Slag is collected by vendor in pots, dumped into pits, and spray quenched. After cooling, it is loaded into the processing system for magnetic separation, screening, and crushing (oversize). Four slag products are made: <1”, 1”x2”, 2”x8”, and >8”. The LMF and EAF slag are treated together, and used bricks are processed separately. Total processing time for slag is one day to one week. The slag exhibits “falling” characteristic. The slag was sold in 1996 at $5/ton, while current price is $2/ton. Road aggregate (stone) is sold at $10-14/ton.
- The baghouse runs at 350°F.
- Most CO_2 discharged from the furnace comes from carbon combustion in their foamy slag practice, than from steel refining.

- A continuous emission monitoring system is employed that monitors CO, SO_2, TOC, and NO_x.

2.2.6 Plant E2 (EAF)

- The slag is collected in pots by a vendor, dumped in pits, and spray quenched. Once the slag is cooled, front-end loaders put it in the processing system magnetic separation and screening. The oversized is crushed, magnetically separated, and screened again. The three slag products are <1", 1"x3", and >3". The >3" is stored and crushed to <1" or 1"x3", depending upon the customer need. LMF slag is processed separately from EAF slag. The slag product is mainly sold for local (<200 mile radius) construction use. Total processing time for the slag is about 1 week.
- The baghouse processes ~2 MMSCFD of exhaust gas from the facility (all of the off-gas is mixed at one point in the operation before being split into three streams for the three baghouses). There is no common stack (each baghouse vents though the top). The gas is spray cooled and the baghouse operates at 200-250°F with polyester bags. A continuous emission monitoring system measures SO_2, O_2, CO, and NO_x content. Average values for the day were 2.32, 20.29, 36.05, and 6.65 PPM respectively. Gas pressure at the monitoring system was 29.6 IWC.

3. SURVEY RESULTS

3.1 SURVEY RESPONDERS

Four plants (A1, D1, E1, and F1) completed and returned the written survey. In addition plants B1, D1, and E3 provided data that is applicable to the survey questions and are included in the analysis as charts. All the data collected is compared in the applicable survey section.

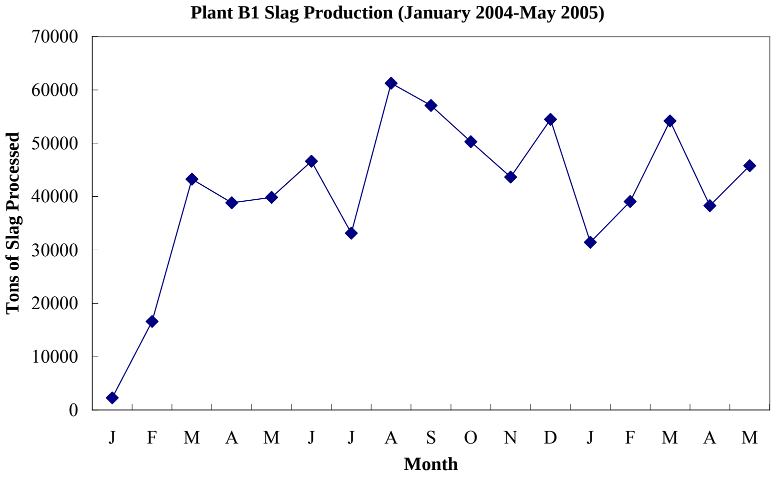
3.2 PRIMARY STEEL PRODUCTION

3.2.1 Furnace Type and Capacity

Plant	#	Type	Tons Per Heat (Liquid)	Tons Per Year (Liquid)	Furnace Lining
A1	1	EAF Twin Shell	158	1,200,000	Mag-Carbon
D1	2	EAF	180	1,600,000	Mag-Carbon
E1	2	EAF	122	2,210,000	Magnesia
F1	1	KOBM	360	3,007,000	Mag-Carbon
	1	EAF	193	1,509,000	Mag-Carbon

3.2.2 Primary Slag Production

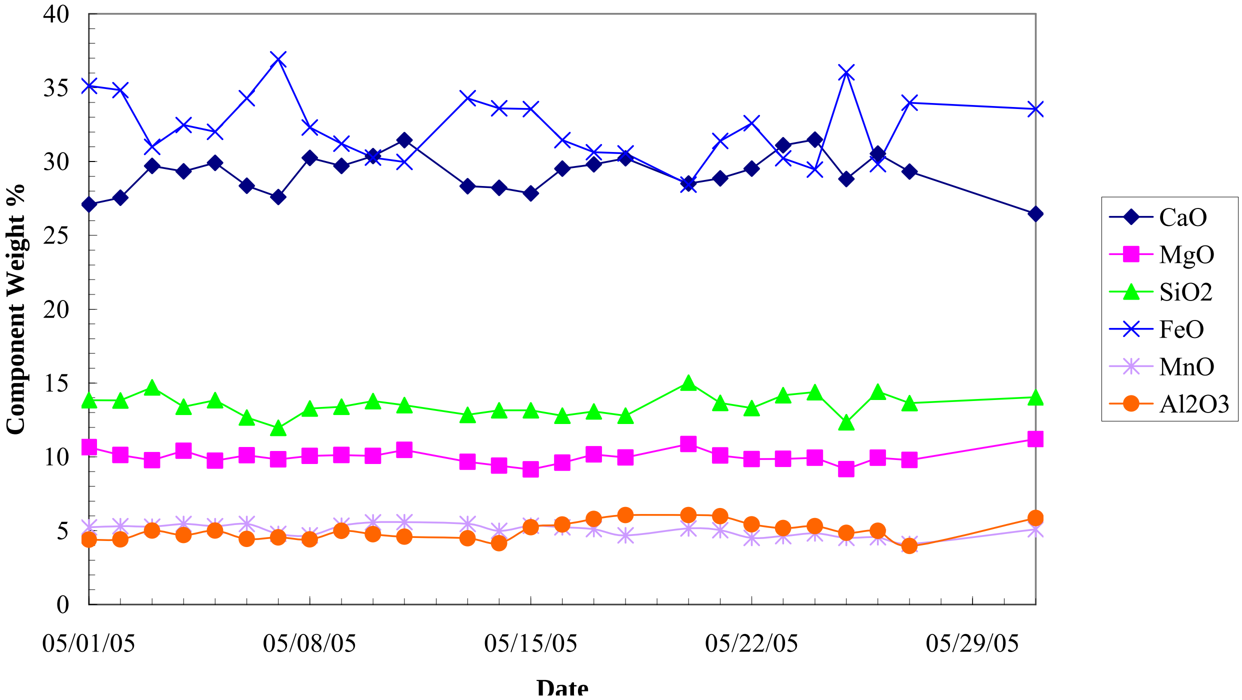
Plant	Process	Tons Per Heat	% Carryover	Tons Per Year	Temp. (°F)
A1	EAF	17	3%	117,931	2850
D1	EAF	15	50%	135,225	3000
E1	EAF	9-9.5	-	-	2980
F1	KOBM	27.5	5%	240,000	2935
	EAF	13.2	6%	106,800	3000



3.2.3 Primary Slag Composition (Weight %)

Plant	Process	CaO	MgO	SiO$_2$	MnO	FeO	P$_2$O$_5$	S	Al$_2$O$_3$	TiO2
A1	EAF	25	8	10	5	38	0.3	0.11	5	
D1	EAF	29.1	9.9	13.4	5.1	32.6	0.7	0.08	5.0	
E1	EAF	32.5	12	16.5	6.6	21.5	0.42	0.32	6.6	0.42
F1	KOBM	45	11	18	5.5	16	0.5	0.07	2.8	1.3
	EAF	36.5	10	12.5	6.5	27	0.35	0.15	6	1

Plant D1 EAF Slag Composition
(Daily Analysis for May 2005)



3.3 SECONDARY STEEL PRODUCTION

3.3.1 Furnace Type and Capacity

Plant	#	Type	Capacity Per Heat	Capacity Per Year	Lining
A1	1	LMF	158	1,200,000	Mag-Carbon
D1	1	LMF	180	1,600,000	Mag-Carbon
E1	2	LMF	120	2,280,000	Magnesia
F1	1	LMF1 & VD1	360	3,007,000	Mag-Carbon
		LMF2	193	1,509,000	Mag-Carbon

3.3.2 Secondary Slag Production

Plant	Process	Tons Per Heat	Tons Per Year	Temp. (°F)
A1	LMF	3.35	25,443	2840
D1	LMF	3	27,045	2800
	Tundish R11	15 lbs.	67.6	2750
	Tundish R17	60 lbs.	270.5	2750
E1	LMF	0.98	18,700	2800
F1	LMF1	5.2	47,632	2880
	LMF2	4.2	36,619	2880

3.3.3 Secondary Slag Composition

Plant	Process	CaO	MgO	SiO_2	MnO	FeO	P_2O_5	S	Al_2O_3	TiO_2
A1	LMF	35	7	1	<1	1	<0.15	1	15	
	Tundish	50	11	6	<1	4	<0.15	1.5	30	
D1	LMF	51.0	10.1	5.4	0.19	0.65	0.02	0.99	29.4	
	Tundish R11	43.2	28.5	17.0	<0.5	<0.5			0.1	
	Tundish R17	36.5	14.2	10.8	<0.5	<0.5			24.6	
F1	LMF1	50.2	6.6	5.1	1.2	2.6	0.01	0.18	31.5	0.6
	LMF2	49.9	8.4	3.8	0.06	0.8	0.002	1.002	33.3	0.6

3.4 SLAG PROCESSING

3.4.1 Slag Cooling, Handling, and Storage

Plant	Slag Vendor	Dump Location	Removal Frequency	Cooling Method	Primary/Secondary Mixed or Separate	Storage
A1	MultiServe	Pot to ground	1 per heat	Water Spray	Separate	Outside Stockpile
D1	MultiServe	Pot to Pad	1 per heat	Air/Spray	Separate	Outside Stockpile
E1	MultiServe	Pot to ground	1 per heat	Spray	Mixed	Outside Stockpile
F1	MultiServe	Pot to ground	42 pots per day (total)	Air/Spray	-	Outside Stockpile

3.4.2 Processing and End Use

Plant	Processing				End Use for Slag (Non-Mag)		
	Ageing Time	Sizing & Sep.	Metallic Recovery	Other	Blast Furnace	Aggregate	Construction
A1	6 months	Yes	Yes			Yes	Yes
D1	-	Yes	Yes			Yes	
E1	Varies	Yes	Yes			Yes	Yes
F1	2 months	Yes	Yes			Yes	Yes

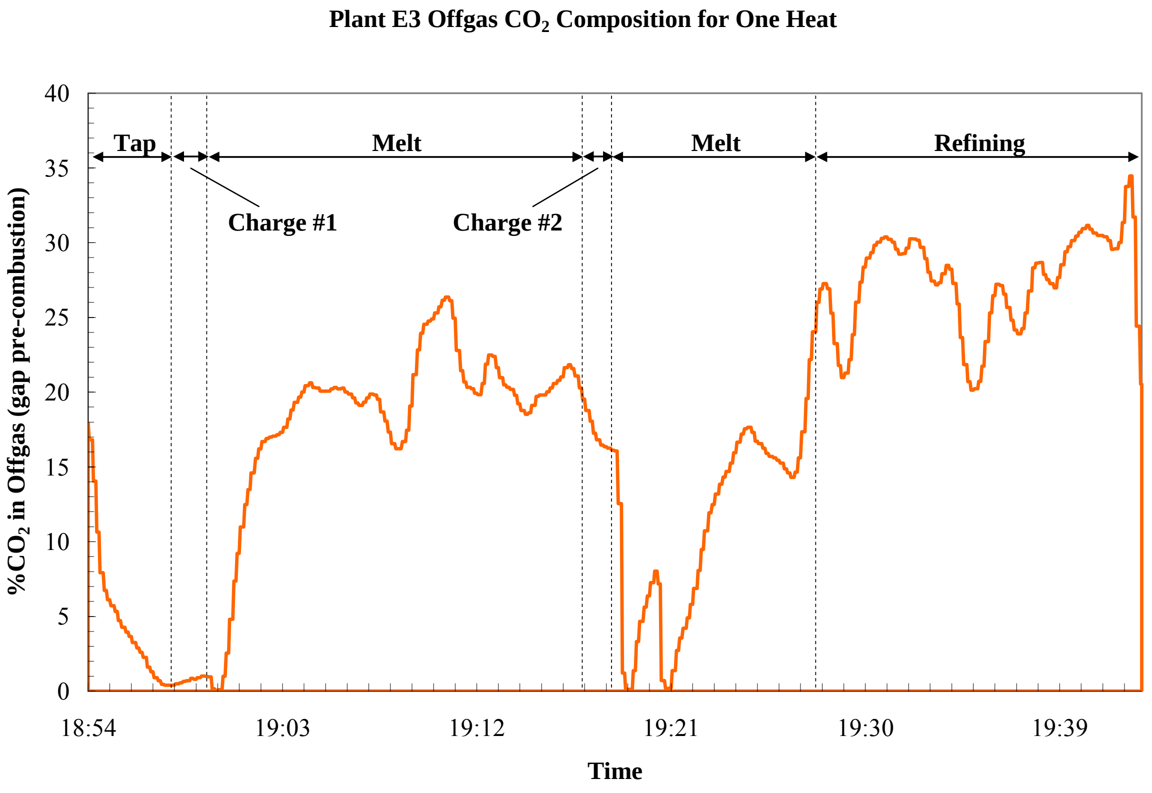
3.5 OFFGAS PROCESSING

3.5.1 OFFGAS PROCESS PARAMETERS

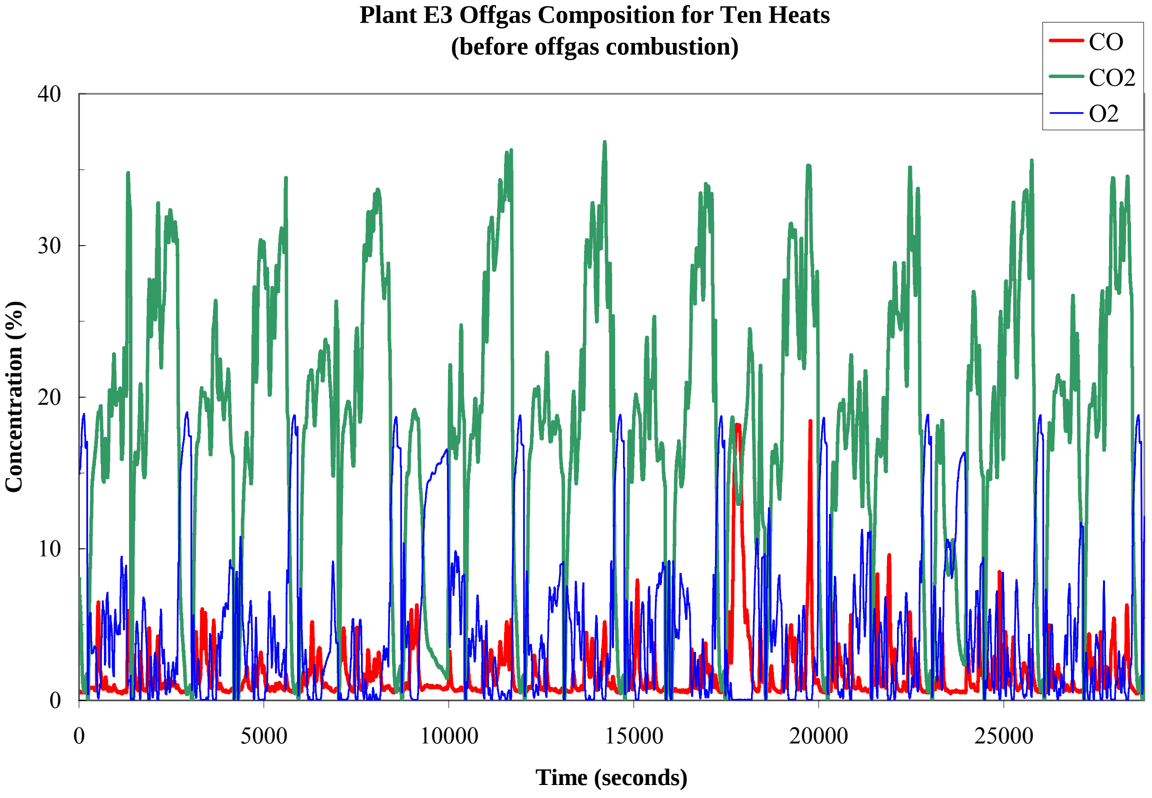
Plant	Location	Volume Flow (ACFM)	Pressure (IWC)	Temp. (°F)
A1	EAF (3/10/05)	721385	-0.5	190
	EAF (4/28/05)	626646	-0.5	157
	EAF (10/14/02)	582887	-0.5	187
	EAF (7/15/04)	784175	-0.5	188
	Reheat (1/9/02)	128050	-0.25	708
F1	KOBM Scrubber	120,000		140
	KOBM Stack	110,000		100
	EAF Booster	350,000	-9	570
	EAF Stack	1,200,000	-1	150

3.5.2 OFFGAS COMPOSITION

Plant	Location	CO_2 %	CO PPM	O_2 %	SO_2 PPM	N_2 %	Monitoring Method
A1	EAF	0.5	48-75	20.5	5-18	79	Periodic test
	Reheat	2.5	0	17.5	-	-	Periodic test
F1	KOBM Scrubber	17	46%	7		30	Periodic test
	KOBM Stack	18	47%	4		31	
	EAF Booster	10	0	19		71	
	EAF Stack	2	0	21		77	



Plant E3 Offgas CO_2 Composition for One Heat



Plant E3 Offgas Composition for Ten Heats (before offgas combustion)

4. SLAG TESTING AND ANALYSIS

4.1 PHYSICAL CHARACTERIZATION

All slag samples were put through a series of physical characterization tests to determine the relevant aggregate properties. The analysis methods are listed below.

Sample Size: Gross weight of sample received from each site.

Moisture: Evaporable moisture content determined by ASTM C566-97.

Bulk Density: Bulk density determined by ASTM C29/C29M-97 (jigging procedure) on the as-received sample (wet) and after drying.

True Density: True density determined by Micrometrics 1305 Multivolume Pycnometer.

% Magnetics: Representative sample ground to <106 μm then separated with three pound magnet.

Particle Size Analysis: Sample particle size analysis performed in accordance with ASTM D448-03a/D692-00 for coarse fraction (≥9.5 mm) and ASTM D1073-01 fine fraction (<9.5 mm).

Sample	Sample Size (kg)	Moisture (Wt. %)	Bulk Density Wet (kg/m^3)	Bulk Density Dry (kg/m^3)	True Density (g/cm^3)	Magnetic (Wt. %)
A1α	16.4	0.00%	2014	2014	4.052	6.21%
A1β	19.0	1.14%	1941	1918	3.881	1.76%
A1γ	14.4	2.59%	1778	1732	2.900	1.23%
B1α	26.4	2.52%	2019	1968	3.614	4.92%
C1α	25.5	4.25%	2138	2047	3.548	3.26%
D1α	25.6	1.56%	2180	2146	3.697	1.29%
D1β	1.6	0.00%	-	-	3.877	-
E1α	23.7	1.44%	1795	1769	3.760	4.02%
E2α	22.1	0.41%	1650	1643	3.822	8.13%

Sieve Size (μm)	Particle Size Distribution - % Passing							
	A1α	A1β	A1γ	B1α	C1α	D1α	E1α	E2α
50800	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%	100.00%
25400	94.54%	100.00%	80.15%	100.00%	100.00%	100.00%	100.00%	100.00%
18796	81.46%	87.38%	77.24%	75.89%	100.00%	93.82%	65.08%	56.95%
12700	60.96%	59.04%	66.97%	59.05%	100.00%	78.44%	27.51%	10.09%
9525	47.68%	39.12%	59.55%	46.94%	95.77%	64.15%	17.69%	3.00%
4750	16.26%	19.75%	45.47%	28.09%	70.82%	35.99%	10.62%	1.37%
2360	3.30%	10.36%	35.93%	17.02%	42.12%	18.29%	7.28%	1.20%
1168	0.86%	6.12%	28.91%	10.56%	24.72%	9.32%	5.29%	1.07%
600	0.41%	3.97%	22.50%	6.92%	14.84%	4.91%	3.93%	0.94%
297	0.26%	2.53%	15.94%	4.61%	9.04%	2.82%	2.95%	0.75%
150	0.16%	1.55%	9.66%	2.85%	4.97%	1.66%	2.16%	0.45%
75	0.08%	0.94%	4.71%	1.60%	2.19%	0.91%	1.46%	0.20%
<75	-0.04%	0.02%	-0.04%	0.03%	0.01%	0.04%	0.02%	0.00%

4.2 CHEMICAL CHARACTERIZATION

Chemical characterization of the slag was performed to determine both composition and phase analysis. Compositional analysis was performed by Mittal at their research center using XRF. The composition values were normalized to bring the total to 100%. Phase analysis was performed at UMR using XRD, and identification of the key phases is listed.

	Composition (Weight %)								
	A1α	A1β	A1γ	B1α	C1α	D1α	D1β	E1α	E2α
CaO	27.34	31.22	47.02	40.90	40.53	33.02	34.49	31.91	35.86
SiO_2	14.84	13.86	6.07	12.89	10.42	12.43	15.08	17.32	9.93
FeO	30.05	24.96	5.02	21.72	21.65	27.93	25.76	20.20	27.98
MgO	10.55	11.61	10.03	11.98	13.81	10.98	11.76	12.85	10.13
Al_2O_3	7.02	8.61	26.55	5.22	6.65	8.74	5.56	6.79	9.22
MnO	6.51	6.07	1.04	4.67	4.50	3.98	4.85	7.07	4.29
TiO_2	0.39	0.42	0.41	0.68	0.47	0.50	0.55	0.49	0.49
ZrO_2	<0.01	0.03	0.20	0.08	0.28	<0.01	<0.01	0.16	0.02
Cr_2O_3	2.48	1.98	0.25	0.31	0.42	0.87	0.78	1.62	0.95
K_2O	0.05	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na_2O	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
S	0.16	0.27	1.35	0.12	0.11	0.21	0.08	0.22	0.30
P	0.16	0.16	0.02	0.42	0.45	0.25	0.32	0.18	0.28
C	0.11	0.26	0.38	0.67	0.40	0.22	<0.1	0.32	<0.1
Sr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01
F	0.33	0.54	1.66	0.33	0.33	0.87	0.75	0.86	0.55

Phase		Phase Present							
Name	Formula	A1α	A1β	A1γ	B1α	C1α	D1α	E1α	E2α
Lime	CaO				x	x			
Periclase	MgO			x					
Coesite	SiO_2			x					
Wustite	FeO	x	x				x	x	x
Alumina	Al_2O_3	x	x						
C_2S	Ca_2SiO_4	x	x		x		x		x
Larnite	Ca_2SiO_4	x	x	x	x	x	x		
C_3S	Ca_3SiO_5		x		x	x			
Hatrurite	Ca_3SiO_5								x
Akermanite	$Ca_2MgSi_2O_7$	x							
C_5MS_3	$Ca_5MgSi_3O_{12}$		x			x	x	x	
$C_{12}A_7$	$Ca_{12}Al_{14}O_{33}$			x	x	x	x		
Clinoenstatite	$MgSiO_3$				x	x			
Magnesiowustite	$MgFeO_2$				x	x	x		
Hercynite	$FeAl_2O_4$					x		x	
Fayalite	Fe_2SiO_4					x			

American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report - Attachment B

Literature Review

January 2008

CO_2 SEQUESTRATION BREAKTHROUGH PROGRAM PHASE I: GEOLOGICAL SEQUESTRATION OF CO_2 BY HYDROUS CARBONATE FORMATION WITH RECLAIMED SLAG

AISI PROJECT TRP9955

LITERATURE REVIEW

by

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January 2006

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1. INTRODUCTION

1.1. PROJECT PURPOSE

The objective of this project is to develop and demonstrate a process for sequestering CO_2 generated from steel production (BOF/EAF) by forming carbonates with the alkaline earth components in slag, generating a higher value slag co-product. The net project result will be the design of a reactor to treat steelmaking exhaust gas rich in CO_2 with raw or minimally processed slag. To achieve this result, the core research focus is to improve the process kinetics of the hydrous carbonate formation reaction, enabling direct removal of CO_2 from steelmaking exhaust. The net plant CO_2 emissions will be reduced by the amount sequestered in the carbonate formation, and the resulting slag product increases in value due to immediate stabilization allowing direct use in a wider range of construction or other applications. In addition, the reaction will produce low-grade sensible heat that can be recuperated for in-plant services.

1.2. METHODOLOGY FOR RESEARCH

Project research will proceed in the stepwise manner detailed in AISI project contract TRP9955: "CO_2 Sequestration Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag." Key tasks include industrial site application survey and visit, literature search, slag characterization, bench evaluation of kinetic factors, and bench scale prototype reactor design. This document serves as the literature search review, and will cover published information pertaining to slag production and characterization, carbonate mineral sequestration, CO_2 capture in slag, and intellectual capital (research knowledge base and patents). The results of the literature review will be used to define the thermodynamic and kinetic test boundary parameters, compare thermodynamic, kinetic, and characterization results, and as idea feedstock for CO_2/slag reactor design.

2. SLAG PRODUCTION, HANDLING, AND USES

2.1. SLAG PRODUCTION

Slag is a co-product from iron and steelmaking. The American Society for Testing and Materials (ASTM) defines steelmaking slag in their publication D5106-03, as "the nonmetallic product, consisting essentially of calcium silicates and ferrites combined with fused and mineralogically combined oxides of iron, aluminum, manganese, calcium, and magnesium, that is developed simultaneously with steel in basic oxygen, electric arc, or open hearth furnaces".[1]

2.1.1. Slag Sources. Slag is produced during each discrete state of iron and steel making, and the corresponding slag produced has its own chemical and physical character. For example, the slag from blast furnace ironmaking is high in silica and lime, while low in iron oxide content. However, slag from steelmaking has a higher lime and iron oxide content. Slag produced during iron or steel refining operations (i.e. hot metal desulphurization and dephosphorization or steelmaking ladle metallurgy) has high phosphorus, sulfur, and impurity contents removed from the melt. Generally each type of slag is differentiated for treatment and end use due to its chemical and physical nature. This project will focus on steelmaking slag, specifically slag produced from BOF and EAF applications. While open-hearth slag piles are being actively processed, this type of steelmaking is not producing significant amounts of new slag to include in this study. From this point forward the term slag will refer to steel slag produced from BOF and EAF operations only.

2.1.2. Tonnage & Value. Slag production rate can be quoted on a per heat or per year basis. The National Slag Association estimates that per metric ton of steel produced, BOF operations generate 75-150 kilograms of slag (150-300 lbs/st), while EAF operations generate less at 65-80 kilograms (130-160 lbs/st).[10] This corresponds to the net 10-15% of crude steel output that van Oss[3] uses in his estimates, and 100-200 kg/t (200-400 lbs/st) per Ionescu et al[29]. In comparison, van Oss[3] estimates the production of blast furnace slag at 25-120% of the hot metal produced per ton, depending on the overall ore grade.

Annual slag production tonnage and value is tracked by the U.S. Geological Service in their minerals commodity and yearbook reports.[2] Table 1.1 shows the amount of steel slag sold in the U.S. (non-metallic fraction), along with the average selling price, for the years 1993-2003 inclusive. Production tonnage in the U.S. has grown about 3.2%/year during this ten year period, with the value ($/t) growing about 5.5% during that time. Most of this growth occurred from 2000-2003, during which the tonnage and value grew 69.2% and 75.0% respectively. This greatly outpaced the rate of construction sand and gravel, which grew at 3.6% in tonnage and 11.1% in value during the 2000-2003 time period.[5] Estimated values for 2004 are 8 million tons (8.8 million short tons) steel slag production, at a value of $40 million.[4] Actual per ton price ranges from $0.50 for steel slag where natural aggregates are abundant, to $11.00 where construction demand is high with little or no local natural aggregate. In 2002 the U.S. Geological Service began tracking U.S. output compared to world output. U.S. output ranks at approximately 10% of the world production, and is directly correlated to steel production.

Table 2.1. U.S. Steel Slag Production, 1993-2003[2]

Year	**Slag Sold (Mt)**	**Value ($, million)**	**Avg. Sell Price ($/t)**	**US total output (Mt)**	**World total output (Mt)**
1993	6.67	22.9	3.43		
1994	7.80	26.9	3.45		
1995	7.16	22.6	3.16		
1996	6.64	21.5	3.24		
1997	7.04	24.9	3.54		
1998	6.20	22.9	3.69		
1999	6.20	23.0	3.71		
2000	5.20	20.0	3.85		
2001	6.50	25.0	3.85		
2002	7.90	29.0	3.67	9-14	90-135
2003	8.80	35.0	3.98	9-14	96-145

2.2. SLAG HANDLING

Slag handling is not heavily documented, mostly because it is not a process requiring a high degree of technology. After cooling to ambient temperature, slag is processed similar to bulk aggregate (sizing, separation, and transport). Other than storage requirements to achieve stabilization, limited literature exists detailing the physical handling of slag from the furnace to end-use. Steel producers have not documented the process in detail, as the most common business approach is to subcontract slag handling and processing to a specialist handling company.

2.2.1. Physical Handling. Physical handling of slag is carried out similar to gravel aggregate. One slag processor (MultiServ) lists the handling steps on their website.[6] In their business model the contractor takes possession of the slag as it is tapped from the furnace (under furnace removal) into transport pots. The contractor transports the slag to a pour pit or pad where it is dumped and allowed to cool naturally or by spray quenching. The cooled slag is dug out of the pit with a front loader and brought to the processing station.

2.2.2. Slag Processing. Slag processing typically consists of crushing, screening, and magnetic separation.[6,9] Magnetic separation may be followed by screening. The oversized material may be crushed and sent back through the process again. Magnetic recovered material is sold back to the steel mill for furnace feed. Van Oss[3] estimates that up to 50% of the slag volume is recovered as magnetic (entrained metal) for return to the furnace. The non-magnetic material is graded by size, and stockpiled for sale.

2.2.3. Slag Stabilization. The end use destination will dictate storage time in the stockpile. This is because slag must go through an ageing period to reach stabilization. During ageing, compounds in the slag (initially free lime) will react with water and carbon dioxide from the air to form hydroxides and carbonates. Formation of these compounds results in a volume change or “swelling” of the slag, and converts these compounds to a more stable form. Stabilization in a stockpile prevents end use in-situ swelling or leaching. Details on the swelling mechanism are discussed in subsequent sections.

Slag swelling is a concern when the slag is used as construction aggregate. Crawford and Burns document the case of an office building on the Canadian side of the international bridge at Sault Ste. Marie, Michigan that experienced wall buckling and floor heave due to swelling of steel slag foundation fill.[23] This was open hearth slag that generated 9% vertical lift on the building floor slab upon in-situ swelling. To prevent in-situ swelling, many state governments now require steelmaking slag to be aged before use. For example, the Missouri Department of Transportation requires slag used in asphaltic concrete to be aged for at least three months after crushing and screening[7], while the Pennsylvania Department of Transportation requires slag to be tested for expansion after six months stockpile curing.[16]

An additional problem that may occur with the use of raw slag is leaching of alkaline materials into the surface water. While testing on slag shows the leachate reporting to the surface water is non-hazardous[18], it may be perceived as a problem by the public. For example, slag used in the Cleveland airport runway produced a “milky white, sulfuric runoff”.[8] While analysis showed that free lime leaching into the surface water precipitated calcium carbonate (milky white), which is stable and non-hazardous, the perception led to a project delay and negative publicity for the use of slag in construction.

2.3. USES

The National Slag Association (NSA) employs promotional and research efforts to identify and develop innovative applications for steel slag’s unique chemical and/or physical properties. The key uses the NSA have identified are as a source of iron and flux materials into blast furnace operations, high quality mineral aggregate, Portland cement, unconfined construction applications, soil conditioning, and environmental pH neutralization of abandoned mines and contaminated sites.[10,11] In 2003, the U.S. Geological survey listed the breakdown of use as shown in Figure 2.1, which supports these same categories.[3] High quality mineral aggregate (asphaltic concrete, road bases, and surfaces) account for more than 63% of the steel slag sold. The next largest use is unconfined construction (fill), which accounts for approximately 12-13%, followed by clinker feed at 5.4%. The “other” category accounts for railroad ballast, roofing, mineral wool, and soil conditioning. Unspecified use is not detailed but probably accounts for recycling into iron making and environmental neutralization.

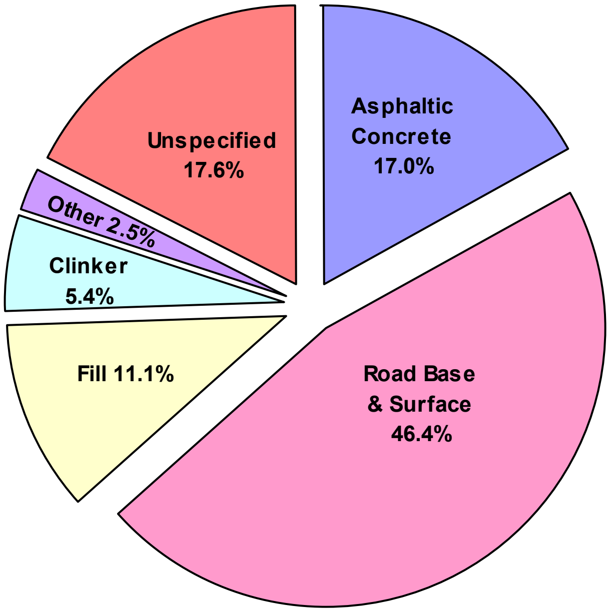

Figure 2.1 Sales of Steel Slag in the United States in 2003, by use[3]

2.3.1. Recycling Into Blast Furnace. Steelmaking slag finds use in recycling into the blast furnace, both for recovery of iron content and for fluxing properties.[9,11] The amount that can be recycled is limited by the chemical composition, specifically phosphorus and sulfur content.[170] As the lime and magnesia are in calcined form, a reduction in energy consumption may be realized compared to conventional flux charge.[9]

2.3.2. High Quality Mineral Aggregate. The physical characteristics of steel slag provide road surfaces with high stability, rutting resistance, skid resistance, and long life.[12] Steel slag qualifies as a premier aggregate for Hot Mix Asphalt (HMA), “Superpave”, and Stone Matrix Asphalt (SMA) applications. Steel slag used in asphaltic concrete is less susceptible to swelling, as the slag particles are coated with a water resistant barrier (asphalt). Steel slag in asphaltic concrete mixes results in 1.5 to 3 times greater stability, 20-80% higher resilient modulus (@ 29°C), and lower resilient Poisson’s ratio.[13] The acceptance of steel slag for these applications has led to the generation of ASTM standard D5106-03 *Standard Specification for Steel Slag Aggregates for Bituminous Paving Mixtures.*[1]

2.3.3. Portland Cement. Steel slag is similar enough in chemical composition and character to Portland cement raw materials that it can be used as a cost effective feed additive.[10] The beneficial features of steel slag result from exposure to high furnace temperatures thus eliminating heat of decarbonation, reducing CO_2 and volatile emissions, and reducing total raw material moisture contents when used in clinker feedstock. Production increases with moderate additions (8-11%) of steel slag can be almost proportionate to the amount utilized.[10] An improved slag for clinker use can be generated by first oxidizing the FeO in the slag to Fe_2O_3, then quenching with water.[170]

2.3.4. Unconfined Construction. Steel slag finds excellent application as an aggregate in unconfined construction resulting in very high stability. Unpaved shoulders, bases, or parking lots, erosion control, and railroad ballast all find improved life and stability compared to standard mineral aggregates.[10,11] As the slag may expand with time, confined applications such as bases under pavements and structures are generally avoided unless the slag is stabilized prior to use.

2.3.5. Soil Conditioning. Steel slag utilization for agricultural purposes was first introduced in North America in 1916 by United States Steel.[9,10] Used first as a lime and phosphate amendment, other trace minerals such as Fe, Mn, Mg, Zn, and Mo have been shown to provide beneficial crop growth. Traditionally, use has been for corn and soybean crops, but sugar cane and rice crops are now being treated.

2.3.6. Environmental pH Neutralization. The free lime and magnesia content of steel slag has led to the investigation of steel slag as a pH neutralizer for acid containing wastes. Specifically steel slag has proven beneficial use in acid mine drainage where it serves as a fill material, bulk filter, and pH neutralizer. Research by the National Mine Reclamation Center in West Virginia on several Appalachian coal mines and Canadian pyrite mines, show that additions of steel slag is a more effective acid discharge neutralizer than lime or limestone, as it provides pH control during a longer period of time, and has no hazardous leachate by products.[14, 15]

3. SLAG CHARACTERIZATION

3.1. PHYSICAL PROPERTIES

Steel slag's unique physical properties result both from its chemical composition and its production method. Comparison to standard construction aggregates show a higher bulk density and specific gravity, higher hardness/toughness, coarser surface texture, and darker color.

3.1.1. Specific Gravity and Bulk Density. The bulk density and specific gravity of steelmaking slag is higher than blast furnace slag and natural aggregates due to the increased content of iron and manganese. Specific gravity values for steel slag averages 3.1-3.7 for BOF and 3.2-3.8 for EAF, in comparison to 2.1-2.5 for air cooled blast furnace slag and 2.85 for dolomite.[13,19,21,38] The resultant bulk density values are 1770-2500 kg/m^3 (156.1 lbs/ft^3), in comparison to 1440-1600 kg/m^3 (89.9-99.9 lbs/ft^3) for dolomite.[16,19] Beaver Valley Slag, a slag processing subcontractor, lists as-sold bulk densities of steel slag from 1410-1930 kg/m^3 (88.0-120.5 lbs/ft^3) depending upon the degree of compaction.[17]

3.1.2. Hardness/Toughness. Mineral hardness can be defined as the resistance to breakage, and toughness is a relative factor indicating the ease of breakage. Of importance for determining the processing and end use for slag is a quantitative factor to determine the amount of work required to break the particles. High toughness and hardness is beneficial for end use of the slag as it provides a more stable material. In construction applications it is desirable for the aggregate to maintain its shape, and resist breaking down into smaller particles. However the higher hardness and toughness, the more energy required to break the slag into desired particle sizes during initial processing (crushing). Estimated Moh's hardness for steel slag is 6-7 compared to 3-4 for dolomite.[21] Crushing work index and grinding work index provide comparison values for crushing (breakage down to 1-2 cm) and grinding (breakage below 1-2 cm) operations respectively. The crushing work index for dolomite is 12.8, which is the same for slag.[19] However, the grinding work index (ball mill) for dolomite is 13.9 versus 17.2 for slag.[19] Work index has the units of kWh/ton, and a comparison shows it takes about 24% more energy to grind steel slag compared to dolomite. Steel slag has the double benefit of requiring about the same energy for crushing as dolomite, but being more resistant to in-situ dust and fine generation. In using slag for asphaltic cement or road surfaces, the slag is more resistant to breakdown during application (mixing and lay down) and for the life of the constructed surface.

3.1.3. Particle Shape. The shape of crushed slag qualifies it as a premier aggregate for road construction applications. The shape of crushed slag is described as cubical, in comparison to dolomite which is rounded or limestone which is flat and elongated.[10] The cubical nature, along with rough surface texture, allows for greater aggregate shear resistance, compared to round or flat particles, which resists rutting of asphalt surfaces. As an estimate to quantify the shape for comparison, the angle of repose can be compared. The angle of repose for slag is 45-50°, while that of crushed dolomite is 37°, indicating it has higher particle-particle resistance when stacked.[20,21]

3.1.4. Surface Texture. The surface texture and hardness of slag provides outstanding skid resistance, a highly sought after feature in pavement construction. The surface texture of slag is primarily a result of its cooling method. Most steel slags are air-cooled under ambient conditions, with final cooling accelerated with a water spray. The solidified material has a vesicular nature from gases entrained during the melt and generated upon cooling. The pores increase the surface roughness and area allowing for higher coefficient of friction and binder affinity. Slag resists polishing during the application life, as the new surfaces generated by impact or wear contain pores which renew the friction resistance. The two terms that quantify skid resistance are polished stone values (PSV, high values desirable) and aggregate abrasion values (AAV, low values desirable). The PSV for BOF slag is 54-57 and EAF slag is 58-63, compared to 53 for dolomite and 41-45 for limestone.[13,38] Likewise the AAV or steel slag is 2-4 compared to 4 for sandy dolomite and 8 for limestone.[13] Another quantification of abrasion resistance is the Los Angeles Abrasion Test, specified by ASTM C131-03 *Standard Test Method for Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine.*[47] This test measures the degradation, as percent loss, due to abrasion in a rotating grinding drum. Steel slag has an exhibited value of 9-18% for BOF and 8-15% for EAF compared to 35-40% loss for air-cooled blast furnace slag and dolomite.[21,38]

3.1.5. Mechanical Swelling. The mechanical swelling of steel slag is a result of hydration and carbonation of some of the compounds present in the matrix. Details of the chemical nature of hydration and carbonation are discussed in subsequent sections, while this section will focus on the mechanical effects from swelling.

Quantification of slag expansion was undertaken by Tsuchiya et al. in 1980 by studying the expansion characteristics of slag during the water immersion test.[22] The method of their test was to measure the rate and total volume of expansion of four LD slags. Employing a constant-temperature-water-immersion test with molds used for measuring California Bearing ratio, data was obtained on expansion with time. Expansion ratios of 2-13% were achieved at one year, with the ultimate expansion reaching 2.0-35.9% (time not given). A comparison between the final expansion ratio and the chemical composition suggests a proportional relationship with the amount of free lime (f-CaO). Slags A, D, B, and C had 3.5%, 6.1%, 8.9%, and 9.2% f-CaO respectively, and a corresponding ultimate volume ratio of 2.0%, 2.6%, 35.9%, and 19.3%. A comparison of the other chemical constituent did not show a proportional correlation. It is assumed that primarily hydrates were formed (as opposed to carbonates), since the slags were subjected to water immersion testing in a closed mold and not exposed to atmospheric carbon dioxide. No characterization was undertaken on the final aged slags.

A second round of tests was conducted on the highest expanding slag (B), where the slag was allowed to field age at zero, one, three, and six months before undergoing the immersion test. Field aging had the effect of significantly reducing the ultimate expansion ratio of the slag. At zero months field aging 35.9% expansion was exhibited, but this dropped to 18.2% expansion at one month field aging and 6.4% expansion at six months of field aging. Field aging and shortened the time needed to complete expansion, but lessened the ultimate expansion value. Qualitatively, these results show that the processes occurring in the field aging and water immersion are different. It is suggested that the free lime in field aging is subject to competing hydration and carbonation reactions from the H_2O and CO_2 in the air. Ultimately some carbonate forms, reducing the available free lime for hydration in the immersion tests. The hypothesis for reducing the time to complete the reaction is that carbonate formation during field aging increases crack formation and propagation, allowing greater surface area for hydration during the immersion tests.

Tsuchiya et al. found that most free lime in LD slag is present in unassimilated lumps, not distributed in solid solution.[171] The free lime lumps are several mm in diameter at a density of one per cm^3, and are observed as white to brown color in a blackish slag matrix.

In 1997 Kandhal and Hoffman published the results from a 1982 feasibility study of using cured steel slag fine aggregate in HMA mixtures.[16] They noted that for raw slag, the unslaked lime will hydrate, causing large volume expansions in a few weeks, while the magnesium oxide hydrates more slowly causing volume changes that may occur after several years. Prior to their work, the Pennsylvania Department of Transportation required that raw steel slag be moist cured under sprayed water conditions in a controlled stockpile for six months to alleviate expansion potential. Even with this requirement, several failures occurred where aged steel slag used as structure backfill expanded 3-6%. As a result, the Pennsylvania Testing Method (PTM) 130 was produced to better characterize expansion characteristics of steel slag. This method was used to generate ASTM D4792-00 *Standard Test Method for Potential Expansion of Aggregates from Hydration Reactions.*[48] Their research focused on the use of fine steel slag for hot-mix asphalt. Because the asphalt binder coats the aggregate particles and seals of the hydration route, this application serves as a better use for steel slag than unbound aggregate. Of use in their research is the evaluation of swelling potential from 10 slag sources. All samples were from Pennsylvania, with three from uncured stockpiles, and seven from stockpiles aged at six months or longer. Expansion tests were undertaken according to PTM-130, which uses a six-inch diameter mold filled with compacted slag and submerged in water at 71°C (160° F) for seven days. After seven days the sample is removed from the water bath, but kept saturated by adding water daily. Expansion measurements continue an additional seven days for a total of 14 days. A dial gauge measures vertical expansion from the initial height of 116.4 mm (4.584 in). Expansion values of 1.1-2.8% were observed for uncured slag, and 0.0-0.3% for cured slag. Further tests were undertaken to determine the particle size effect on expansion potential. Samples from the four highest expanders of the original ten stockpiles were graded at 4.8

mm (0.185 in). The undersize (<4.8 mm) and oversize (4.8-50.8 mm) particles were then subjected to PTM-130 testing. Coarse particles showed 1.13-2.83% and 0.27-0.67% expansion for uncured and cured respectively. Fine particles showed 0.87-2.7% and 0.03-0.23% expansion for uncured and cured respectively. These results indicate homogeneity in expansion potential versus particle size.

The testing time range for Tsuchiya et al. and Kandhal et al. was significantly different (>400 days vs. 14 days). However, a comparison of data from both sources at 14 days gives an average expansion on uncured slag of 0.7% for Tsuchiya and 1.9% for Kandhal. The difference lies in both the sample source (Tsuchiya was LD slag and Kandhal was unspecified), and that the Kandhal testing allowed the second half of the testing to have contact with air. The higher expansion rate may be a result of carbonation expansion taking place in addition to hydration expansion. Insufficient data was available from Tsuchiya to compare the cured slag expansion.

The literature sources reviewed have stated several times that the primary constituents in slag that lead to swelling are free lime (CaO) and free magnesia (MgO). However in the slag mechanical swelling studies reviewed[16,22], no characterization work was undertaken to compare the phases before and after the swelling test. The volume increase contribution of free oxides alone versus other phases could not be determined. A comparison of the molar volumes of lime and magnesia to that of their corresponding hydroxides and carbonates provides an estimate of their individual expansion capacities. Lime has a molar volume of 16.76 cm^3 (1.022 in^3), and upon hydration this increases 97% to 33.08 cm^3 (2.019 in^3). The formation of calcium carbonate leads to 120% growth (36.89 cm^3 (2.251 in^3)) from the oxide. Magnesia shows similar dramatic change, growing from 11.25 cm^3 (0.6865 in^3) to 24.63 cm^3 (1.503 in^3) upon hydration (119% increase), and to 28.03 cm^3 (1.710 in^3) upon carbonation (149% expansion) from the dry state. Other compounds in the slag (primarily silicates of the alkaline earth metals) also show a volume increase during hydrate and carbonate formation. A thermodynamic review of these minerals, including molar volume change, is covered in Section 3.4.

3.2. CHEMICAL PROPERTIES

The final chemical composition of steel slag is a result of the fluxing agent used during steelmaking, the charge composition (hot metal and scrap), and refining agents. The primary fluxing agents are limestone (standard and dolomitic), lime (standard and dolomitic), dolomite, and fluorspar. Refining agents include aluminum, ferromanganese, ferrosilicon, and calcium-silicate, all used to remove oxygen, sulfur, phosphorus, and other impurities in the molten steel. Most of the fluxing agent and impurities will report to the slag phase for removal from the furnace.

3.2.1. Elemental Chemical Composition. A study in 2000 by Proctor et al. at ChemRisk, a risk assessment consulting firm, measured the elemental breakdown of slag samples from 58 active mills with BF, BOF, and/or EAF production.[18] This study represents approximately 47% of North American steel production. Data from this study for BOF and EAF production is shown in Table 3.1.

Table 3.1. Elemental Chemical Composition of Slag by Furnace Type[18]

	Detection Frequency (%)		**Average Conc. (mg/kg)**		**Concentration Range (min – max, mg/kg)**	
Metal	BOF	EAF	BOF	EAF	BOF	EAF
Al	100	100	23841	35009	100 – 108800	14100 - 71600
Sb	35	31	3.3	4	3 - 8.8	1.1 - 18
As	0	11	ND	1.9	ND	0.5 - 5.8
Ba	100	100	75	557	24 – 260	160 - 1800
Be	6	91	0.5	1.1	5 – 5	0.6 - 6.3
Cd	24	84	2.5	7.6	8 – 15	0.1 - 19
Ca	100	100	280135	250653	206900 – 367200	172300 - 324400
C	100	100	2600	2936	500 – 5800	100 - 12100
Cr (tot)	100	100	1271	3046	440 – 2000	320 - 6200
Cr (VI)	0	29	ND	1.2	ND	1 - 9.1
Co	59	96	3.8	4.8	2 – 12	2.5 - 11
Cu	100	100	30	178	12 – 120	62 - 540
Fe	100	100	184300	190211	115700 – 229000	32700 - 312000
Pb	100	100	50	27.5	2.4 – 330	4.5 - 220
Mg	100	100	55318	54460	28700 – 72000	23600 - 91500
Mn	100	100	32853	39400	12900 – 65700	18900 - 63800
Hg	41	18	0.1	0.04	0.1 - 0.1	0.1 - 0.7

Mo	47	98	11	30	0.8 – 73	1.6 - 81
Ni	94	100	4.9	30	2.1 – 10	5.2 - 310
P	100	98	3197	1781	470 – 5720	580 - 4290
Se	82	100	15	18	7.7 – 25	7.5 - 36
Si	100	100	59653	74524	30900 – 114100	39900 - 152700
Ag	53	78	9.1	8.4	2.3 – 100	1.3 - 100
S	100	100	1112	1891	440 – 5000	600 - 3310
Tl	12	2	7.2	11	11 – 11	11 - 11
Sn	100	100	6.5	10	2.7 – 26	3.2 - 34
V	100	100	992	513	430 – 1700	170 - 1500
Zn	94	100	46	165	8.5 – 150	31 - 690

The primary elements indicated are Al, Ca, Fe, Mg, Mn, and Si which are to be expected in normal steelmaking slags. Fluxing agent serves as the source for Ca and Mg, oxygen kill additions account for Al and Si, and oxidation/entrapment in the slag accounts for Fe and Mn. Using the average values for the primary elements in BOF slag, we find their oxides account for 93.5% of the slag mass. The secondary elements of importance are C, Cr, P, and S, which are present as oxides, or carbonates, sulfates, and phosphates with the primary elements. These are the impurities removed by steelmaking, which report to the slag.

3.2.2. Toxicity Potential. In addition to slag characterization, Proctor et al. sought to determine the potential for slag to leach chemicals into the soil or groundwater.[18] This is a critical parameter for determining slags usability in unconfined construction applications. Water leachate tests using EPA method 1311[49] were performed for toxicity characterization leaching potential (TCLP) on each critical metal in the slag. The elements C, S, Mg, Ca, and P were considered major elements in the earths crust, and essential human nutrients, and were excluded from the analysis. Analysis of the leachate testing showed a pH of 11.8 for both BOF and EAF slag. Comparison to the TCLP regulatory standards was made for As, Ba, Cd, Cr VI, Cr (total), Pb, Hg, Se, and Ag. None of the elements exceeded the U.S. EPA standards, and most were at least one order of magnitude below, indicating that under acidic soil conditions the metals present in steel slag do not leach to any appreciable degree, and steelmaking slag should not be considered hazardous waste.

3.2.3. Chemical Compounds. Steel slag rarely contains free elements, and at ambient equilibrium conditions all constituents normally exist as compounds. Typically these are oxides, carbonates, or sulfates. Several sources provide a chemical compound breakdown of steel slag, as summarized in Table 3.2.

Table 3.2. Steel Slag Chemistry (Compound basis), by Source

	NSA[12]	**Emery**[13]	**BVS**[24]		**Noureldin**[21]	**Tsuchiya**[22]		**Sorrentino**[172]
Type	Steel	BOF	Steel (high Si)	Steel (high Fe)	Steel	High Exp.	Low Exp.	Steel
CaO	42.9	41.3	35.3	37.7	34	46.0	42.5	50.03
FeO/Fe_2O_3	25.0	20.0	9.6	30.8	23	25.4	28.4	22.67
SiO_2	14.9	15.6	31.4	17.9	16	11.9	11.8	15.22
MgO	8.1	6.9	6.2	5.8	8	7.2	7.0	6.59
MnO	5.0	8.9	1.9	4.8	10	4.9	5.7	2.38
Al_2O_3	5.0	2.2	8.9	2.7	3	1.2	1.2	1.68
P_2O_5	0.8	NR	NR	NR	NR	2.1	NR	2.06
S*	0.08	- -	1.9	0.52	NR	NR	NR	NR
TiO_2	NR	0.5	0.46	0.39	1	1.2	1.3	0.7
Na_2O	NR	NR	0.03	0.05	NR	NR	NR	NR
K_2O	NR	NR	0.48	0.28	NR	NR	NR	NR
free CaO	NR	3.3	NR	NR	3	8.9	3.5	10.40

* Sulfur exists principally as calcium sulfate

A range of reported data exists, but in general the major compounds are oxides of the Ca, Mg, Fe, Si, Mn, and Al. These species account for >97% of the slag mass. The data from the National Slag Association represents a U.S. average, while that from Emery, Beaver Valley Slag, and Noureldin represent an approximation for their geographic regions. The data from Tsuchiya lists analysis from an individual source. Geiseler[38] compared the amount of free CaO between BOF and EAF slag, estimating <10% and <3% respectively, which corresponds with the data listed in Table 3.2. Little differentiation exists in literature to characterize BOF versus EAF, and for the purposes of this project unless specified the compositions stated are for steel slag without segregation by furnace type.

A comparison can be made between steelmaking slag (BOF/EAF) and other ferrous processing slags. Table 3.3 compares the data for steelmaking slag from blast furnace, hot metal dephosphorization, and stainless steel production.

Table 3.3. Comparison of Ferrous Processing Slags, by source

	NSA[12]	**NSA**[25]	**Isoo**[26]	**Johnson**[27]
Type	Steel	Blast Furnace	Hot Metal Dephos	Stainless Steel
CaO	42.9	32-45	56.8	46.7
FeO/Fe_2O_3	25.0	1-1.5	8.3	1.2
SiO_2	14.9	32-42	13.8	27.9
MgO	8.1	5-15	3.7	9.8
MnO	5.0	0.2-1.0	4.4	
Al_2O_3	5.0	7-16	3.3	2.9
P_2O_5	0.8		6.9	
S	0.08	1-2	0.3	
TiO_2	NR			1.1
Cr_2O_3				2.8
F	NR			1.6

The key component when comparing steelmaking to other ferrous processing slags is that steelmaking slag contains a high amount of iron oxide (FeO/Fe_2O_3). This specie attributes the high density and dark color. While attempts are made during processing to remove any magnetic material (free Fe) from the slag for recycling into production, a significant amount of iron oxide is distributed throughout the slag matrix and cannot be easily recovered by physical separation. As to be expected with these slags, their processing method contributes to their chemical character. The flux type and reducing environment results in high lime and magnesia, with low FeO content in blast furnace slag. Hot metal dephosphorization slag has high P_2O_5 content, and stainless steel slag has appreciable amounts of chromium oxide.

3.2.4. Neutralization Potential. A beneficial chemical characteristic of steelmaking slag is its neutralization potential. As the primary constituents in slag are lime, magnesia, and other basic compounds, leaching of this material results in the liberation of high concentrations of alkalinity to the dissolving fluid. Work by Proctor et al. measured a pH of steelmaking slag leachate at 11.8.[18] Emery also estimated steelmaking slag leachate from slag solubility data at 12.5.[13] This character of slag led to steelmaking slag use for neutralization of acid mine drainage. Neutralization potential is the amount of acidity that can be neutralized by the slag (tons acid neutralized/ton slag expressed as a percentage), and is a measure of the sum total of carbonates, alkaline earths, and bases available. Simmons estimated the neutralization potential of the slag studied at 47-77%.[15] Slags generally have a lower neutralization potential than limestone (less alkalinity by mass); however, it is more effective at releasing the alkalinity. As the lime and magnesia in slag is in loose combination with silica, iron oxide, and alumina, it does not “burn” immediately, but releases the alkalinity during longer periods of time until exhausted. This observation is supported by slag phase analysis, as free lime, which dissolves in water rapidly, is present in small amounts (~3% according to Table 3.2). Slag has large amounts of combined lime, which thermodynamically will release into water, but at a much slower rate than free lime.

3.3. MINERALOGY

The slag chemistry, as previously described, along with the cooling history, will lead to an equilibrium set of minerals in the slag. Most steel slags are air cooled to solidification, and may be spray quenched to ambient temperature. The water spray assists in speeding up the processing, but has little effect on the bulk slag mineralogy.

3.3.1. Minerals Present in Steel Slag. A wide range of minerals have been observed in steelmaking slags. Table 3.4 contains a summary of the predominant minerals from published work. This table includes work from Corus RD&T (Ceramic Research Centre)[28], Emery[13], Monaco and Wu[31], Suito[42], Bradaskja[30], Luxán[50], and Sorrention.[172] The work by Corus utilized DTA and high temperature XRD to characterize the solidification sequence of steelmaking slag (type not specified). Emery's findings were based on literature review, while the work by Monaco and Wu was based on K-OBM slag. The LD converter slag studied by Suito et al. is listed in Table 3.4; however, their data on phosphorus enriched synthetic slags is not included. Bradaskja et al. studied minerals in EAF and VOD slags. Only the predominant minerals from EAF slag are listed. Luxán et al. carried out a study of EAF black slags in Spain, which are defined as a lime content <40% resulting from the cold loading of scrap.

Table 3.4. Predominant Minerals Found in Steel Slag, by Source

Mineral	**Monaco**[31]	**Corus**[28]	**Emery**[13]	**Suito**[42]	**Bradaskja**[30]	**Luxán**[50]	**Sorrentino**[172]
Lime	X	X	X				X
Periclase	X	X	X		X		
Hatrurite	X	X	X				X
Larnite	X	X	X	X	X	X	X
Srebrodolskite	X	X	X	X			
Brownmillerite	X				X		
Wustite	X	X	X	X	X		X
Calcium Ferrite	X		X	X			X
Gehlenite						X	
Bredigite						X	
Magnetite						X	
Magnesioferrite						X	
Manganese Oxides						X	

Good agreement exists between researchers on the predominate minerals found in steelmaking slag. These are alkaline earth metal oxides (lime and periclase), calcium-silicate combinations (hatrurite and larnite), iron oxide (wustite), and calcium-ferrite combinations (calcium ferrite and dicalcium ferrite). Many other species are present, all of them solid solutions or complex combinations of the oxides of calcium, magnesium, iron, aluminum, and silicon. This work will focus on the predominant minerals listed and not an exhaustive analysis of all species contained.

Table 3.5. Properties of Minerals Found in Steel Slag

Chemical Formula	**Name**	**Synonym**	**Density (g/cm^3)**	**Molar Volume (cm^3)**
CaO	Lime	-	3.35[51]	16.76
MgO	Periclase	Magnesia	3.58[51]	11.25
$3CaO \cdot SiO_2$	Hatrurite (Alite)	Tricalcium Silicate	3.15[39]	72.4
β-$2CaO \cdot SiO_2$	Larnite	Dicalcium Silicate	3.34	51.60[33]
$2CaO \cdot Fe_2O_3$	Srebrodolskite	Dicalcium Ferrite	4.04	67.18[33]
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Brownmillerite	-	3.73[39]	130.3
$Fe_{0.947}O$	Wustite	-	5.87[51]	12.25
$CaO \cdot Fe_2O_3$	Calcium Ferrite	-	5.08[51]	42.47
$2CaO \cdot Al_2O_3 \cdot SiO_2$	Gehlenite	-	3.04	90.24[33]
α'-$2CaO \cdot SiO_2$	Bredigite	-	3.40[52]	50.69
Fe_3O_4	Magnetite	-	5.20[51]	44.52
$MgO \cdot Fe_2O_3$	Magnesioferrite	-	4.49	44.57[33]
Mn_3O_4 MnO_2	Hausmannite Pryolusite	Manganese Oxide	4.86[51] 5.03[51]	17.30 49.89

A comparison of the minerals shows many complex combinations of simple oxides. The combinations containing iron and manganese oxides lead to the high density of the slag composite.

3.3.2. Metastable Minerals Subject to Stabilization. While a wide range of minerals in steelmaking slag have been observed, the focus of this project are those minerals that will provide sequestration of carbon dioxide. Several minerals in steelmaking slag are meta-stable, meaning that under dry vacuum conditions they will stay in their present state. However, exposure of these minerals to ambient atmospheric conditions will lead to spontaneous reaction with water and carbon dioxide in air to form more stable compounds. Ambient atmospheric conditions are defined as atmospheric humidity and carbon dioxide content at ambient temperature and pressure. Of the minerals listed in Tables 3.4 and 3.5, those containing oxides of calcium and magnesium are meta-stable in the raw slag, and will sequester carbon dioxide under ambient atmospheric conditions in the formation of more stable compounds. A thermodynamic analysis provides insight to the mechanism of these reactions.

3.4. THERMODYNAMICS OF STABILIZATION

Stabilization is the process that slag goes through to transform from the raw to most stable state. The basis of this study is the naturally occurring process that involves exposure of the raw slag to ambient atmospheric conditions (temperature, pressure, air composition, and humidity). Under these conditions, specific minerals in the slag will react spontaneously, and release heat as a result (exothermic). As the slag is subject to both water and carbon dioxide, competition exists between hydroxide and carbonate formation of each compound. A thermodynamic review will determine both the heat released in each reaction, and the final stable state of each compound (hydroxide or carbonate).

The key minerals identified for carbon dioxide sequestration are the free oxides and silicates of calcium and magnesium. These minerals form both hydroxides and carbonates, and determination of their respective Gibbs free energy of formation at ambient conditions (G°) will determine the final stable state. The subsequent analysis concerns spontaneous reactions to form hydroxides and carbonates at ambient temperature of 25°C (77°F). An increase in temperature pushes the system away from forming hydroxides/carbonates, and ultimately, a temperature will be reached in which the reaction goes backwards (decomposition). Hydroxide formation will be studied discretely and as a step in the formation of carbonate, while carbonate formation will be studied in both dry and wet processes.

3.4.1. Hydroxide Formation.

The reaction of water with alkaline earth metal oxides and silicates in the slag will lead to the formation of hydroxides. This water can be sequestered either from the air (ambient humidity) or from liquid form (submersion), and the concentration available will play a role in the rate of the reaction (covered in subsequent section). A study of the reaction thermodynamics will provide the state of the equilibrium products and any heat produced. A review of the literature provides this information for CaO, MgO, $2CaO{\cdot}SiO_2$, and $3CaO{\cdot}SiO_2$ at standard conditions (298°K, 1 atm.).

Equations 1-4 show the formation of the respective hydroxide from each compound, while Table 3.6 provides the heat released (*ΔH°_r*), Gibbs free energy (*ΔG°_r*), and volume change (ΔV) of each respective reaction.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \qquad (1)$$

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s) \qquad (2)$$

$$2CaO \cdot SiO_2(s) + 4.3H_2O(l) \rightarrow 1.7CaO - SiO_2 - 4H_2O(s) + 0.3Ca(OH)_2(s) \quad {}^{41}(3)$$

$$3CaO \cdot SiO_2(s) + 5.3H_2O(l) \rightarrow 1.7CaO - SiO_2 - 4H_2O(s) + 1.3Ca(OH)_2(s) \quad {}^{41}(4)$$

Table 3.6. Formation of Hydroxides from Steelmaking Slag Oxides & Silicates

Eq	**Product Formula**	**Product Name**	**$\Delta H°_r$ (kJ/mole)**	**$\Delta G°_r$ (kJ/mole)**	**Molar Vol. (cm^3) (each)**	**ΔVol. (%) (total)**
1	$Ca(OH)_2$	Portlandite	-65.2	-57.9	33.08[51]	97%
2	$Mg(OH)_2$	Brucite	-37.3	-27.3	24.63[51]	119%
3	$1.7CaO \cdot SiO_2 \cdot 4H_2O$ $0.3Ca(OH)_2$	C-S-H Portlandite	-38.2[41,43]	-15.8[33,41,43]	108[41] 9.92	127%
4	$1.7CaO \cdot SiO_2 \cdot 4H_2O$ $1.3Ca(OH)_2$	C-S-H Portlandite	-122.2[41,43]	-84.6[32,41,43]	108[41] 42.98	113%

Free lime and magnesia readily react with water at ambient conditions to form calcium hydroxide (portlandite) and magnesium hydroxide (brucite) respectively, as shown in Equations 1 and 2. These reactions have been extensively studied, as they are widely used industrial minerals. Thermochemical data for their respective reactions can be obtained from FactSage.[51] Their reaction with water is spontaneous and exothermic, with lime as the stronger reactant. Calcium hydroxide begins to decompose at 325°C (617°F), but has a quoted dehydration temperature of 518°C (964°F).[34,35] Magnesium hydroxide begins to decompose at a slightly lower temperature of 200°C (392°F) as reported by Butt et al.[36] and has a quoted dehydration temperature of 285°C (545°F).[34] The reactions of these oxides with water lead to a substantial volume change (97% and

119% respectively), which is why they are listed as key compounds in slag swelling studies.

The hydration of calcium silicates has been studied in cement chemistry, as they are key components in the manufacture of cement and concrete. Dicalcium silicate and tricalcium silicate together account for approximately 75% of ordinary Portland cement (OPC) by weight.[44] The hydration of dicalcium silicate and tricalcium silicate is documented by Tennis and Jennings[39], Bentz[41], and Fuji and Kondo.[43] Their work provides the reactions listed in Equation 3 and 4. Their hydration route is similar in that they both form calcium silicate hydrate and calcium hydroxide (in varying ratios). More than 30 crystalline phases of calcium silicate hydrate (C-S-H) are known. The preparation of C-S-H from dicalcium silicate and tricalcium silicate forms a C-S-H gel, which may vary in composition (as indicated by the dashes in the chemical formula). The hydrate reaction path for these minerals used by Bentz and Tennis and Jennings has been adopted for cement modeling and studied to provide thermochemical data. A ratio of 1.7:1 $CaO:SiO_2$ is adopted by the researchers listed; however, the amount of water varies. Thermochemical data for heat of formation and molar volume are obtained from Bentz, and data for free energy of formation is obtained from Fujii and Kondo. Fujii and Kondo use 2.62 moles of water for C-S-H, as opposed to four moles by Bentz, which provides different listed heats of formation. However, normalizing both to the same hydration level (4 moles) gives the same heat of formation for C-S-H (-3288 kJ/mole for Fujii and -3283 kJ/mole for Bentz). The hydration of tricalcium silicate is the strongest listed, providing nearly twice as much heat as the slaking of lime. Both dicalcium silicate and tricalcium silicate will spontaneously react with water at ambient conditions. The change in volume by the hydration provides a significant volume increase (127% and 113% respectively), indicating that they are a significant contributor to slag swelling.

3.4.2. Carbonate Formation. Formation of carbonates in slag can occur either dry (from non-hydrated minerals) or wet (from hydrated minerals). The ambient conditions (amount of water and length of time present) will determine if the slag forms carbonates from the dry state, or if hydroxides are formed as an intermediate step. A study of the reaction thermodynamics reveals the energy released, as well as the equilibrium reached between hydroxides and carbonates.

3.4.2.1 Dry Carbonate Formation. Carbonates of calcium and magnesium oxide will form directly if no water is present. Dry carbonation of lime occurs to form calcium carbonate (calcite) as shown in Equation 5.

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \tag{5}$$

This reaction is significantly more exothermic than the hydroxide formation, and with a lower free energy, this is a more stable compound. The dissociation (calcining) temperature of calcium carbonate depends on the partial pressure of CO_2 (pCO_2) in the surrounding atmosphere. It can range as low as 650°C (1202°F) at pCO_2 near zero, to 898°C (1648°F) for pCO_2 at unity.[20] Cement kilns normally operate in the 950-1100°C (1742-2012°F) range to increase the decomposition rate.

Dry carbonation of magnesia occurs to form magnesium carbonate (magnesite) as shown in Equation 6.

$$MgO(s) + CO_2(g) \rightarrow MgCO_3(s) \tag{6}$$

As with calcium carbonate formation, this reaction is significantly more exothermic than the corresponding hydroxide formation, and with a lower free energy this is a more stable compound. Butt et al. report the dissociation temperature of magnesium carbonate ranges from 320°C (608°F) at pCO_2 near zero to 410°C (770°F) at pCO_2 near unity.[36]

An alternate dry reaction may occur utilizing both CaO and MgO to reform dolomite ($CaMg(CO_3)_2$) as shown in Equation 7.

$$CaO(s) + MgO(s) + 2CO_2(g) = CaMg(CO_3)_2(s) \tag{7}$$

As the formation free energy reveals, dolomite is even a more stable form for CaO and MgO conversion than conversion to their respective carbonates. However, dolomite formation requires the intimate association of both CaO and MgO molecules, and as slag is a heterogeneous mixture, the formation of dolomite may be more difficult to achieve than the respective single carbonate compounds. Dolomite in its pure state has a dissociation temperature of approximately 600°C (1112°F), which is expected, as it is a combination of calcium and magnesium carbonate.[37]

The dry formation of carbonates from dicalcium silicate and tricalcium silicate are given by Goto et al.[45] Respectively, they will form carbonates according to the dry reactions shown in Equations 8 and 9.

$$2CaO \cdot SiO_2(s) + 2CO_2(g) \rightarrow 2CaCO_3(s) + SiO_2(s) \tag{8}$$

$$3CaO \cdot SiO_2(s) + 3CO_2(g) \rightarrow 3CaCO_3(s) + SiO_2(s) \tag{9}$$

Both reactions are highly exothermic and readily produce more stable compounds than their respective hydroxide formations at atmospheric ambient conditions. Table 3.7 summarizes the data from Equations 5-9 on dry carbonate formation.

Table 3.7. Summary Data from Dry Carbonation Calculations

Eq	**Product Formula**	**Product Name**	**ΔH°_r (kJ/mole)**	**ΔG°_r (kJ/mole)**	**Molar Vol. (cm^3) (each)**	**ΔVol. (%) (total)**	**CO_2 Seq. Pot. (kg/kg)**
5	$CaCO_3$	Calcite	-178.1	-129.3	36.89[51]	120%	0.78
6	$MgCO_3$	Magnesite	-116.7	-64.5	28.03[51]	149%	1.09
7	$CaMg(CO_3)_2$	Dolomite	-302.1	-201.6	64.36[51]	130%	0.91
8	$CaCO_3$ SiO2	Calcite Quartz	-232.4	-132.3	36.89 22.68[51]	87%	0.51
9	$CaCO_3$ SiO_2	Calcite Quartz	-421.1	-270.3	36.89 22.68[51]	77%	0.58

In each of these reactions, the formation of carbonate compounds results in a significant volume increase compared to the oxidized states. The carbonates of CaO and MgO are larger in volume than their respective hydrates, indicating that hydration followed by carbonation will lead to continued swelling in the slag. The total molar volume increase represented by dry carbonation of the silicates, shows a significant volume change (77-87%), but the final molar volume is less than that of the hydrates. This indicates that swelling will occur with the silicates upon hydration, but this will be followed by subsequent shrinkage upon carbonate formation.

While a thermodynamic analysis shows dry carbonation of the preceding compounds is possible, the reactions are dependent on the availability (partial pressure) of CO_2, which is low at atmospheric ambient conditions (pCO_2~33.4 Pa (3.30×10^{-4} atm)). Research in Finland (Zevenhoven et al.[46]) is concentrating on dry mineral carbonation primarily with magnesium oxides and silicates. They concluded that a catalyst will be required (and possibly elevated temperature and pressure) to achieve reaction rates for dry carbonation in a reasonable time. The highest reaction rates occurred in the presence of humid (water saturated) gas. Hydrates should form more readily due to the higher availability of water in normal ambient air. The partial pressure of water vapor in air ranges from pH_2O=3141 Pa (3.10×10^{-2} atm) for saturated air at standard conditions to pH_2O=0.1 MPa (1 atm) when rain falls on the slag. It is anticipated that hydrates will form more readily, due to availability of water then convert to the more stable carbonate compounds.

In Equations 5-9, oxides and silicates in the slag are combining with ambient CO_2 to form more stable carbonates. The CO_2 sequestration potential for each compound indicates the mass of CO_2 captured per mass of reactant (kg CO_2/kg reactant). The CO_2 sequestration potentials for each compound are listed in Table 3.7. The oxides have a higher sequestration potential than the silicates, indicating that if the slag cooling can be controlled to favor more lime and magnesia, then more CO_2 can be sequestered per mass of slag. The CO_2 sequestration potential is to grow in proportion to the mineral volume change associated with carbonation. This indicates a correlation may be obtained between the slag expansion potential and the CO_2 capture amount.

3.4.2.2 Hydrous Carbonate Formation. While dry carbonation can take place, the most likely scenario for the hydroxide and carbonation reactions to take place simultaneously. This would be the case for slag exposure to ambient air, which contains water and CO_2. A simplification for understanding is the sequential reaction of hydration followed by carbonation. In practicality, this may be the case of raw slag that is submerged in water (e.g. water quench granulation of blast furnace slag), where the assumption is that due to the small slag particle size, and immediate contact with water hydration takes place both immediately and to completion. Once the slag is removed from the quench tank and exposed to air, carbonation can take place. The hydroxides formed upon quenching are meta-stable in that given time they will sequester CO_2 to form carbonates by the following reactions. Equations 10-14 show the hydroxide to carbonate formation for $Ca(OH)_2$, $Mg(OH)_2$, $Ca(OH)_2+Mg(OH)_2$, 2C-S-H, and 3C-S-H, respectively. Table 3.8 summarizes the resultant enthalpy, free energy, and volume change data from these reactions, respectively.

$$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \qquad (10)$$

$$Mg(OH)_2(s) + CO_2(g) \rightarrow MgCO_3(s) + H_2O(l) \qquad (11)$$

$$Ca(OH)_2(s) + Mg(OH)_2(s) + 2CO_2(g) \rightarrow CaMg(CO_3)_2(s) + 2H_2O(l) \qquad (12)$$

$$1.7CaO - SiO_2 - 4H_2O(s) + 0.3Ca(OH)_2(s) + 2CO_2 \rightarrow 2CaCO_3(s) + SiO_2(s) + 4.3H_2O(l) \qquad (13)$$

$$1.7CaO - SiO_2 - 4H_2O(s) + 1.3Ca(OH)_2(s) + 3CO_2 \rightarrow 3CaCO_3(s) + SiO_2(s) + 5.3H_2O(l) \qquad (14)$$

Table 3.8. Sequential Carbonate Formation from Hydrates in Steel Slag Components

Eq	**Product Formula**	**$\Delta H°_r$ (kJ/mole)**	**$\Delta G°_r$ (kJ/mole)**	**Molar Vol. (cm^3) (each)**	**ΔVol. (%) (overall)**	**ΔVol. (%) (hydrate)**	**CO_2 Seq. Pot. (kg/kg)**
10	$CaCO_3$	-112.7	-71.4	36.89	120%	12%	59%
11	$MgCO_3$	-79.3	-37.2	28.03	149%	14%	75%
12	$CaMg(CO_3)_2$	-199.6	-116.4	64.36	130%	12%	66%
13	$2CaCO_3$ SiO_2	-188.6	-118.1	73.78 22.68	87%	-18%	35%
14	$3CaCO_3$ SiO_2	-302.2	-190.7	110.67 22.68	77%	-12%	41%

As shown by the free energy data in Table 3.8 for Equations 10-14, all hydroxide species will react to form carbonate at atmospheric ambient conditions. The heat released equals the heat of dry carbonation minus the heat of hydration. The carbonate compounds of these oxides and silicates are more stable than the hydroxides, and in all cases the hydroxides will convert to the more stable form given time. The conversion to carbonates leads to a small volume increase in the case of the oxides, leading to further slag swelling. The conversion of the silicate hydrates to carbonates leads to a volume decrease. The competing increase and decrease of hydration and carbonation of the various components, will lead to cracking of the slag during the stabilization period. The cracking will produce smaller slag particles (proportional to the amount of oxides and silicates available to react with water and carbon dioxide), and open new surfaces for reaction in the slag matrix, thus increasing the overall slag stabilization rate. This is the phenomena observed by Tsuchiya et al.[22] in their slag swelling study. The CO_2 sequestration potential is lower for the hydroxide compounds compared to dry carbonation due to the extra mass of water in each hydroxide. The amount of carbon dioxide captured for a given mass of slag is thus maximized under dry conditions.

3.4.3. Mineral Modification for Slag Stabilization. An alternative to time-based hydrate and carbonate stabilization involves modification of the slag mineralogy to produce phases less susceptible to swelling. Mineralogical modification seeks to eliminate formation of free lime, which is viewed as the primary source of slag swelling.

Dippenaar lists two alternative methods that eliminate the need for stockpile stabilization.[170] Both methods involve chemical additions to the molten slag to inhibit precipitation of free lime during solidification upon cooling. The first method (Reeves and Lu) adds fayalite (Fe_2SiO_4), and the second method (Hiltunen) injects oxygen and silica. Further details on each method are not provided.

Sorrentino et al. has researched the mineralogical modifications that occur upon cooling from addition of silica and alumina to the slag melt.[172] Their work is an extension of an oxidation treatment proposed to stabilize slag. The oxidation treatment injects oxygen and silica into the molten slag. During oxidation, divalent iron oxide (wustite and magnesiowustite), and iron metal oxidize to produce Fe_2O_3. The reaction is exothermic and produces sufficient energy to dissolve the added silica. Upon crystallization the added silica combines with free lime to produce calcium silicates, thus eliminating the free lime.

The experimental work by Sorrentino et al. submitted industrial slag to oxidation only, oxidation with silica addition, and oxidation with alumina addition. Untreated slag contained a solid solution of dicalcium silicates, magnesiowustite, calcium ferrite, and free lime (~10%). Oxidation treatment at 1500°C eliminated magnesiowustite to precipitate magnesium oxide (periclase) and ferric oxide (hematite). The main phases after oxidation are dicalcium ferrite, formed from the free lime and ferric oxide, dicalcium silicate solution, and periclase, with the free lime amount dropping to ~1%. After oxidation with silica addition the main phases are dicalcium silicate surrounded by a solution of iron oxide and an unidentified eutectoid precipitate. In the case of slag oxidized with addition of alumina, calcium aluminate, dicalcium silicate, and calcium ferrite are formed. The free lime amount dropped to less than 0.5%.

4. CO_2 CAPTURE AND GEOLOGICAL SEQUESTRATION

4.1. OVERVIEW OF CO_2 CAPTURE

4.1.1. Implications of CO_2 Control in the Steel Industry. The driving factors for CO_2 sequestration are extremely complex and involve political, economic, and scientific factors. There is uncertainty or disagreement about almost every aspect of the anthropogenic greenhouse gas theory, and it is extremely unlikely that anyone in government, or indeed possibly in science, is able to command a comprehensive view of the whole situation.[128] Regardless of personal, corporate, or governmental views of the anthropogenic greenhouse gas theory, a binding agreement for the industrial countries was put forward at the world summit in Kyoto, Japan in 1997. This agreement, called the Kyoto Protocol, proposes the industrial nations to cut their collective emissions of specific gases (CO_2, CH_4, NO_x, SF_6, hydrofluorocarbon's, and perfluorocarbon's) by an average of 5.2% below the 1990 levels by 2012. This agreement came into force February 2005 and is currently supported by 156 countries.

The industries working in the countries that have signed the Kyoto Protocol have the responsibility to work within the scope of their respective legislation in reducing emissions of the gases listed. The iron and steel industry is highly reliant on carbon based fuels both directly (coke for iron oxide reduction) and indirectly (EAF use of electricity from coal burning power plant). The emission of CO_2 has been targeted most heavily by the supporting countries, with the net result that the iron and steel industries will need to make changes in operation and methodology to meet this cutback. Long-term changes may require the development of carbon-free steelmaking, but that is many years in the future. Short-term goals can be achieved by reducing the carbon intensity of iron and steelmaking. These include injecting hydrogen rich fuel in the blast furnace (natural gas instead of coke), alternative ironmaking technologies (DRI, ITmk3, COREX, etc.), maximizing scrap recovery and use in steelmaking, and optimizing energy use in all areas of ferrous processing. Medium-term goals for the iron and steel industry should include greater industrial symbiosis, such as limestone replacement by slag cement clinker, and the use of byproduct gas and heat for power generation and industrial heating.[128] Permanent sequestration of CO_2 from industrial sources is being investigated as a medium to long term option, and if developed properly may provide a commercially favorable route.

4.1.2. Industrial CO_2 Capture (Non-Geological). Carbon dioxide capture from gaseous streams is a commercial technology, although this technology is not set up for permanent sequestration CO_2. The natural gas industry commonly uses liquid amine based chemicals (monoethanolamine (MEA) and diethanolamine (DEA)) in a stripping tower or polymer membranes (polyimide, polyamides, and cellulose acetate) to sweeten raw natural gas by the removal of carbon dioxide. These technologies operate at high pressures and large flow rates, but may not optimized for the high temperatures that may be seen in blast furnace or steelmaking furnace exhaust ducts. Each of these technologies removes carbon dioxide from the natural gas stream to form a concentrate, but subsequently exhausts the concentrate to the atmosphere. Permanent sequestration in a non-gaseous form must be added as a separate process.

Other non-geologic technologies are being researched for use in the steel and power industries for capture of CO_2 from the offgas. Gielen presents the results of a study using Selexol^{TM} (dimethyl ether of polyethylene glycol made by Union Carbide) to remove CO_2 from blast furnace offgas.[120] The estimated capture cost is 16.7-18.8 US$/t of CO_2 for conventional blast furnace (2003 basis), and could reduce Japanese emissions by 6.5% (80 Mt/yr) if implemented. Solid regenerable carbonates can be used at a potentially lower cost than liquid amine systems. Work by Green et al.[129] and Corti[130] with sodium and potassium bicarbonate, and Robertson[131] with magnesium carbonate, shows solid carbonates have a high CO_2 capture potential (~80%) with a short cycle (<5 minutes), are easier to regenerate than liquid-amines which require steam stripping to remove the CO_2, and require a small reactor size. As with amine systems, a sequestration system must be added to this cost of each system to provide permanent disposal of CO_2.

4.2. GEOLOGICAL METHODS FOR SEQUESTRATION

Geological sequestration of carbon dioxide is actively being researched as it provides a permanent disposal source, as opposed to biomass uptake that will eventually release the captured CO_2 again to the atmosphere. The two significant geological bodies available to permanently capture increased amounts of CO_2 from the atmosphere are the oceans and mineral bodies in the earths crust.

Natural neutralization of projected CO_2 emissions by marine sediments in ocean bodies would result in an estimated sequestration of 70-80% of the carbon dioxide; however, the process may take several centuries to 1500 years to complete.[53,62] Injection of liquefied carbon dioxide into deep ocean zones to eliminate the millennium required for natural equilibrium is an active research area. Alternatively the liquefied CO_2 can be injected into subterranean formations, as researched by the Pacific Northwest National Laboratory.[169] While these methods greatly speed up the reaction of carbon dioxide with seawater or geologic formations, they both require technologies for capture, liquefaction, transport, and injection. To date these methods have proven prohibitively expensive for common industrial use.

Solid based CO_2 sequestration holds great potential for industrial operations, as a wide variety of minerals are available to form permanent carbonates sinks. The distribution of the mineral body in relation to the locality of the CO_2 generation source will be the primary cost hurdle. The design of a system that can accomplish a reaction of the mineral with gaseous CO_2 will simplify the unit process by eliminating gas based capture and liquefaction systems. Transport of the CO_2 to the mineral body or of the prepared mineral to the CO_2 source becomes the driving economic factor, providing the reaction rate is sufficiently fast.

Three classes of mineral carbonate disposal strategies have been proposed.[53] The first approach mimics the natural weathering process whereupon mineral alkalinity neutralizes carbonic acid. Natural carbonate weathering generates bicarbonates that go into surface or ground water solution, eventually reporting to the ocean as the final geological sink. Natural silicate weathering extracts alkalinity (e.g. Ca^+ or Mg^+) into surface water, which in turn combines with bicarbonate (HCO_3^-) in the ocean to precipitating solid carbonates (e.g. $CaCO_3$ or $MgCO_3$). A strategy to accelerate the two steps of this process provides a permanent ocean-based disposal of bicarbonate salts. The second strategy is similar, but the carbonate or bicarbonate brines are injected into an underground reservoir, as opposed to ocean disposal. The third strategy involves the formation of solid carbonates for surface or underground disposal. The latter strategy is most similar to the current research involving slag-CO_2 sequestration.

4.2.1. Minerals for Solid Carbonate Sequestration. The most common minerals studied for solid carbonate sequestration are based on the alkali or alkaline earth metals. Respectively, the base ions are monovalent sodium and potassium, or divalent calcium and magnesium. Table 4.1 lists many of the potential minerals readily available for solid carbonate sequestration.

Table 4.1. List of Potential Minerals for Solid Carbonate Sequestration (from Lackner[53])

Mineral	**Chemical Formula**	**Resource Size (1000 Gt)**	**Chemical Preprocess**	**Disposal Form**
Lime	CaO	Synthetic	None	$CaCO_3$
Brucite	$Mg(OH)_2$	Small/Synthetic	None	$MgCO_3$
Calcium hydroxide	$Ca(OH)_2$	Synthetic	None	$CaCO_3$
Periclase	MgO	Small	None	$MgCO_3$
Wollastonite	$CaSiO_3$	Small	None	$CaCO_3$
Peridotite			Extraction of MgO or $Mg(OH)_2$	$MgCO_3$
Serpentine	$Mg_3Si_2O_5(OH)_4$	100,000	Acid dissolution leading to MgO or $Mg(OH)_2$	$MgCO_3$
Olivine	$(Mg,Fe)_2SiO_4$	100,000	Acid dissolution leading to MgO or $Mg(OH)_2$	$MgCO_3$
Forsterite	Mg_2SiO_4	Pure deposits are very small	Acid dissolution leading to MgO or $Mg(OH)_2$	$MgCO_3$
Potassium feldspar	$KAlSi_3O_8$	Very large	Dissolution in water or brine	K_2CO_3
Sodium feldspar	$NaAlSi_3O_8$	Very large	Extraction of sodium alkalinity	Na_2CO_3

As the disposal source of this study is a solid carbonate, the source of alkaline ions cannot be a carbonate (which require aqueous discharge), but will most likely be a silicate mineral rich in magnesium or calcium, thus the bicarbonate forming minerals listed in Lackner are precluded from Table 4.1. Significant sources of magnesium and calcium silicates are available on all continents, some of which are feasible for use in industrial systems.[53] Magnesium ions can be extracted from serpentine or olivine rock, and periodite deposits containing these minerals are widespread. Total estimates are several hundred thousand gigatons. Simple oxide minerals, such as lime, periclase, or their hydroxides are not readily available in natural mineral form and can only be used where these compounds are synthetically produced. Weathering of feldspars is a natural phenomenon that captures CO_2, but extraction of sodium and potassium from these minerals has not been widely studied.

4.2.2. Solid Carbonate Capture Chemistry. Carbon sequestration on a geologic scale requires neutralization of carbonic acid. Divalent metal oxides or hydroxides (such as Mg or Ca) would react with carbonic acid as shown in Equations 15-18 as given by Lackner.[53]

$$MeO + H_2CO_3 \rightarrow MeCO_3 + H_2O \tag{15}$$

$$Me(OH)_2 + H_2CO_3 \rightarrow MeCO_3 + 2H_2O \tag{16}$$

$$MeO + 2H_2CO_3 \rightarrow Me(HCO_3)_2 + H_2O \tag{17}$$

$$Me(OH)_2 + 2H_2CO_3 \rightarrow Me(HCO_3)_2 + 2H_2O \tag{18}$$

While these equations show the thermodynamic possibility of carbonate capture with metal oxides and hydroxides, the availability of these minerals are very limited. A more appropriate route would be direct carbonate formation from the silicates as shown in Equations 19-20 from Lackner.[53]

$$(MeO)(SiO_2)_m + H_2CO_3 \rightarrow MeCO_3 + H_2O + m(SiO_2) \tag{19}$$

$$(MeO)(SiO_2)_m + 2H_2CO_3 \rightarrow Me(HCO_3)_2 + H_2O + m(SiO_2) \tag{20}$$

The formation of a bicarbonate salt in solution allows for the use of carbonate minerals as shown in Equation 21.

$$MeCO_3 + H_2CO_3 \rightarrow Me(HCO_3)_2 \tag{21}$$

This reaction is shown for academic interest only, as this route produces a bicarbonate salt requiring aqueous or oceanic disposal, which is counter to the goal of this research to bind CO_2 into a solid slag product. Lackner states that it is easier to transform carbonates into bicarbonates than it is to drive silicic acid out of its minerals, and that in forming bicarbonates from silicates, only half as much silicate is required compared to carbonate formation only.[53] The first statement is not supported thermodynamically as, for example, the free energy of formation of the carbonate from forsterite (Mg_2SiO_4) is -230.2 kJ/mole, while bicarbonate formation from magnesium carbonate +221.2 kJ/mole. His observations also suggest that bicarbonates may represent a more convenient form of sequestration. However, as bicarbonates readily dissolve in water, they require dilution into the environment. The ocean is large enough to accept the bicarbonates formed, but the practical and environmental logistics of this route are not well defined. Solid carbonate formation, however, provides a specific and well-defined capture method not subject to the same geologic intrusion. The environmental impact from solid disposal is confined to the smallest possible region.

4.2.3. Thermodynamic Stability. Mineral carbonate formation is a highly thermodynamically stable route for disposal of carbon dioxide. Solid carbonate formation is exothermic; thus, it will be difficult to decompose these minerals under natural atmospheric conditions. Carbon dioxide can be released through a reaction with a strong acid, such as sulfuric; however, under natural conditions even that produced from burning sulfur rich coal is insufficient to free sequestered carbon dioxide. Alternatively, carbon dioxide may be released through natural calcination, which may take place upon mineral heating through volcanic action. The amount of carbon dioxide released through this method on a global scale will be very limited. The thermodynamic stability of solid carbonates eliminates the need for long-term monitoring and continued maintenance of the disposal site.[53]

4.2.4. Formation of Solid Carbonates from Natural Minerals. Several methods are currently being researched to produce a viable large-scale industrial solid carbonate disposal method. These methods primarily focus on the silicate minerals, with magnesium ores favored more than calcium ores, as magnesium silicates are usually more reactive than the calcium silicates. Some work has been done on simple oxides, but they are less naturally abundant. Cement chemistry can provide valuable insight to mineral carbonation, as can a study of biological carbonate forming processes. The information discussed in this section focuses mainly on the carbonation of natural minerals, which are minerals obtained from ore bodies for the primary purpose of reaction with carbon dioxide. Carbonation of “derived” minerals (industrial co-products such as slags and ash) will be covered in the section on carbonate formation in steelmaking slag. The methods researched for carbonation of virgin minerals have a direct impact on work to do the same with slags, as the chemical reactions are the same.

4.2.4.1 Silicates (Calcium and Magnesium). A consortium managed by the U.S. Department of Energy – National Energy Technology Laboratory (NETL) has done the largest amount of work with solid mineral sequestration. This group, comprised of NETL, Los Alamos National Laboratory, Arizona State University, and Albany Research Centre (ARC), has extensively researched the mechanisms and applications of using silicate based minerals for permanent carbon dioxide sequestration. Other groups at the University of Ohio, University of Pennsylvania, and Helsinki University of Technology have added to the knowledge of mineral silicate-to-carbonate formation through research of their own.

Butt, Lackner, and Wendt at Los Alamos National Laboratory have carried out extensive research on carbon dioxide disposal in carbonate minerals.[35,36,63,64] Their initial research focused on the carbonation of calcium and magnesium silicate minerals. The reactions are exothermic, therefore chemically stable; however, the main constraint for cost implementation is the reaction speed. Two approaches were researched to improve the reaction rate: solid-gas reaction at high-temperature and reactions in aqueous solutions.

The focus of solid-gas reactions was to determine the maximum temperature for stable formation of the carbonate from silicate. Calculations were made for a variety of common minerals to determine the maximum carbonation temperature in an atmosphere where pCO_2=0.1 MPa (0.99 atm). The results are shown in Table 4.2. In all cases the reaction products are the alkaline earth metal carbonate plus free silicate/aluminate/water, where applicable.

Table 4.2. Thermodynamic Properties of Mineral Carbonation Reactions (from Lackner[35])

Mineral	**Formula**	**T_{deh} °C**	**T_{max} °C**	**ΔH kJ/mole**	**ΔQ kJ/mole**
Lime	CaO	-	888	-167	87
Periclase	MgO	-	407	-115	34
Portlandite	$Ca(OH)_2$	518	888	-68	114
Brucite	$Mg(OH)_2$	265	407	-37	46
Wollastonite	$CaSiO_3$	-	281	-87	37
Clinoenstatite (Pyroxene)	$MgSiO_3$	-	201	-81	23
Forsterite (Olivine)	½Mg_2SiO_4	-	242	-88	24
Diopside (Pyroxene)	½$CaMg(SiO_3)_2$	-	164	-71	19
Grossular (Garnet)	⅓1/3$Ca_3Al_2Si_3O_{12}$	-	192	-67	28
Anorthite (Feldspar)	$CaAl_2Si_2O_8$	-	165	-81	39
Pyrope (Garnet)	⅓$Mg_3Al_2Si_3O_{12}$	-	260	-92	40
Talc	⅓$Mg_3Si_4O_{10}(OH)_2$	439	201	-44	64
Tremolite (Ampibole)	1/7$Ca_2Mg_5Si_8O_{22}(OH)_2$	566	164	-37	72
Chrysotile (Serpentine)	⅓$Mg_3Si_2O_5(OH)_4$	535	407	-35	78

The temperature T_{max} is the maximum carbonation temperature for $pCO_2=10^5$ Pa (0.99 atm). The temperature T_{deh} refers to the dehydroxylation temperature at $pH_2O=10^5$ Pa (1 atm). The enthalpy of reaction, ΔH, is normalized for one mole of CO_2 at the temperature T_{max}. The heat, ΔQ, is the energy required to heat the original mineral and the CO_2 to the higher of T_{max} or T_{deh}, from 25°C (77°F). They state in most cases that the energy released from carbonation exceeds that required to heat the reactants to T_{max}; so, theoretically, the reaction can be made self-sustaining. Grinding followed by direct carbonation in a rotary kiln or fluidized bed is recommended to achieve minimal cost. While this data proves useful in comparison to the thermodynamic phase stability diagram calculated for slag phases, Lackner et al. do not provide reaction rates for the direct carbonation reaction in their initial work.[35]

Following their initial study, Lackner et al. performed experiments primarily on magnesium-based ores. This is because two to two and one-half tons of magnesium-based rock is required to bind one ton of CO_2, as opposed to seven tons of calcium-based rock. Carbonation of serpentine ($Mg_3Si_2O_5(OH)_4$) is exothermic, but difficult to perform directly. They were able to carbonate samples of 100 μm serpentine to 25% stoichiometric maximum upon exposure to CO_2 at 34 MPa (336 atm) and 500°C (932°F) for 2 hours.[63] Due to the slow kinetics of silicate carbonation, their work has mainly focused on hydrochloric acid extraction to produce magnesium hydroxide. Magnesium hydroxide is then free to react faster with CO_2. Their experiments showed that near complete carbonation of the hydroxide can take place in less than 30 minutes at 50 MPa (49.3 atm) pressure and 550°C (1022°F).[63] A side comment was provided stating that water vapor plays an important role and may catalyze the reaction, while at the same time inhibits carbonation by reducing the overall surface area through annealing.

Direct carbonation of $Mg(OH)_2$ was studied in further detail specifically to determine kinetic rates and factors.[36] The rate of carbonation was found to be most rapid very near the dissociation temperature, as shown in Figure 4.2.

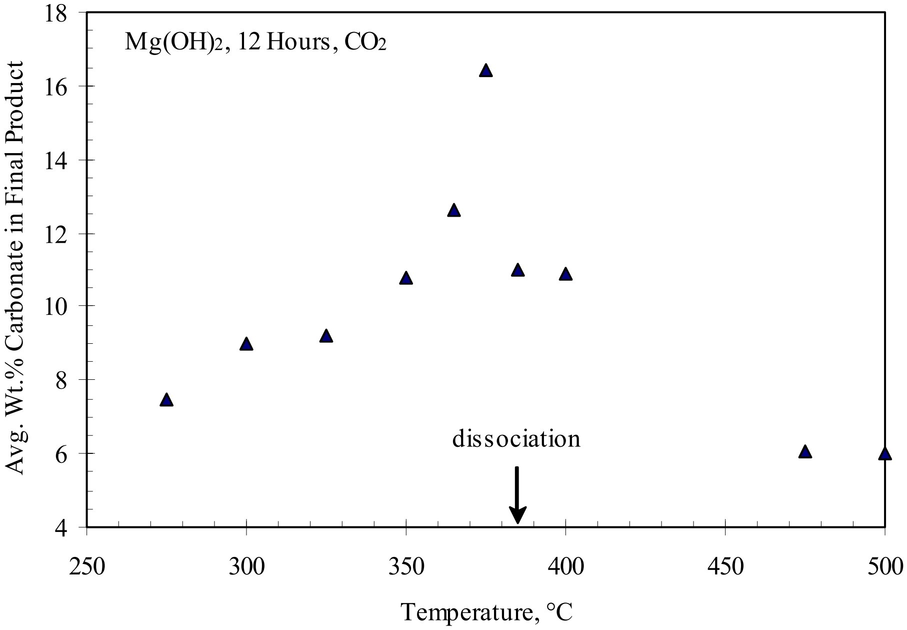

Figure 4.1. $Mg(OH)_2$ Conversion to Carbonate as a Function of Temperature at pCO_2=77.5 kPa (0.765 atm), from Butt et al.[36]

Tests on magnesium hydroxide particles (average particle size 28.7 μm) exposed to pCO_2=77.5 kPa (0.76 atm) for 12 hours show 2% carbonation at room temperature and a peak of 16% carbonation at 375°C (707°F), just below the dissociation temperature of 385°C (725°F).[64] Overall, the efficiency of carbonation at atmospheric pressure is relatively slow due to the formation of a product (carbonate) barrier that inhibits outward diffusion of water and inward diffusion of CO_2. The kinetics of both dehydroxylation and simultaneous dehydroxylation-carbonation obey the contracting-sphere model.[64] As the carbonation rate is thermally activated, the rate should increase with temperature. Following thermodynamic principles the dissociation temperature can be shifted higher, thus allowing the carbonation reaction to take place at a higher temperature, by increasing the system pressure. Carbonation tests at a pressure of 5.3 MPa (52 atm) allowed the reaction to proceed at 565°C (1049°F), resulting in 90% carbonation compared to 16% at standard atmospheric dissociation temperature.

Other key qualitative conclusions are made regarding kinetic factors. It was noted that the carbonation rate is rapid after an initial induction period. The induction period is caused by the outgassing of H_2O from dehydroxylation that inhibits inward diffusion of CO_2. Also that water is required to provide a reasonable reaction rate, and that kinetics of carbonation are better in a low velocity CO_2 stream compared to a higher velocity of CO_2. Their envisioned final process will require the use of moderately high pressure CO_2 with a relatively slow flow rate.

McKelvy et al. at Arizona State University have undertaken work to develop an atomic level understanding of the dehydroxylation/carbonation process applied to Mg-rich minerals to be used for solid carbonate disposal of CO_2.[65-68] Their work is used to support the work of Butts et al., and therefore, focuses primarily on brucite ($Mg(OH)_2$) and serpentine ($Mg_3Si_2O_5(OH)_4$). Magnesium hydroxide exhibits a lamellar crystallographic structure. During dehydroxylation the $Mg(OH)_2$ crystal structure contracts by 50% perpendicular to and 5% parallel to its lamella, respectively.[67] The resultant distortion induces high levels of interlamellar and intralamellar strain, which facilitates cracking and the formation of MgO nanostructures with very high surface areas near 100-200 m^2/g.

An understanding of the structural changes during dehydroxylation led to the discovery of rehydroxylation for dramatically enhancing gas-phase carbonation reactivity. Single crystal fragments were 93% dehydroxylated at 375°C (707°F) under dry helium to form high surface area intermediate structures. The samples were exposed to dry and humid CO_2 at 375°C (707°F), resulting in rapid carbonation to 1%, after which carbonation ceased. Cooling to ambient temperature (23°C (73°F)) in dry CO_2 resulted in negligible further weight gain (total of 1.4% $MgCO_3$). However, cooling to 23°C (73°F) in humid CO_2 induced rapid rehydroxylation and carbonation providing significant weight gain (total of 8.1% $MgCO_3$). Further work with serpentine validates these observations. Serpentine heat pretreated to 600°C (1112°F) for several hours can achieve 70-85% carbonation in one hour (~150°C (302°F) and 11.7-18.7 MPa (115-185 atm) CO_2), exceeding the conversion rate for olivine (Mg_2SiO_4) by an order of magnitude.[65] The method of simultaneous dehydroxylation/rehydroxylation to provide access to fresh, carbon-reactive, intermediate materials with high surface area may be applicable to other Ca- or Mg-rich lamellar hydroxide based minerals.

To better understand the interplay between dehydroxylation and carbonation, a series of tests were run on $Mg(OH)_2$ as a function of CO_2 reaction pressure at a constant temperature (585°C (1085°F)) and time (16 hours).[66] Figure 4.3 shows the experimental results.

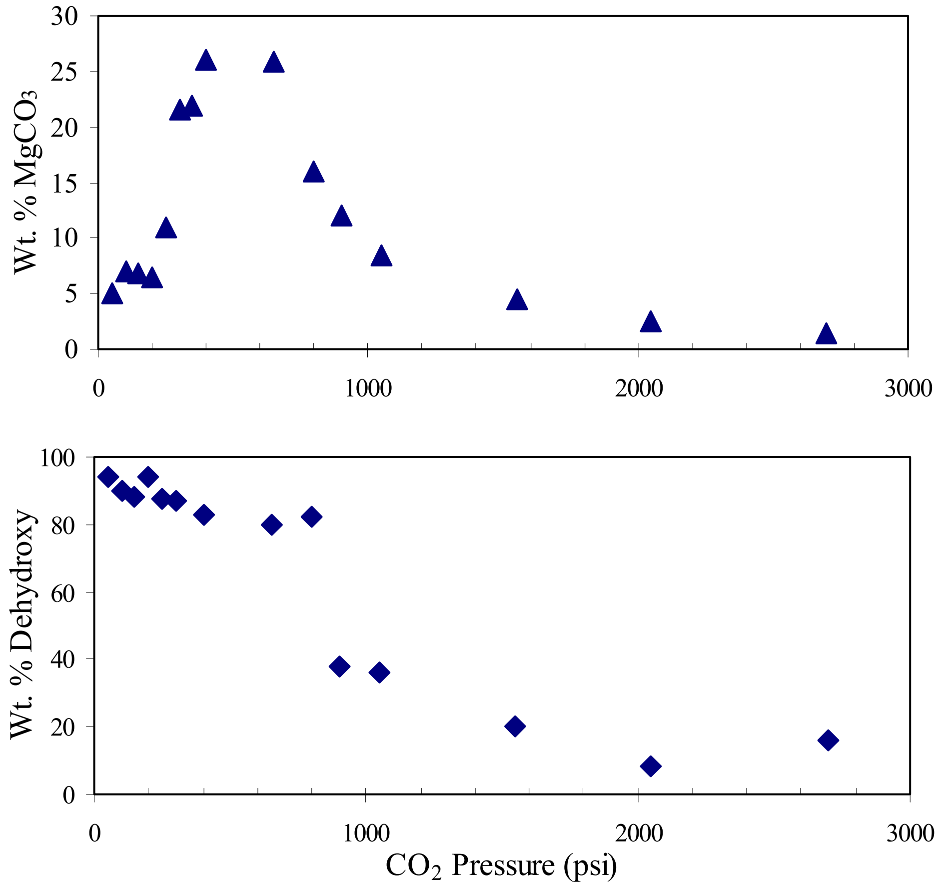

Figure 4.2. Wt. % $MgCO_3$ formed (above) and Wt. % Dehydroxylation (below) Vs. CO_2 Pressure for $Mg(OH)_2$ Single Crystal Fragments Reacted at 585°C (1085°F) for 16 Hours, from McKelvy et al.[66]

The first observation is that the extent of dehydroxylation exceeds the extent of carbonation by 20:1 at pressures to ~5.52 MPa (54.4 atm, 800 psi) and by 4:1 at pressures above this point. As the stability pressure for $MgCO_3$ is 5.44 MPa (53.7 atm, 789 psi) at 585°C (1085°F), the shift to the formation of more carbonate with respect to hydroxide above ~5.52 MPa (54.4 atm, 800 psi) is to be expected.

The second, and more important, observation is that the maximum carbonation rate takes place near the $MgCO_3$ stability pressure. The extent of carbonation increases proportional to CO_2 pressure up to ~5.52 MPa (54.4 atm, 800 psi), after which the further increase of CO_2 pressure decreases the carbonation rate significantly. Investigation revealed that carbonation was occurring at reaction temperature/pressure in the high-pressure region, but carbonation took place upon sample cooling in the low-pressure region (normally samples were cooled ~30 minutes to ambient temperature in a CO_2 atmosphere). This was confirmed by quenching and evacuating samples from the high- and low-pressure regions immediately after reaction. Quenched samples in the high-pressure region showed the same carbonation as those undergoing normal cooling, while quenched samples in the low-pressure region showed negligible carbonation. The extensive dehydroxylation of the samples in the low-pressure region under normal cooling (80-95%) resulted in formation of high surface area materials produced from lattice cracking, delamination, and morphological reconstruction. Upon cooling, substantially enhanced carbonation was exhibited. This phenomenon can be harnessed to engineer better sequestration materials. The high-pressure decrease in CO_2 reactivity is a result of a passivated carbonate layer slowing diffusion of the water and carbon dioxide species, combined with a high external CO_2 pressure slowing the outgassing of H_2O which is necessary to free up sites for carbonation.

To achieve reaction rates suitable for industrial processes (<1 hr), pretreatment activation is required for the alkaline-earth-metal-based silicate minerals. Serpentine as a hydroxide can be activated by dehydroxylation as detailed previously. Olivine (Mg_2SiO_4) is hydroxide free and is only susceptible to mechanical activation (via intense grinding). Olivine is of interest as it is similar to the phases observed in steelmaking slag. McKelvy et al. studied the mechanism of olivine carbonation under aqueous mineral carbonation.[68] Olivine samples (<37 μm) were reacted at 185°C (365°F) with 15.2 MPa (150 atm) CO_2 in a solution of 0.64 M $NaHCO_3$ and 1.0 M NaCl at 1000-2000 rpm stirring speeds. Without pretreatment activation 30-50% carbonation was achieved within one hour. Conditions such as these are unrealistic for bulk treatment of slag and show the stability of Mg-silicates even though thermodynamically the carbonation is exothermic.

Field emission scanning electron microscopy and energy dispersive spectroscopy were used to understand the barrier to rapid carbonation in olivine. An amorphous SiO_2 rich passivating layer forms on the olivine surface that is very effective at locally hindering carbonation. The volume contraction from silica formation from olivine can disrupt and crack the silica-rich surface layer, allowing the carbonation reaction to proceed, albeit slowly. Mechanical stirring was found to be effective at exfoliating the cracked silica surface layer thus exposing fresh olivine for carbonation. Particle-particle and particle-wall interaction are able to abrade the silica surface layer, as found through studies of slurry-flow dynamics. An order of magnitude increase in carbonation was observed through the use of a flow-loop compared to a batch reactor. A further ~50% increase was observed by incorporating flow mixers in the flow-loop. Enhanced carbonation can be correlated to increased turbulence.

O'Connor et al. at the Albany Research Center (ARC) have been conducting research to optimize the process conditions for direct aqueous carbonation of silicate minerals.[69-74] The process uses an aqueous slurry of fine particles reacted with CO_2 in a stirred autoclave. The concentration of solids ranges from 15-30 wt.%. Additions of $NaHCO_3$ and NaCl to the solution were found to improve the reaction rate dramatically. The bicarbonate ion is not consumed in the reaction, but found to act as a catalyst. The addition of NaCl may provide a complexing ion (Cl^-), which combines with the Mg^{2+} cations, thus reducing the activity in solution and increasing the solubility from magnesium silicate.[88] Experiments were carried out at elevated temperature and pressure (155-185°C (311-365°F) and 11.7-18.7 MPa (115-185 atm), respectively). The following key conclusions can be drawn from the analysis.[69]

- Conversion of silicate to carbonate requires mineral dissolution into the aqueous phase. The mineral dissolution reaction is surface controlled.
- The primary mechanism for carbonate formation is precipitation
- Chemically bonded water in serpentine prevents rapid carbonation. Every 1% loss on ignition amount of material reduces effective carbonation potential by ~7%
- Heat-treated serpentine has 10 times the surface area compared to natural olivine (~70 m^2/g versus ~7 m^2/g), resulting in the higher reactivity. Olivine pretreatment should focus on increasing the mineral surface area.

Size-by-size analysis showed that a sharp demarcation by particle size exists for carbonation. More than 99% of the CO_2 reported to the <500 mesh (<25 μm) product. The >25 μm particles are primarily magnesium silicate (>99%) and the <25 μm particles are primarily magnesite (>75%).

Further work was undertaken to characterize the carbonation process and determine rate parameters.[70] The rate controlling parameter for the direct carbonation of olivine and serpentine were chemical kinetics and diffusion through the product layer respectively. The rate constant for direct conversion of olivine is of the order of 10^{-7} cm/s, while the diffusivity coefficient in serpentine is of the order of 10^{-10} cm^2/s. The diffusivity value is much lower than that of CO_2 into water ($2x10^{-5}$ cm^2/s), but similar to helium into silica ($2.4\text{-}5\text{-}5x10^{-10}$ cm^2/s), suggesting the pores are not filled with water and/or the process is controlled by the diffusion of other components.

Mechanical agitation, primarily through attrition grinding to less than 10 μm, was found to be an effective activation method for olivine (non-hydroxide) material.[71] Comparison tests were conducted at 15% solids, in a 0.64M $NaHCO_3$ + 1M NaCl aqueous solution at 155°C (311°F) and pCO_2=15.2 MPa (150 atm) for one hour. Standard feed olivine (<75 μm, no pretreatment) achieved 47% stoichiometric conversion at a rate of 0.010 $gMg/m^2/h$ (grams of Mg converted to carbonate per m^2 of surface area per hour of reaction time). Dry attrition grinding to <10 μm increased the stoichiometric conversion to 82% and rate to 0.045 $gMg/m^2/h$. Wet attrition grinding further increased the stoichiometric conversion amount to 100%, but reduced the rate to 0.006 $gMg/m^2/h$. Activation mechanisms are size reduction to increase surface area (wet grinding) and destruction of the crystal lattice to form an amorphous material (dry grinding).

The initial work at ARC focused on the use of a batch autoclave to achieve the high pressure and temperature required for suitable reaction rates.[74] Scale-up estimates to a full size plant revealed the batch autoclave as too costly for industrial use. A high-pressure high-temperature (HPHT) slurry flow loop reactor was designed to mimic a plug flow reactor with 100% recycle. The reactor can handle multiphase slurry (gas/liquid/solid) to 200°C (392°F) and 17.24 MPa (170.1 atm). Carbonation rates achieved were similar to the batch autoclave for the attrition ground material; however, the coarse mineral feed achieved a much higher extent of reaction. During autoclave batch testing, <400 mesh (<37 μm) olivine showed an extent of reaction at 4.2%, where in the HPHT flow loop, an extent of 72.0% was shown. In addition, coarser feed at <200 mesh (<75 μm) achieved 67-78% extent of reaction. It is thought that the turbulent environment in the slurry reactor resulted in high particle-to-particle interaction, therefore continually exposing fresh surfaces to reaction.

Park et al. at the University of Ohio investigated carbonation of olivine and serpentine similar to the work of O'Connor et al.[75] Direct (dry) carbonation on <125 μm particles of olivine, serpentine, and magnesia was carried out in pure CO_2 for 24 hours at 350°C (662°F) and total pressure from 0.1-2.5 MPa (1-25 atm). Quantitative data is not provided, but the discussion states that the degree of direct carbonation was negligible for all materials. Surface area measurements from BET analysis showed the presence of micropores between 20-50 Å. It was suggested that the pores were plugging up very fast at the beginning of the reaction resulting in a low carbonate conversion. Aqueous carbonation studied were carried out from 100-200°C (212-392°F), 1.5-2.5 MPa (15-25 atm), and 2-10 wt.% solids, with $NaHCO_3$ and NaCl additives. Again, quantitative results are not given; however, qualitatively increasing temperature and pressure increased carbonation rate, as did increasing $NaHCO_3$ concentration to1M and NaCl concentration to 2M.

Kutcha et al. at the University of Pennsylvania investigated the activation of serpentine minerals for enhanced CO_2 sequestration.[76,80] Focusing on various chemical and mechanical means for activation, he was able to demonstrate that the surface area of raw serpentine, which is ~8m^2/g, can be increased to >330 m^2/g. The pretreatment routes studied include particle comminution, magnetic separation, acid treatment, and HCl extraction. The extent of carbonation is significantly affected by particle size. Under identical test conditions, olivine particles in the 106-150 μm size range achieved 10.6% conversion, while particles <37 μm achieved 91.5% conversion. Magnetic separation was undertaken to remove the magnetite fraction from serpentine after grinding (to <37 μm). During heat treatment in air, magnetite naturally present in serpentine will oxidize to form hematite that forms a passive layer on the mineral surface and inhibits carbonation.

Magnetite removal did not increase carbonation conversion, but allowed the serpentine to be pre-heated in air, as opposed to a CO_2 non-oxidizing environment, thus simplifying the pretreatment process. Heat treatment results were similar to those presented earlier by McKelvy et al. Acid pre-treatment was conducted with HNO_3, H_2SO_4, HCl, and a combination of orthophosphoric acid, oxalic acid, and EDTA. Sulfuric acid proved the most effective acid for chemical activation, resulting in a surface area >330 m^2/g. However, all acids extracted Mg^{2+} from serpentine, therefore reducing the sequestration potential of the solid mineral. Molten salt extraction was studied using HCl to extract magnesium to a hydrated magnesium chloride which can be used to produce magnesium hydroxide. The process is energy and chemical intensive.

Zevenhoven et al. at Helsinki University of Technology has also focused on the capture of CO_2 emissions through direct dry mineral carbonation of magnesium silicate minerals.[46] Their approach is to optimize the kinetics of dry carbonation from serpentine or olivine in order to simplify the process (compared to a wet chemistry route). Tests on 50 μm particles of serpentine at 200°C (392°F) for 3 hours at 0.1 MPa (0.99 atm) and 1.5 MPa (14.8 atm) in N_2/CO_2 dry and wet gas mixtures showed no measurable carbonation. Heating the same serpentine to 1000°C (1832°F) for 10 minutes then cooling to 200°C (392°F) in a N_2/CO_2 dry atmosphere at 0.1 MPa (0.99 atm) also resulted in no measurable carbonation. Tests on 20 μm pure $Mg(OH)_2$ involved heating to 1000°C (1832°F) for 10 minutes, followed by cooling at 10°C/min to 200°C (392°F) at 0.1 MPa (0.99 atm) in various atmospheres of N_2, CO_2, O_2, and H_2O. All tests showed a conversion to $MgCO_3$, at an increasing rate below 300°C (572°F). A catalytic effect of water in the gas stream was seen on the carbonation amount, and no influence of oxygen content could be discerned.

A theoretical kinetic model was setup and applied to the results obtained. The forward rate constant (k_+) can be expressed by Equation 22.

$$k_+ = \frac{\beta}{(1-X)pCO_2 - \frac{Z \cdot X}{K_p}} \frac{dX}{dt} = k_0 e^{-\frac{E_{act}}{RT}} \tag{22}$$

Where β is the heating rate (°K/s), X is the fractional conversion of MgO to $MgCO_3$, pCO_2 is the partial pressure of CO_2 (bar), Z is the molar mass ratio M_{MgCO3}/M_{MgO} (2.0918), K_p is the equilibrium constant, dX/dt is the change of conversion X with time t, R is the gas constant, and T is the temperature (°K). The Arrhenius constant parameters k_0 and E_{act} must be calculated for each test. The equilibrium constant (K_p) can be obtained from Equation 23 relating the temperature (°K) and partial pressure of CO_2.

$$\ln K_p = \frac{11839}{T} - 20.219 = -\ln pCO_2 \qquad (23)$$

Equation 23 was applied to the test results to determine the effect of temperature on the rate constant. Each test condition resulted in an increase in rate constant up to ~320°C (608°F), then a rate decrease with increasing temperature. The temperature of 320°C (608°F) was identified as the turnover temperature, and corresponds to the maximum thermodynamic stability temperature given by Equation 24.

Further tests were undertaken to determine the effect of solid and gaseous catalysts, as well as operating pressure. Separate tests were conducting with 1 wt.% NaCl, $NaHCO_3$, or Al_2O_3 mixed into the $Mg(OH)_2$, and 500 PPM (vol.) SO_2 mixed into the gas phase. Following the same heat-up and cooling pattern of the previous tests, no discernable effect of these catalytic materials on carbonation rate was observed. The effect of pressure at 1.5 or 2.5 MPa (14.8 or 19.7 atm) total could not be accurately quantified due to competing dehydroxylation and carbonation reactions and limitations of the testing apparatus.

Teir et al. also at the Helsinki University of Technology studied the production of precipitated calcium carbonate (PCC) in the Finnish paper industry as a model for carbon dioxide sequestration using calcium silicate based minerals.[77-78] Calcium carbonate is produced in the paper industry as a filler and coating, and is produced by reacting lime with exhaust gas. The synthetic calcium carbonate has a higher purity than natural limestone due to purification during processing. The production of lime releases CO_2 from calcining and combustion heating; therefore, even though the subsequent sequestration from exhaust gas reduces CO_2 emissions; the net process is a CO_2

generator. If PCC can be produced from calcium silicate (e.g. wollastonite), the production of CO_2 can be significantly reduced.

PCC is primarily produced through carbonation of slaked lime. Limestone is calcined at 1000˚C (1832°F) produced dry CaO. The dry lime is mixed with water at 30-50˚C (86-122°F) to form a slurry at 20 weight %. The slurry is screened to remove impurities from the original limestone. A high shear mixer maintains suspension of the slurry in a stirred tank reactor where it is reacted with CO_2 from an exhaust gas source (after scrubbing). The particle size, shape, and surface properties of the PCC are controlled through the carbonation temperature. The pH of the lime slurry is near 12 at the beginning of the process but drops to approximately eight at equilibrium. The reaction rate is greater with increasing pressure, and the PCC reactors normally operate at 0.2-0.3 MPa (2.0-3.0 atm).

Wollastonite was investigated in a process model as an alternative feedstock to the production of PCC to calculate the net CO_2 reduction. The chemical composition of pure wollastonite is $CaSiO_3$, and it is normally found with limestone deposits. A review of published research was undertaken to ascertain the most promising methods for the process modeling. Direct dry and aqueous carbonation of wollastonite has been tested at 25°C (77°F) and atmospheric pressure for 0-600 hours and found to be too slow for further investigation. Indirect carbonation with hydrochloric or acetic acid, where the acid is used to extract Ca^{2+} ions for subsequent reaction with CO_2, was selected for further study. The carbonation of wollastonite in a batch autoclave was studied by the Albany Research Center. Carbonate conversion of 70% could be achieved, but required attrition grinding to 2-4 μm and a high pressure high temperature batch reactor (185°C (365°F) and 15.2 MPa (150 atm)), followed by separation from the SiO_2. This process was discarded from further study due to complexity. A detailed process model was setup with Aspen Plus 12.1® and Outokumpu HSC-4 software for the standard PCC process in comparison to acid extraction. Using the acetic acid process, a net 0.34 t CO_2 could be sequestered per ton of PCC produced; however, the processing cost is several times higher than sales of the CO_2 emissions credits would return, notwithstanding the fact that three to five times more rock would have to be mined and transported, which was not taken into account in the process model. Naturally occurring calcium silicates do not represent a feasible source for industrial carbonate fixation.

4.2.4.2 Oxides (Calcium and Magnesium). The simple oxides of calcium and magnesium are more effective for sequestering carbon dioxide than their respective silicates, however due to their high reactivity they are rarely found in nature. These oxides do occur in slag, and work by researchers in Spain on the natural form of these minerals is valuable for better understanding sequestration of carbon dioxide in slag.

Abanades et al. at the Instituto de Carboquímica (CSIC) in Spain have done extensive research on the use of CaO as a sorbent to capture CO_2 from industrial combustion processes, primarily for large-scale power generation systems[54-60]. His work is partially funded by the European Coal and Steel Community (7220-PR-125). This work has focused on the characteristics of CaO to serve as a regenerative sorbent, and the design of a fluidized bed capture system to effectively use this sorbent. The reaction of carbon dioxide with lime is very simple and proceeds strongly exothermically as detailed previously. The equilibrium limit in terms of CO_2 capture efficiency from gas phase in a lime carbonation-calcination reaction is shown by the reaction in Equation 24, where T is expressed in °K[55]. This equation was developed from data by Baker.[61]

$$C_{CO_2,eq} = \frac{1.462x10^{11}}{T}\exp(\frac{-19130}{T}) \tag{24}$$

The work by Abanades et al. has focused on a reactor operating at 650°C (1202°F) and atmospheric pressure. Using coal combustion flue gases at 12-15 vol. % CO_2 capture efficiencies higher than 90% have been exhibited. Although the initial capture rates of CO_2 are high, the regenerative performance of CaO as a sorbent drops rapidly upon cycling through the carbonation-calcination process as shown in Figure 4.1.

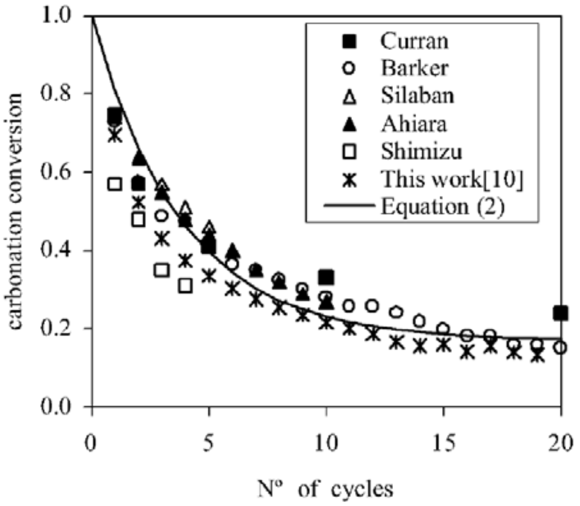

Figure 4.3. The Decay in CO_2 Sorbent Capture Capacity With the Number of Carbonation/Calcination Cycles (from Abanades[58])

The sharp decline in activity for carbonate conversion is due to limited diffusion of the CO_2 through the carbonate product layer and pore closure combined with grain growth, which leads to internal sintering and overall shrinkage of the particle.[59] The latter factors reduce the effective contact area for CaO-CO_2 reaction within the fluidized bed. While data from Abanades et al. work is useful in slag-offgas reactor and in understanding the carbonation kinetics of calcium oxide, it is not focused on a permanent solid carbonate disposal method, but a solid sorbent to compete with liquid sorbent (amine) systems.

Fernandez et al. from the University of Barcelona studied the carbonation of MgO slurries at atmospheric pressure.[89] Calcined magnesite (89.3% MgO) was mixed with water to form a slurry through which CO_2 was passed. The reactivity was found to be directly related to the specific surface area of the MgO. A specific surface area of 43.1 m^2/g yielded 90% MgO conversion in 50 minutes, while 210 minutes was required to reach the same yield with a specific surface area of 1.8 m^2/g. Specific surface area could be controlled by time and temperature during calcining, with an increase in both reducing the specific surface area (due to internal sintering). A decrease in particle size (from 235 μm to 40 μm), increase in CO_2 partial pressure (from 0.05 to 0.1 MPa (0.5 to 1.0 atm)), increase in solid-liquid ratio (5-50 g/l), increase in CO_2 flow rate (90-690 cm^3/min), and increase in temperature (5-45°C (41-113°F)) were all beneficial in speeding up the reaction rate. The kinetic relation expressed by Equation 25 was found to be valid for MgO slurry carbonation for the first 10 minutes.

$$1-(1-X_{MgO})^{\frac{1}{3}} = kt \tag{25}$$

X_{MgO} is the fraction carbonated; *k* is the rate constant (min^{-1}), and *t* is time (min). A plot of the rate constant versus temperature yields an activation energy of 29.1 kJ/mol. Studies of the reaction mechanisms indicate that the process is mixing controlled and chemical reaction controlled, with reaction of the magnesium carbonate on the particle surface with CO_2 to form magnesium bicarbonate as the rate-determining step.

4.2.4.3 Cement Minerals. A study of cement can provide valuable insight to slag carbonation, as they have many of the same mineral phases. Cement and slag both contain calcium silicates, calcium aluminates, and calcium ferrites. While cement chemists are primarily concerned with the hydraulic activity of these phases, work has been undertaken to understand long-term carbonate formation and the corresponding structural and physical changes that take place.

Berger et al. studied the carbonation of calcium silicates and calcium aluminates in their research of cement chemistry.[81-86] Even though this work was undertaken for accelerated curing of cement, the chemistry involved pertains directly to geological CO_2 sequestration. Initial work tested the compressive strength of pure cement minerals carbonated after hydration. Pure Ca_3SiO_5, β-Ca_2SiO_4, $Ca_3Al_2O_6$, and $C_{12}Al_{14}O_{33}$, were mixed with water at 92 wt.% solids for five minutes then compacted to 5.86 MPa (57.8 atm) in a cylinder and exposed to CO_2 at 0.39 MPa (3.8 atm) for five minutes. The Ca_3SiO_5 and β-Ca_2SiO_4 minerals produced an appreciable temperature rise upon reaction and the resultant strength was similar to standard cement. The aluminate samples showed no appreciable temperature rise or increase in strength from carbonation.

The carbonation of tricalcium and β-dicalcium silicate was studied further to understand the process chemistry. Powdered Ca_3SiO_5 (3300 cm^2/g) and β-Ca_2SiO_4 (4500

cm^2/g) were mixed with 12.5 wt.% water and subjected to pCO_2~0.1 MPa (1 atm) for varying times. From X-ray diffraction studies and ignition loss determinations the initial chemical reactions occurring for the silicate was found to be according to Equation 26.

$$nCaO \cdot SiO_2 + yH_2O + (n-x)CO_2 \rightarrow xCaO \cdot SiO_2 \cdot yH_2O + (n-x)CaCO_3 \qquad (26)$$

This initial reaction takes place with CO_2 accelerating the hydration of the silicate to form C-S-H gel and $CaCO_3$. The stoichiometry of the gel is similar to that formed in conventional cement hydration. However, the gel carbonates rapidly to eliminate lime and produce calcite and silicate gel, yielding an overall reaction shown by Equation 27.

$$nCaO \cdot SiO_2 + nCO_2 + zH_2O \rightarrow SiO_2 \cdot zH_2O + nCaCO_3 \qquad (27)$$

The carbonation reaction kinetics of β-Ca_2SiO_4 and Ca_3SiO_5 powders were determined as a function of material parameters and process conditions. Both silicates follow a decreasing-volume diffusion-controlled kinetic model expressed in Equation 28.

$$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2 = K_T^{'}t \qquad (28)$$

In this equation, α is the degree of carbonation, K_T' is the apparent rate constant, and *t* is the time of reaction (hours). A plot of $\log[1-(1-\alpha)^{1/3}]^2$ versus log(*t)* yields a straight line with slope approximately equal to 1.0. Substituting in the temperature dependency of K_T' as an Arrhenius equation provides a direct relationship for the degree of carbonation, as shown in Equation 29.

$$\alpha = 1-\left\{1-\left[K_o^{'} \exp^{\frac{-E_a}{RT}} A^2 t\right]^{\frac{1}{2}}\right\}^3 \qquad (29)$$

K_o' is the pre-exponential term in the Arrhenius relationship times the diffusion coefficient; E_a is the activation energy; R is the gas constant; T is the temperature (°K), and A is the average particle surface area (assumed monodispersed size). The values for the reaction parameters for both silicates are shown in Table 4.3.

Table 4.3. Reaction Parameters for Calcium Silicate Carbonation, from Goodbrake[85]

Phase	**K_o' (h^{-1})**	**E_a (kcal/mol)**	**ΔH_f (kcal/mol)**
Ca_3SiO_5	$3.44x10^4$	9.8	-83
β-Ca_2SiO_4	$2.39x10^9$	16.9	-44

These values were obtained from Arrhenius plots for both silicates. The reaction conditions were fixed at 0.1 MPa (0.99 atm) CO_2 at 100% relative humidity.

The carbonation mechanisms for anhydrous powders are best described by Equation 26. A small amount of C-S-H gel forms, which rapidly loses CaO and water to form amorphous silica. The carbonation heats of formation are shown in Table 4.3 and are strongly exothermic. Both silicates form aragonite during carbonation, as long as the water stays in the vapor phase. If water condenses on the sample, they will form calcite initially, which transforms to aragonite as the sample dries.

4.2.4.4 Other Mineral Based Processes. Several other processes are worth mentioning in brief for their value in comparison with geological sequestration. Golomb at the University of Massachusetts Lowell investigated the formation of a stabilized limestone-CO_2 emulsion for carbonate sequestration into seawater.[79] Finely ground calcium carbonated (10-20 μm) is mixed with liquid or supercritical CO_2 in water to form a stable emulsion. The $CaCO_3$-coated CO_2-globules are stable and settle in water, thus allowing dissemination into the ocean. Lackner mentions that citric acid and EDTA are two chelating agents shown to break apart serpentine mineral; however, this method has not been researched in detail.[53] TecEco, a company in Australia envisions the use of forsterite and serpentine minerals as feedstock for making a magnesium oxide based cement (Eco-cement) that would sequester CO_2 from the air as it cures.[87] The company fails, however, to properly credit the CO_2 released through calcining, and at best (even with a solar powered Tec-Kiln), this process provides a zero sum for total carbonate sequestration.

4.2.4.5 Biomimetic Processes. Several biological processes form calcium carbonate from (dissolved) calcium oxide. These processes (e.g. shellfish exoskeletons) use a natural catalyst to increase the formation rate compared to a geologic process. The use of carbonic anhydrase catalyst to mimic the biological process (biomimetic) for industrial scale carbon dioxide sequestration has been proposed by Bond, Medina, and Simsek-Ege.[163-166] Carbonic anhydrase, a zinc metalloenzyme, increases the hydration of CO_2 to form carbonic acid, which is defined as the rate-limiting step of the fixation of carbon dioxide into calcium carbonate in aqueous solution. The overall objective of their research is to develop an industrial CO_2 scrubber using carbonic anhydrase to catalyze the rate of CO_2 hydration for subsequent fixation into stable mineral carbonates. Bovine carbonic anhydrase (BCA) was tested in a laboratory scale exhaust-seawater contactor and found to reduce the time for calcium carbonate precipitation from 20 minutes to less than 10 seconds. This process was repeated 15 times with the same catalyst (BCA immobilized on alginate beads) and exhibited less than 1% loss in experimental yield. BCA was also found to be stable to 70°C and resistant to SO_x and NO_x inhibition at levels expected in normal power plant exhaust gas.

5. OFFGAS GAS CO_2 SEQUESTRATION IN SLAG

5.1. CO_2 EMISSIONS IN STEELMAKING

The primary direct source of carbon dioxide emissions in the steel industry is the production of iron followed by the production of steel. Traditional ironmaking technology, based on blast furnace production, is a large producer of CO_2 emissions. To achieve a net reduction in carbon dioxide emissions, three different areas are being investigated for the iron and steel making industries: energy conservation, alternative iron and steel making technologies, and CO_2 sequestration. These three areas are listed in order of immediate effectiveness and cost impact. Energy conservation can be implemented immediately in all plants, and both reduces the net amount of CO_2 generated (directly and indirectly) and results in a cost reduction to the manufacturing plant. Many alternative iron and steel making technologies are available or in development. Most focus on cost reduction for the production of iron and steel, primarily through energy or material requirement reductions. A serendipitous side benefit is the reduction in energy or raw material correlate to a reduction in CO_2 generation. Both the energy conservation and alternative production technology areas will provide the bulk of CO_2 reduction in the iron and steelmaking industries. Sequestration technologies will provide a direct reduction in CO_2 emissions, but generally do not provide a direct commercial benefit to the steel producer at the present time. If CO_2 regulations develop to the point where emission credits are bought and sold, the cost-benefit of installing a sequestration technology versus emissions penalty will be undertaken. This section will primarily focus on carbon dioxide emissions from steelmaking (BOF, EAF, and other), which is reflected in the data presented subsequently.

5.1.1. Amounts. Carbon dioxide production in the steel industry has been well studied both by geographic region and technology, mainly to establish a baseline amount for meeting future regulations.

Research by Stubbles research in 2001 shows the historical trends of U.S. domestic steel production, energy use, and CO_2 emissions.[110] Advances in technology, such as replacement of OH production with BOF and EAF, mini-mills, continuous casting, and thin slab casting have reduced U.S. steel industry required energy per ton from 47.4 GJ (45 million BTU) in 1950 to 17.9 GJ (17 million BTU) in 2000. By percentage of total domestic energy consumption, the U.S. steel industry dropped from 5% in 1970 to 1.6% in 2000. Raw steel production increased slightly during this same time period, from approximately 95 to 100 million tons. Carbon dioxide emissions have only been tracked since 1990, but show a similar trend to reduction in energy use. Presented as carbon equivalent (CE) units (equal to 12/44 or 0.27 x tons CO_2), Figure 5.1 shows the U.S. steel industry values during that time, along with predicted trends until 2030.

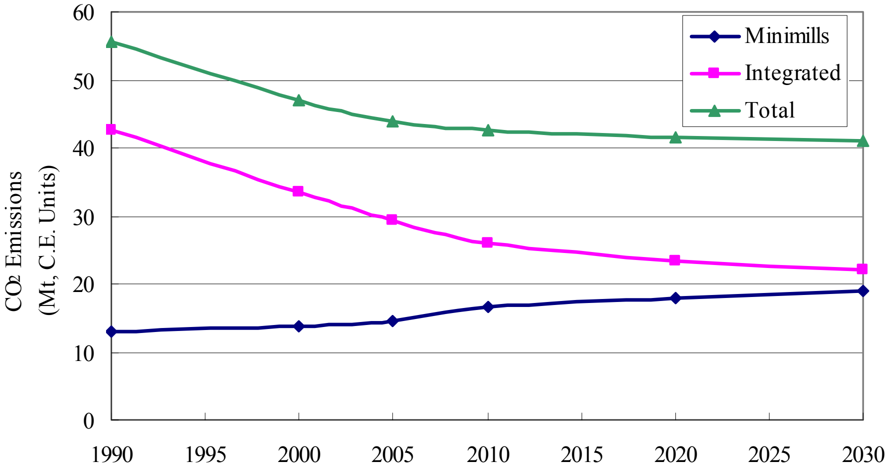

Figure 5.1. U.S. Steel Industry CO_2 Emissions from 1990-2030 as Carbon Equivalent Units, data from Stubbles[110]

Integrated mills produce significantly more CO_2 than mini-mills because of their reliance on coke making and blast furnace ironmaking. In 2000, mini-mills were responsible for the production of 13.65 million tons of CO_2 (CE units), of which 80% (10.86) came from electrical production at the power plant. The integrated mills produced 33.46 million tons of CO_2 (CE units) of which 64% (21.47) came from the production and use of coke. Based on the 2000 steel production rate, the steel industry on an average produced ~0.4 carbon equivalent tons of CO_2 per ton of steel shipped. Reduction in electrical use in the mini-mill and reduction of coke production/use in the integrated mill represent the largest factor that can affect CO_2 generation in these types of plants, respectively.

On a domestic and global scale, steel industry production represents only a small fraction of anthropomorphic CO_2 emissions. The U.S. steel CO_2 emissions in 2000 was 43 million metric tons (CE units), which ranks as 2.9% of the U.S. total output (1500 million tons) and 0.6% of the world output (7000 million tons). Even the total world anthropomorphic output of 7 billion tons (CE units) is but a small fraction of the natural amount produced, which is estimated at 190 billion tons annually. Most of the CO_2 produced annually (total) is taken up by the oceans or biomass. An estimated net positive 2-3 billion tons per year is being added to the 750 billion tons in atmospheric storage.[110]

Worrell et al. has also evaluated the U.S. domestic steel industry for the purpose of identifying energy and carbon dioxide emission reduction opportunities.[111] A comparison can be made using the data for iron and steelmaking only (part of Worrell's data set includes ferroalloy and ferrous foundry productions). In 1994, the primary energy used for integrated steelmaking was about three times greater than that used in secondary steelmaking (1439 PJ compared to 425 PJ). The energy intensity, expressed as energy per metric ton of steel produced, of production was 26.0 GJ/t and 11.8 GJ/t, respectively, for the integrated and secondary route. The total sector primary energy intensity is 20.4 GJ/t for 1994, which compares favorably to 20.9 GJ/t from Stubbles estimate. Total carbon dioxide emissions from steelmaking in 1994 were 34.4 million metric tons CE, which is 27% less than Stubbles estimate of 47.2 million metric tons CE (52 million short tons). Carbon dioxide emission intensity for the whole steelmaking sector averaged 0.38 tons CE per ton steel produced, which compares to about 0.52 tons CE per ton steel produced.

Afonin provides similar data for the steelmaking sector in Russia.[113] Based on 1998 data, the total CO_2 emissions from the integrated steelmaking sector stand at 48.6 million tons carbon equivalent, which is 8.5% of all Russian CO_2 emissions. On an intensity basis, this equals 1.4 tons CE per ton steel produced. Russia produces more CO_2

emissions than the U.S. (total tons equivalent) in steelmaking, but produces about one-third the amount of steel, which accounts for the higher CO_2 intensity output.

Birat et al. has studied iron and steelmaking in the French and European sectors to understand the best CO_2 mitigation route.[114-118] In 1989, the French steel industry produced a total of 26.3 million metric tons CO_2 total, at an intensity of 0.42 tons CE per ton steel, based on integrated steelmaking. This is comparable to U.S. emission rates of 2000. By 1994, the CO_2 intensity had dropped to 0.40 tons CE per ton steel, which is approaching the theoretical limit. France has an extremely low CO_2 emission rate of 0.03 tons CO_2 per ton steel based on EAF with 100% scrap due to their high reliance on nuclear power. Recycling is being researched as the most powerful method of reducing CO_2 emissions for the material community as a whole. This includes use of the steel in the EAF and use of the slag to offset limestone used in cement production.

Carbon dioxide generation data from the steel industries of other countries has not been studied as in-depth, but some information is available from the literature. Holappa reports data from Finnish ironmaking that can be used to estimate the carbon dioxide intensity for that region, which is approximately 0.53 tons CE per ton steel for integrated steelmaking.[118] Data from Emi[119] and Gielen[120] show the 2005 carbon intensity rate for Japanese integrated steelmaking is 0.46 tons CE per ton steel.

Anderson et al. reported the results of a thorough study comparing the carbon dioxide emissions and energy requirements for 30 different steelmaking routes.[121] To the BF/BOF baseline of 89% hot metal/11% scrap, they have compared standard ironmaking/steelmaking (DRI/EAF) and alternative iron sources/steelmaking routes, such as FASTMET, FASTEEL, ITmk3, COREX, and HIsmelt. The amount of material from alternative iron sources was compared at 80%, 50%, and 30%. The carbon dioxide emission data from this publication is shown in Figure 5.2. This data was published in 2002.

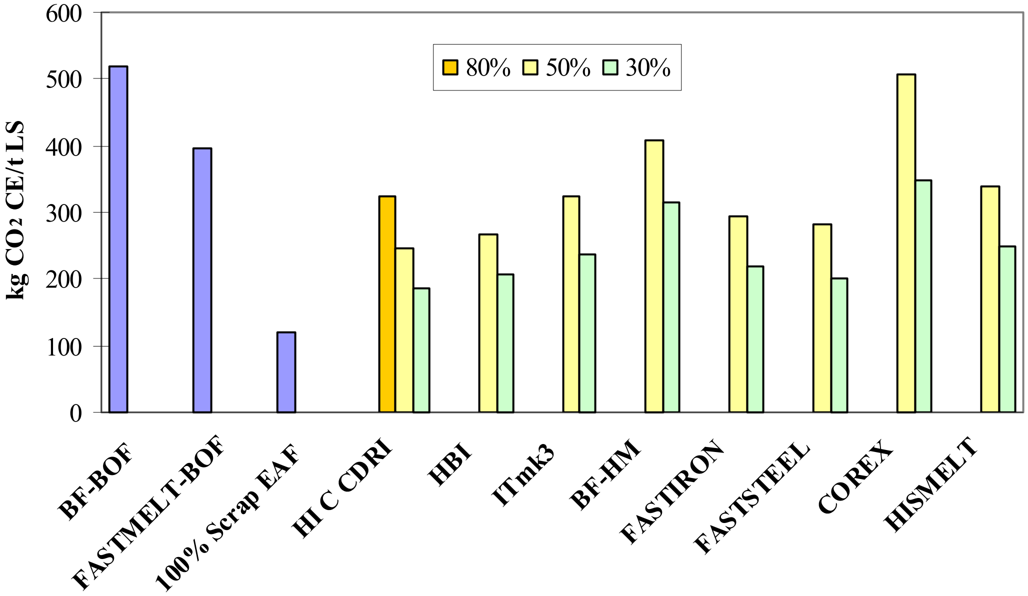

Figure 5.2. CO_2 emissions (CE) for Various Steelmaking Processes, data from Anderson 2002[121] (Percentage values show the amount used in EAF, with balance from scrap)

The highest CO_2 producer is the traditional BF-BOF route at 519 kg CE per ton of liquid steel. The lowest CO_2 producer is 100% scrap in an EAF at 119 kg CE per ton liquid steel. All other processes are for EAF production and fall in between these boundaries. As the amount of scrap blending is increased, the carbon dioxide production decreases. The COREX process at 50% scrap produces just 2% less CO_2 emissions as BF-BOF. This value is higher than that published by Kepplinger et al.[122] for 1999 data, even when credits for slag substitute in to clinker feed are used because of differences in offgas credits and carbon use in foamy slag. Anderson et al. reports 508 kg CE while Kepplinger et al. reports 424 kg CE, both per ton of liquid steel. Comparison of 100% scrap in an EAF with Goodfellow et al. shows that the indirect sources produce almost 70% of the CO_2 generated, with the largest fraction from electricity generation.[123-124] Goodfellow shows that U.S. EAF production with 100% scrap produces ~140 kg CE/t LS (compared to 119 kg CE from Anderson) due to high electrical generation from hydrocarbon sources (69%). However, Canadian EAF production with 100% scrap produces ~89 kg CE due to less electrical supply from hydrocarbon fuel (32%), and French EAF production is at 46 kg CE due to an even lower reliance on hydrocarbon based fuels (5%).

5.1.2. Offgas Composition. The composition of steelmaking offgas, especially as it changes during the heat, is an important factor when considering the design of a sequestration system. The concentration of CO_2 will change during the various stages of the steelmaking heat, such as charging, blowing, refining, and tapping. In addition, other offgas constituents, such as CO, O_2, N_2, and H_2, may affect the performance of the sequestration technology.

Evenson et al. reports on an expert system relying on feedback control from offgas analysis in EAF operations.[125] A sampling probe installed at the entrance to the fixed duct just after the combustion gap provides real time analysis for CO, CO_2, H_2, and O_2. Sampling at this location allows chemical analysis before combustion air. A second sampler was placed at the end of the water-cooled duct downstream of the combustion chamber. Table 5.1 shows the upstream and downstream offgas composition for the average of 30 heats. This data is reported for an upstream flow rate of 15900 Nm^3/hr (9358 SCFM) and a downstream flow rate of 68400 Nm^3/hr (40259 SCFM), yielding a dilution flow ratio of 4.3.

Table 5.1. Average (30 Heats) EAF Offgas Composition at Deacero SA de CV, data from Evenson[125]

Component	Upstream Composition	Downstream Composition
CO	21 ± 2.5%	0 ± 0%
CO_2	22.7 ± 2.4%	10.3 ± 1%
H_2	8.1 ± 1.2%	N/A
O_2	0.6 ± 0.5%	11.3 ± 0.7%

Grant reports EAF offgas data from a U.S. based shop (location not specified) in his work with post-combustion optimization.[126] Figure 5.3 shows the offgas composition profile at the inlet of the fixed duct just after the combustion gap (same as Evenson et al. upstream location) for a period of 15 heats. A comparison to data from Evenson shows the CO average similar (~18%), the CO_2 average a little lower (~15%), the H_2 average similar (~6%), and the O_2 value higher (~4%), with the latter value showing less combustion of the CO. These variances are due to differing operations at the two plants.

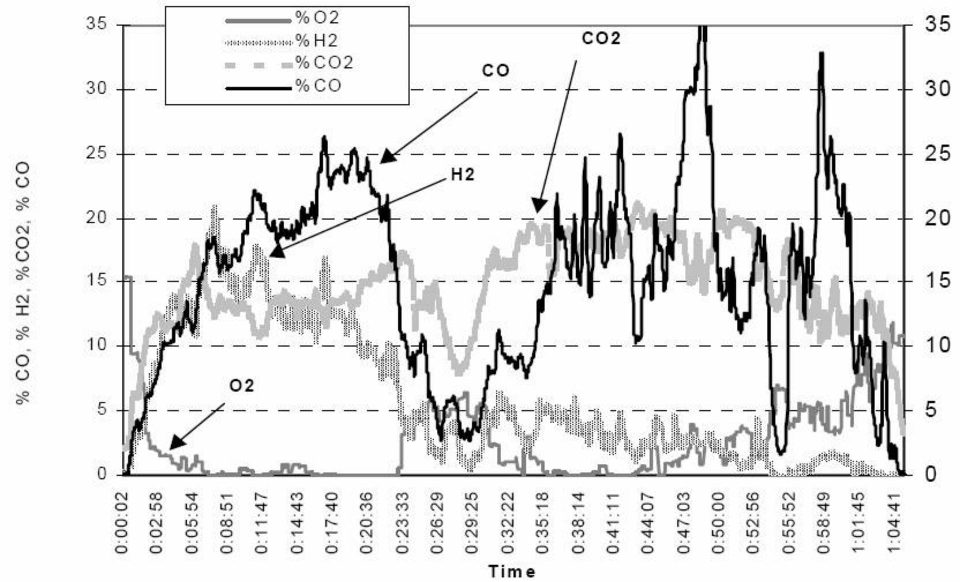

Figure 5.3. EAF Offgas Composition at the Entrance of the Fixed Duct, from Grant[126]

Allendorf et al. reports on the development of a laser-based sensor for real-time measurement of BOF steelmaking offgas (CO and CO_2 concentration); however, no industrial performance data is listed.[127,167,168]

5.1.3. CO_2 Emission Reduction. Reduction of carbon dioxide emissions from steelmaking is being studied directly in Europe and Japan, and indirectly in the U.S. as an offshoot of energy conservation.

The Europeans and Japanese have undertaken proactive research initiatives for the purpose of reducing carbon dioxide emissions, and in some cases, to develop carbon-free steelmaking. Most of the research involves the use of new technologies to replace or augment the traditional blast furnace ironmaking. Emi lists pulverized coal, plastic, and LNG injection, increased blast temperature, and decreasing moisture as current technologies to reduce CO_2 emissions by up to 23% in Japanese iron making.[119] Alternative iron technologies, such as ITmk3, HIsmelt, and Tecnored may provide 20-25% reduction but are still in development. Birat lists several carbon free technologies being proposed, but they are many years from large-scale commercial development.[117] These technologies include hydrogen reduction and direct electrolytic production of iron. Both technologies require a source of electricity that is not carbon based to provide a net reduction in CO_2 emissions. In both European and Japanese markets, recycling was identified as the powerful method with immediate implementation to provide a net reduction of CO_2 emissions. Life cycle analysis, such as detailed by Holappa, take into account all products from the steelmaking hub (steel, slag, offgas, wastewater, scrap, waste heat, dust, etc.) and determine a use or recycling role that each can serve.[118] Regulations and methods should be sought to increase the scrap usage in these countries.

Work in the U.S. has focused on energy reduction as the primary goal, which will, in turn, reduce CO_2 emissions. These reductions will mostly be realized from indirect sources as the U.S. relies heavily on hydrocarbon fuels for electrical generation (~69%).

Worrell et al. investigated 47 energy efficient practices and technologies, which can directly impact energy consumption and CO_2 emissions.[111] All practices were evaluated according to fuel, electricity, and primary energy savings per ton, annual operating costs, retrofit capital costs, carbon dioxide emission reductions, and percentage of production to which the measure can be applied nationally. Ranking the measures for cost of conserved energy shows continuous casting, natural gas injection (into BF), and increasing bed depth (in BF) were the three best methods of improvement for integrated manufacturing. For secondary steelmaking oxy-fuel burners, scrap preheating, and post-combustion were the three best methods of improvement. If all measures identified were implemented, a net 18% in energy savings and 19% reduction in carbon dioxide emissions would be realized. The data from this study was implemented into a spreadsheet model by Molburg and Thimmapuram for quicker evaluation in the future.[112]

Stubbles provides the history of energy reduction in the U.S. steel industry. The drive towards near net shape final product has provided the largest gains. Continuous casting and thin slab casting have reduced energy consumption 36.9 GJ/t to 21.1 GJ/t (35 million BTU/t to 20 million BTU/t). The move towards strip casting and closure of inefficient facilities should drop the industry amount to ~14.8 GJ/t (14 million BTU/t) by 2010.[110]

The data from Anderson et al. clearly shows that steel production from scrap provides the lowest amount of CO_2 emissions (and energy requirement). The U.S. automotive scrap market is running near the 100% recycling rate, and it is doubtful with increasing scrap demand from China that the U.S. can improve much in this area.[121]

5.2. CARBONATE FORMATION IN STEELMAKING SLAG

Steelmaking slag can be considered a mineral source, thus the work accomplished for geological sequestration is applicable for understanding the mechanisms for sequestration of carbon dioxide. Steel slag, however, is a derived mineral, in that it contains a mixture of many minerals found in nature, but it is not naturally produced. Because it is an industrial co-product, it is subject to environmental regulations and controls not imposed on natural minerals containing the same phases. The high content of CaO, MgO, and SiO_2 in slag leads to the formation of silicates, which are similar to those minerals studied under geological sequestration (olivine and wollastonite). The presence of high iron oxide content, however, leads to phases not as widely studied for geological sequestration, and gives rise to unique work with steelmaking slags.

5.2.1. Current Slag Sequestration Research. Several groups of researchers are investigating the carbonation of steelmaking slag for use as an industrial sequestration reagent. This research has focused on a wide variety of carbonation routes from aqueous dissolution to exposure to supercritical carbon dioxide to steam-CO_2 reactors. The majority of the processes focus on using slag as a sequestering agent. Some of the research involves the use of slag to make an end product such as blocks or construction material or waste containment.

Huijgen and Comans at the Energy Research Centre of the Netherlands (ECN) have done the largest amount of recent research on the use of steelmaking slag for mineral-based CO_2 sequestration.[90-94] The literature review covers much of the background geological sequestration research described earlier, including mineral selection, thermodynamics, pre-treatment and processing methods, and kinetics.[90]

Huijgen and Comans selected steel slag for experimental work on mineral CO_2 sequestration due to its high theoretical capacity (0.25 kg CO_2/kg slag). Slag was mixed with water and reacted with CO_2 in a batch autoclave reactor. Process conditions were particle sizes of <38 μm to <2000 μm, temperature from 25-225°C (77-437°F), reaction time from 2-30 minutes, and partial pressure of CO_2 from 0.1-2.9 MPa (0.99-28.6 atm). Particle size was found to have a strong effect on conversion rate, increasing from 25% conversion with the <2000 μm fraction to 70% conversion with the <38 μm fraction. The percent conversion is inversely proportional to the square root of the particle size (volume based mean diameter). As Ca conversion was not effected by the stirring rate in the reactor, they concluded that Ca-diffusion through the matrix is the rate-limiting step. A temperature increase of 50-175°C (122-347°F) improved the Ca conversion from 48% to 70% (at 106 μm particle size). The data fits an Arrhenius equation well in this range, yielding an activation energy of 3.6 kJ/mol which is consistent with solid-state diffusion control. Reaction time and CO_2 partial pressure had milder effects on Ca-conversion, with both factors increasing conversion from 40-45 to 50-55%. They concluded that the process can yield Ca-conversion more than 80% at relatively mild conditions ($d<38$ μm, $T=200$°C (392°F), $pCO_2=1.0$ MPa (9.9 atm), $t=15$ minutes).

Scanning electron microscope analysis of the carbonated steel slag helps reveal the rate determining mechanism. Figure 5.4 shows a back-scattered electron (BSE) image of a polished steel slag sample after carbonation. The core of the particle is calcium silicate and calcium ferrite, two common slag phases. Upon carbonation the Ca diffuses outward from the calcium silicate phase leaving a Ca-depleted SiO_2 phase behind. The Ca on the rim of the particle reacts to form $CaCO_3$. The calcium carbonate rim and silica phases both provide a hindrance for further carbonation by limiting the diffusion rate of Ca to the surface.

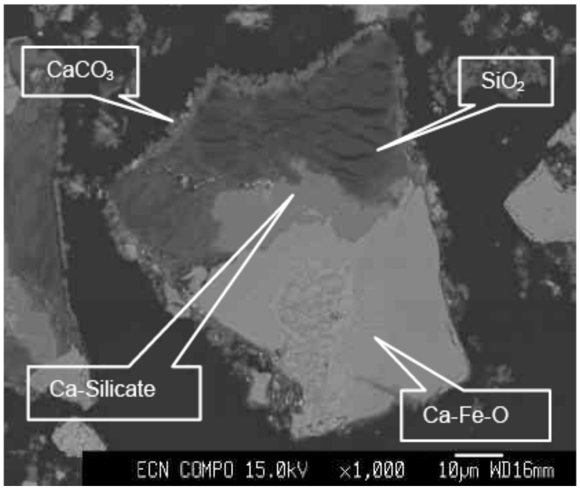

Figure 5.4. BSE-image of carbonate steel slag particle, from Huijgen[92]

A comparison of wollastonite with steel slag shows the latter to have a higher reactivity to sequester CO_2. Figure 4.5 shows the comparison of steel slag and wollastonite for a range of temperatures.

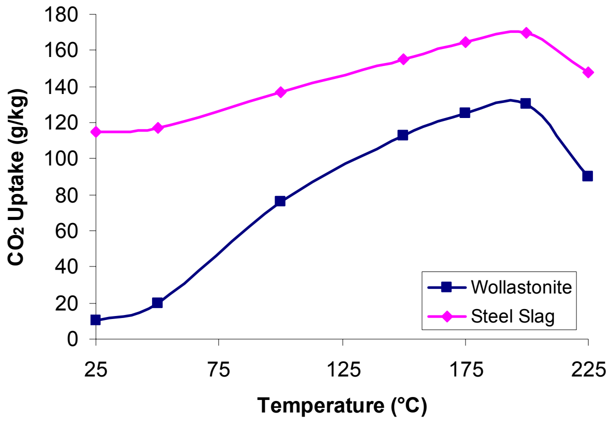

Figure 5.5. CO_2 uptake of Wollastonite versus Steel Slag in a Batch Autoclave (d<106 µm, pCO_2=2.0 MPa (19.7 atm)), data from Comans[91]

At constant process conditions (particle size <106 µm and pCO_2 of 2.0 MPa (19.7 atm)), steel slag was able to sequester 115 g CO_2 per kg slag versus 10 g CO_2 per kg wollastonite at ambient temperature, a reactivity more than 11 times greater. Peak reactivity was achieved at ~200°C (392°F), in which steel slag and wollastonite reached 170 and 135 g CO_2 per kg, respectively. A decrease in reactivity above 200°C (392°F) was due to the lowering of CO_2 dissolution into water, making the delivery of CO_2 to the particle surface the limiting factor. The peak values obtained for slag are 68% of the stated theoretical maximum (0.17 kg versus 0.25 kg).

As an extension of their work with precipitated calcium carbonate formation from primary silicate ores, Teir et al. at the Helsinki University of Technology have investigated the carbonation of slags from the iron and steel industry.[95] The Finnish steel industry produces approximately 1.3 Mt of steel slag per year. It is available at 10 €/t compared to wollastonite at 200 €/t. They propose to use an acetic acid process for extraction of Ca^{2+} ions that would then be used to precipitate calcium carbonate by reaction with CO_2 in a slurry crystallizer. Blast furnace and steel slag were obtained from Ruukki steel plant at Raahe, Finland, which produces 0.57 Mt and 0.30 Mt annually of these materials respectively. Annual CO_2 emissions from the plant are estimated at 4.74

Mt. Blast furnace slag showed rapid extraction of Ca^{2+}, with 97% extracted in 20 minutes at 60°C (140°F) compared to 38% extraction achieved with wollastonite under the same conditions. Further work is planned with this process.

Stolaroff et al. proposed to form dilute aqueous alkali-metal solution formed from steel slag or concrete that can be used to extract CO_2 from ambient air.[96-99] Steel slag at three different size fractions (45-74 μm, 74-300 μm, and 300-600 μm) was leached with de-ionized water and a pH buffer at ambient temperature to measure the amount of Ca^{2+} extracted. The initial rate and extend of calcium dissolution is higher for smaller particle sizes and lower pH. Approximately 50% of the Ca^{2+} is leached within the first minute, and 80% within the first hour. A process reaching near terminal concentration of Ca^{2+} may be reached in a few hours.

Their recommended industrial process uses the slag in a water spray bed, as shown in Figure 5.6. In this method, slag is heaped on concrete pads. Water is sprayed on the slag, leaching Ca^{2+} and forming $Ca(OH)_2$. The water is collected and pumped back through the sprayers. As the solution falls through the air, it captures CO_2 from the atmosphere creating $CaCO_3$, which is deposited on the slag. A calculation of CO_2 absorption into the aqueous solution shows that a 0.8 mm (0.03 inch) droplet falling from 10m (33 ft) height will utilize 84% of the Ca in solution in forming carbonate. Estimates are made of water use, pumping energy, and materials flow to yield 32000 tons of CO_2 sequestered per year for 140000 tons of slag, at an average cost of \$8/ton-CO_2.

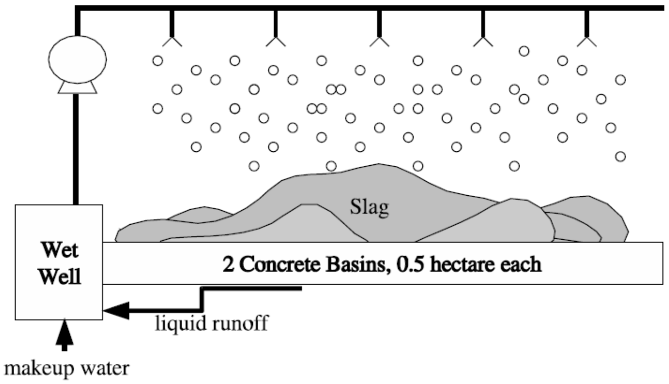

Figure 5.6. Spray Bed for Carbonation of Steel Slag, from Stolaroff[98]

Hills, Johnson, et al. have studied the accelerated carbonation of stainless steel slag and other materials for the purpose of rapid stabilization to prevent leaching of heavy metals during disposal.[27,100-103] The primary constituent in the slags tested was calcium silicate. Carbonation was carried out in a 100% CO_2 atmosphere at 0.3 MPa (3.0 atm) for 24 hours. The slag was mixed with water in varying ratios, and the maximum carbonation (20% weight gain) was achieved with 12.5 wt.% water in solids. No carbonation occurs at 0% water, and increasing the water above 12.5 wt.% decreases the carbonation. Comparison of the results with industrial materials (pulverized fly ash, municipal solid waste incineration ash, de-inking ash, and ordinary Portland cement) shows a directly proportional trend of carbonation weight gain with weight percent CaO in material. X-ray diffraction revealed that the carbonation reaction took place by γ-Ca_2SiO_4 conversion to calcite (this is a falling slag). Calcite was found to be the form of the carbonate product. Further testing showed that grinding prior to carbonation led to 10 times the compressive strength achieved, but this was not correlated to the amount of CO_2 captured.

A second set of tests was conducted on the stainless steel slag only, using the optimum conditions found earlier. The bulk slag was graded into three size fractions (bulk <40 mm, 4-8 mm, and <125 μm), which were then ground for five minutes in a mill. Ground samples were mixed with 12.5 wt.% water and exposed to 100% CO_2 at 0.3

MPa (3 atm) for 1 hour. The theoretical maximum uptake capacity following carbonation can be calculated from the original chemical composition by Equation 30.

$$CO_2\% = 0.785(CaO - 0.7SO_3) + 1.09Na_2O + 0.93K_2O \qquad (30)$$

This calculation was developed for cement chemistry and does not take into account the MgO amount, which averaged about 9.8% in this slag. Results calculated by Johnson show a theoretical capacity of 45-50% depending upon the size fraction. This compares to an actual measured capacity of ~18%, showing that one-hour reaction time was insufficient to reach carbonation equilibrium. Grinding the slag prior to carbonation again showed a 10-fold increase in compressive strength.

The carbonation reaction steps and mechanisms have been studied extensively for cementitious materials, which can be applied directly for the same process in slags.[103] CO_2 from the air permeates through the solid, which is the diffusion controlled rate-limiting step. The presence of water solvates CO_2 and a high surface area favors transport of the CO_2 to the solid surface. CO_2 hydrates to H_2CO_3, which is then ionized to H^+, HCO_3^-, and CO_3^{2-}. The pH drops approximately three units, typically from 11 to eight. The cementitious phases Ca_3SiO_5 and Ca_2SiO_4 are dissolved. The calcium silicate grains are covered by a calcium silicate hydrate gel, which quickly dissolves releasing Ca^{2+} and SiO_4^{4-} ions. Calcium carbonate and calcium silicate hydrate nucleates, which is favored by slightly high temperatures and finely divided material which acts like nuclei. Vaterite and aragonite can precipitate, but ultimately all carbonate takes the form of calcite. A calcium silicate hydrate gel forms and is progressively decalcified converting ultimately to silica hydrate and $CaCO_3$.

Several key factors are found to influence the carbonation process of cementitious materials. Increasing the Ca content and Ca/Si ratio favor effective carbonation. Ferrite and Ca_3AlO_6 promote the formation of ettringite ($Ca_6(Al,Cr,Fe,Mn,Si)_2(SO_4)_3(OH)_{12}$-$26H_2O$), which readily decomposes to calcium carbonate in the presence of CO_2. The heavy metals Pb, Cd, and Ni increase the susceptibility of carbonation of cementitious materials by 40%. Organics will adversely affect carbonation. Water is necessary to promote carbonation, but too much blocks the pores and limits the reaction. Higher microporosity, surface area, and permeability all enhance carbonation rate. The rate of carbonation is directly proportional to the concentration of CO_2 in the gas phase. Carbonation peaks at 50-70% relative humidity and 60˚C (140°F). Above or below these ranges carbonation is less favorable.

Microstructural changes to the parent material due to carbonation include increased susceptibility to hydration, higher compressive strength, reduced porosity (initial pores fill up with $CaCO_3$), lower tortuosity, decrease in pore size distribution (large pores filled but micro-cracks occur due to carbonate volume expansion). Chemical changes induced by carbonation include reduced leachability of Zn, Pb, Ni, Cd, Co, Ba, Sr, Cl^-, increased leachability of Cu, Mn, NO^{3-}, and SO_4^{2-}, and no change in leachability of Hg, As, Cr.

Different methods of carbonation have been tried in the search for a commercially favorable route. Exposing solids to dry CO_2 under pressure leads to dehydration, causing water starvation of the carbonation reaction. At low pressures a dynamic system is favored to a static system as the flowing CO_2 helps remove the water vapor produced by the reaction. At elevated pressures larger amounts of CO_2 are introduced throughout the sample before pore closure occurs, aiding carbonation. Vacuum carbonation in the presence of a desiccant has shown more complete carbonation, due to diminished resistance of water transport from the carbonating solid leaving an open pore network. Supercritical carbon dioxide penetrates into fine pores displacing water and replacing structurally bound water with CO_2. A pilot plant was operated to contain Galligu (a calcium sulfide waste from soap manufacture) through an accelerated carbonation process. Galligu was mixed with a cement binder and reacted with gaseous CO_2 in an enclosed rotary chamber (similar to a rotary kiln). A continuous process is available for 50 t/hr throughput from Forkers, Ltd.[103]

Several Japanese researchers have focused on the carbonation of steelmaking slag for the purpose of ocean farming. Isoo, Takahashi, et al. at NKK Corporation have developed a process to make large blocks from steelmaking slag that are used as growth sites for marine life.[26,104-105] This grew out of work from Germany who produced bricks from blast furnace slag and exhaust gas in the 1940s. Dephosphorization slag (56.8% CaO and 13.8% SiO_2) was ground to a median diameter of 0.61 mm. Exposure to the atmosphere led to the formation of 0.9% $Ca(OH)_2$ and 2.5% $CaCO_3$ after one month. The slag was placed in large (1m x 1m x 1.2m) molds and reacted with CO_2 saturated with water vapor (~0.1 MPa (1 atm)) for 12 days. The block center temperature was measured at 70°C (158°F). The main carbonate product was calcite, and approximately 6% by weight CO_2 was reacted (~20% of theoretical amount). Blocks weighing 2.4 tons ($1m^3$) contain about 130-160 kg CO_2. The blocks were placed on the ocean floor near Hiroshima, Japan for 22 months and exhibited great nucleation sites for seaweed growth. The amount of CO_2 in the slag blocks placed in air or sea did not change during a three-year period. Tonomura et al. from Nippon Steel carried out a study to scatter ground dephosphorization slag particles in the ocean as fertilizer for plankton growth.[106] The increase in plankton growth was correlated to carbon dioxide uptake. Tamari proposes an accelerated stabilization technology for EAF/LMF slag with steam aging in pits.[107] A reduction in stockpile aging time from six to two months can be achieved by passing 110°C (230°F) steam through the slag; however, this only produces hydrates, and no work was done to optimize the carbonation process.

Two university projects have focused on the use of steel slag to sequester CO_2 either from industrial or atmospheric sources. Students at Clarkson University won the 15th Annual Environmental Design Contest sponsored by WERC at the University of New Mexico with their process of using steel slag to extract carbon dioxide from a coal-burning power plant.[108] No technical details were provide. Researchers at the University of New Hampshire have investigated the use of carbon sequestering carbon materials in highway construction, including steel slag.[109] A report is not available from the project web site; however, they are sponsoring a conference entitled “Accelerated Carbonation for Environmental and Materials Engineering” to be held June 12-14, 2006 in London, England.

6. INTELLECTUAL CAPITAL FOR GEOLOGICAL SEQUESTRATION

6.1. PATENTS

A variety of patents have been filed worldwide dealing with stabilization, accelerated aging, and waste-gas processing with slag. The bulk of these are found in the U.S., Japan, and Korea, and a review of these patents is provided.

6.1.1. U.S. Patents and Applications. The U.S. patents and applications found relevant to the current research are shown in Tables 6.1 and 6.2, respectively.

Table 6.1. U.S. Patents Relating to CO_2 Sequestration in Steelmaking Slag

Number	Date	Inventor(s)	Assignee	Title
4191731	04-Mar-80	Miura et al.	Nippon Steel Corp.	Wet process using steel slag for waste gas desulfurization
5569314	29-Oct-96	Mikhail et al.	Energy Mines & Resources	Thermal stabilization of steelmaking slag
5879430	09-Mar-99	Morishita et al.	Sumitomo Metal Industries	Method and apparatus for aging steel-making slag
6053010	25-Apr-00	Morishita et al.	Sumitomo Metal Industries	Apparatus for aging steel-making slag
6890497	10-May-05	Rau et al.	U.S. DOE	Method for extracting and sequestering carbon dioxide

Patent 4191731 by Miura et al. involves crushing slag (BF and converter) to form an aqueous slurry through which waste gas, containing sulfurous acid, is passed.[132] The process forms gypsum from the calcium oxide components in the slag. Optimum sulfur removal occurs in the pH range 4.5 to 8.

Patent 5569314 by Mikhail et al. involves crushing EAF or BOF slag to <0.2 mm, thermally hydrating the slag with moist air at 100-400°C (212-752°F), then carbonating the slag in the range 500-900°C (932-1652°F).[133] The optimum conditions are 150°C (302°F) for thermal hydration and 550°C (1022°F) for carbonation. No reactor time or pressure is specified for either step.

Patents 5879430 and 6053010 by Morishita al. describe the equipment and methodology to steam age slag in a pressure vessel.[134-135] The goal is to stabilize the hydroxide forming compounds. Steelmaking slag is crushed to <25 mm diameter and packed into a pressure vessel. The interior of the vessel is pressurized with saturated steam to 0.2-0.98 MPa (2-10 kg/cm^2) for 1 to 5 hours. The slag should be charged at <200°C (392°F), and the vessel operates at 130-190°C (266-374°F). The equipment is designed for batch operation on an industrial scale (40-50 metric tons).

Patent 6890497 by Rau et al. describes a method to extract and sequester CO_2 from a gas stream by reaction with carbonates of alkali metal and alkaline earth metal carbonates, preferably carbonates of calcium and magnesium.[136] The waste products are metal cations and bicarbonates in solution or dehydrated metal salts, which require disposal in a large body of water. The CO_2 source is passed through an aqueous solution to extract CO_2 by forming carbonic acid. The carbonic acid is reacted with a metal carbonate to form bicarbonate. Chemical additives are added to prevent carbonate precipitation (phosphates, metals, or organic compounds). The metal ion and bicarbonate stream are released into the ocean below the carbonate compensation depth (where the rate of carbonate dissolution and precipitation are equal). Temperature, pressure, and times for optimum reaction rates are not specified.

Table 6.2. U.S. Patent Applications Relating to CO_2 Sequestration in Steelmaking Slag

Number	**Date**	**Inventor(s)**	**Title**
2004/0093988	20-May-04	Poupardin et al.	Method for oxidizing treatment of steel plant slag to obtain cement-based materials
2004/0213705	28-Oct-04	Blenco et al.	Carbonation of metal silicates for long-term CO_2 sequestration

Patent application 2004/0093988 by Poupardin et al. describes a process to treat raw steel industry slag for conversion to a hydraulic binder equivalent to Portland cement clinker.[137] Steel industry slag is subjected to an oxidizing treatment, with oxygen or air, at 0.1-1.5 MPa (0.99-14.8 atm) at a temperature from 1450-1650°C (2642-3002°F). The raw slag should have at least 45 wt.% CaO and <30 wt. % Fe_2O_3. If necessary, mineral additives are added to the slag in the form of lime (CaO or $CaCO_3$, <30 wt. % added), alumina (bauxite, 0-10 wt. % added), or silica (0-5 wt. % added). These minerals are added in proportion to ensure that the converted slag has >13 wt. % Fe_2O_3, >40 wt. % $3CaO \cdot SiO_2$, >10 wt. % $2CaO \cdot Fe_2O_3$ and/or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and <2% free CaO.

Patent application 2004/0213705 by Blenco et al. relates to work sponsored by the U.S. DOE at UT-Battelle.[138] The process involves reacting a metal silicate with a caustic alkali-metal hydroxide to produce a hydroxide of the metal formerly in the silicate, reacting carbon dioxide with the alkali metal hydroxide or alkali metal silicate to form an alkali metal carbonate or bicarbonate, and reacting the metal hydroxide originally produced with the alkali metal carbonate or bicarbonate to produce a carbonate of the metal originally contained in the silicate. An example of this process using olivine (Mg_2SiO_4) is show in Equations 31-34.

$$MgSiO_4(s) + 2Na(OH)(aq) + H_2O(l) \rightarrow 2Mg(OH)_2(\downarrow) + Na_2SiO_3(aq) \quad (31)$$

$$Na_2SiO_3(aq) + 2CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(aq) + SiO_2(\downarrow) \quad (32)$$

$$2Mg(OH)_2(s) + 2NaHCO_3(aq) \rightarrow 2MgCO_3(\downarrow) + 2NaOH(aq) + 2H_2O(l) \quad (33)$$

$$Net: Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \quad (34)$$

The metal silicates identified are calcium-based (wollastonite, calcic plagioclase, basalt, and montmorillonite), magnesium based (olivine and serpentine), and iron based (fayalite). The reactions take place at a pressure near 5.0 MPa (49.3 atm) in an aqueous caustic solution containing NaOH, KOH, LiOH, or mixtures thereof. Fly ash and waste concrete are listed as a mineral source, but slag is not mentioned.

6.1.2. Foreign Patents and Applications. The foreign patents and applications found relevant to this research are shown in Tables 6.3, 6.4, and 6.5 for Korean, Japanese, and World patents, respectively. The Korean and Japanese patents provide abstracts only in English, and this information is summarized after the respective tables.

Table 6.3. Korean Patents Relating to CO_2 Sequestration in Steelmaking Slag

Number	**Date**	**Inventor(s)**	**Assignee**	**Title**
1020000041665	15-Jul-00	H.S. Kim et al.	Pohang Iron & Steel	Seasoning method of electric furnace slag with hot carbonated water
1020000042037	15-Jul-00	H.S. Kim et al.	Pohang Iron & Steel	Method of neutralizing waste water generated in aging treatment of electric furnace slag using carbon dioxide gas
1020020050429	27-Jun-02	U.H. Bae et al.	POSCO Research	Pretreatment method of steel slag by using carbon dioxide
1020030052340	27-Jun-03	U.H. Bae et al.	POSCO Research	Surface treatment method of steel making slag
1020040026383	31-Mar-04	U.H. Bae et al.	POSCO Research	Method for preparing calcium carbonate using steel making slag and carbon dioxide

The two patents by H.S. Kim et al. both relate to the stabilization of the electric arc furnace slag using water and carbon dioxide gas. Patent 1020000041665 shows a method by which EAF slag is placed in a chamber with hot water through which carbon dioxide or waste gas containing carbon dioxide is bubbled.[139] The CaO in slag reacts with water to form $Ca(OH)_2$ then with the CO_2 to form $CaCO_3$, thus stabilizing the slag against further expansion. Patent 1020000042037 provides a method of treating the resultant wastewater, which is further reacted with carbon dioxide or waste gas containing carbon dioxide to neutralize the alkali components.[140]

The first two patents by U.H. Bae et al. show methods for passivating steel slag, to prevent sudden pH increase upon exposure to (ocean) water. Patent 1020020050429 focuses on the formation of a calcium carbonate layer on the slag particles.[141] Slag particles of <25 mm are reacted with exhaust gas containing 3-30% CO_2 for at least 2 days. The stabilized slag will be used for artificial fish reef. Patent 1020030052340 is a refinement of the first method where the slag is ground to <10 mm and reacted with a CO_2 containing atmosphere at >70% humidity for 4-36 hours.[142]

The third patent by U.H. Bae et al. describes how to make calcium carbonate from steelmaking slag and a CO_2 containing waste gas.[143] Steel slag is crushed to <45 μm, and mixed with water to form an aqueous suspension. The aqueous liquor (containing Ca species at a pH of 12 or higher) is separated from the undissolved material by filtration. The Ca-liquor is then reacted with exhaust gas until the pH drops to seven.

Table 6.4. Japanese Patents Relating to CO_2 Sequestration in Steelmaking Slag

Number	**Date**	**Inventor(s)**	**Assignee**	**Title**
57152411	20-Sep-82	H. Naoe et al.	Nippon Steel	Treatment for stabilization of slag in steel making
3013517	22-Jan-91	H. Yasuyuki et al.	Sumitomo Metal	Method for aging steel making slag
3159938	09-Jul-91	Y. Masaharu et al.	Nakayama Steel Works	Method for short-period aging of steel manufacturing slag
4175250	23-Jun-92	H. Toru et al.	Sumitomo Metal	Aging treatment of steel-making slag and apparatus therefor
4202033 4202034 620744	22-Jul-92 22-Jul-92 26-Jul-94	H. Toru et al.	Sumitomo Metal	Aging treatment of steel making slag
6127985	10-May-94	I. Hideo	Nippon Steel	Method for accelerating aging of steel making slag
8059307	05-Mar-96	K. Hiroshi	Sumitomo Metal	Accelerated aging method for steel making slag
8165151	25-Jun-96	Morishita et al.	Sumitomo Metal Ind.	Aging of steel mill slag and apparatus therefor
8259282	08-Oct-96	M. Hishiro et al.	Kawasaki Steel	Stabilization treatment of steel making slag

8259283	08-Oct-96	T. Hiroyuki	Kawasaki Steel	Method for aging steel making slag
9025142	28-Jan-97	I. Koichi et al.	Nippon Kokan	Steam aging treatment of steel making slag
10338557	22-Dec-98	I. Hideto et al.	Sumitomo Metal	Aging treatment of steel making slag
2000203903	25-Jul-00	K. Makoto	Nippon Kokan	Production of artificial stone material and production equipment therefor
2003134958	13-May-03	H. Mitsutaka et al.	Nippon Tekko Renmei	Method for promoting CO_2 absorption in ocean using iron and steel slag
2005047789	24-Feb-05	T. Naoto et al.	Nippon Steel	Stabilization treatment method of steel slag and stabilized steel slag

The Japanese have prodigiously researched slag stabilization as evident by the amount of patents filed. The patents are summarized in bullet form to simplify the review.

- 57152411: Steelmaking slag is immersed in hot (sea) water at >60°C (140°F) for eight hours to seven days to accelerate stabilization of free lime.[144]
- 3013517: Steelmaking slag is crushed to <25 mm and placed in a concrete tank. Wastewater at 60-95°C (140-203°F) is fed into the tank and the slag is immersed for 12-48 hours.[145]
- 3159938: Steelmaking slag is stabilized by the addition of hot water or steam. A continuous process using three tanks (receiving, aging, and discharge) is employed.[146]
- 4175250: Steelmaking slag is placed in an insulated tank through which steam pipes are inserted. The bulk slag is subjected to 100°C (212°C) steam to shorten stabilization.[147]

- 4202033: Optimization of the steam addition in 4175250 by layering crushed slag on a steam pipe and covering the slag with a vinyl sheet. Steam rate feedback control is used.[148]
- 4202034: Same as 4202033, but the slag is allowed to natural age for three months before the introduction of steam.[149]
- 6127985: Steelmaking slag is screened to provide two to four size fractions (<1 mm, 1-30 mm, and >30 mm) and is put into separate stockpiles. It is claimed that this method improves the air permeability and water retaining properties since the surface area to volume ratio increases for each size, thus shortening the natural aging process.[150]
- 6206744: Each steelmaking slag batch is chemically analyzed to determine the basicity (CaO/SiO_2). Slag with a basicity >4 is crushed, graded, and aged with steam.[151]
- 8059307: A cylindrical hermetic vessel is designed to house the slag and react it with steam under reduced pressure. The vessel is portable and truck mounted, allowing transportation of the slag to stations (loading, steaming, and disposal).[152]
- 8165151: Steelmaking slag is crushed to <25 mm and placed in a pressure vessel. Steam at 0.20-0.98 MPa (1.9-9.7 atm) is introduced for 1-5 hours. The vessel is top loading and bottom unloading.[153]
- 8259282: Steelmaking slag is treated with steam at atmospheric pressure, then held for >1 hour in a steam/CO_2 mixture to prevent subsequent leaching of Ca and Mg.[154]
- 8259283: Steelmaking slag is aged in an atmosphere at >80°C (176°F) and >60% relative humidity for a time (t). The time is determined by the concentration of CaO+MgO in the slag.[155]
- 9025142: Steelmaking slag is held in steam for >1 hour, then force cooled and reheated. At least two cycles of heating/cooling are used in the claim to reduce steam consumption.[156]

- 10338557: The amount of steam required for slag aging is pre-determined from the charging basicity and fluorine concentration at the time of blowing in the steelmaking process.[157]
- 2000203903: Steelmaking slag and water are mixed to form a slurry then packed into a $1m^3$ ($35.3\ ft^3$) mold. A carbon dioxide containing gas is blown through the mold to carbonate the CaO, thus forming a solidified artificial block.[158]
- 2003134958: The nutrient demand ratio for a specific sea area is determined, then granulated steelmaking slag corresponding to the demand ratio (composition and size) is spread into the water to aid growth of phytoplankton. The growth of phytoplankton will reduce the local carbon dioxide level in the surface layer of the ocean, thus allowing subsequent sequestration from the atmosphere.[159]
- 2005047789: Steelmaking slag is treated with a gas containing carbon dioxide and 75-100% relative humidity in an air, pressurized, or steam atmosphere. The amount of water added is controlled to prevent formation of free water on the slag.[160]

Table 6.5. World Patents Relating to CO_2 Sequestration in Steelmaking Slag

Number	**Date**	**Inventor(s)**	**Assignee**	**Title**
WO2004108624 (Japan)	16-Dec-04	T. Naoto et al.	Nippon Steel	Method for stabilization treatment of steel making slag, stabilized steel making slag, and material and method for environmental preservation of water area using said slag
WO2005035462 (Brazil)	21-Apr-05	J.L. Pimental et al.	Companhia Siderúrgica de Tubarão	Process of inertization (dampening) of steel making slag for economical reuse

World patent WO2004108624 is a precursor to Japanese patent 2005047789.[161] Water or carbonic acid water (via steam) is added to steelmaking slag to accelerate the aging process. The amount of water added is less than the amount necessary for which free water is present but more than 10 wt.%. In this manner, carbonation is carried out without binding together of the slag particles.

World patent WO2005035462 by Pimental et al. is aimed at accelerating the hydration and carbonation of free MgO and CaO species in steelmaking slag. Slag is homogeneously crushed and spread out in an inertization yard to a predefined thickness. The slag layer is then aerated and dampened to accelerate the hydration and carbonation reactions. Volumetric expansion is determined by sampling and testing to PTM-130.

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American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report - Attachment C

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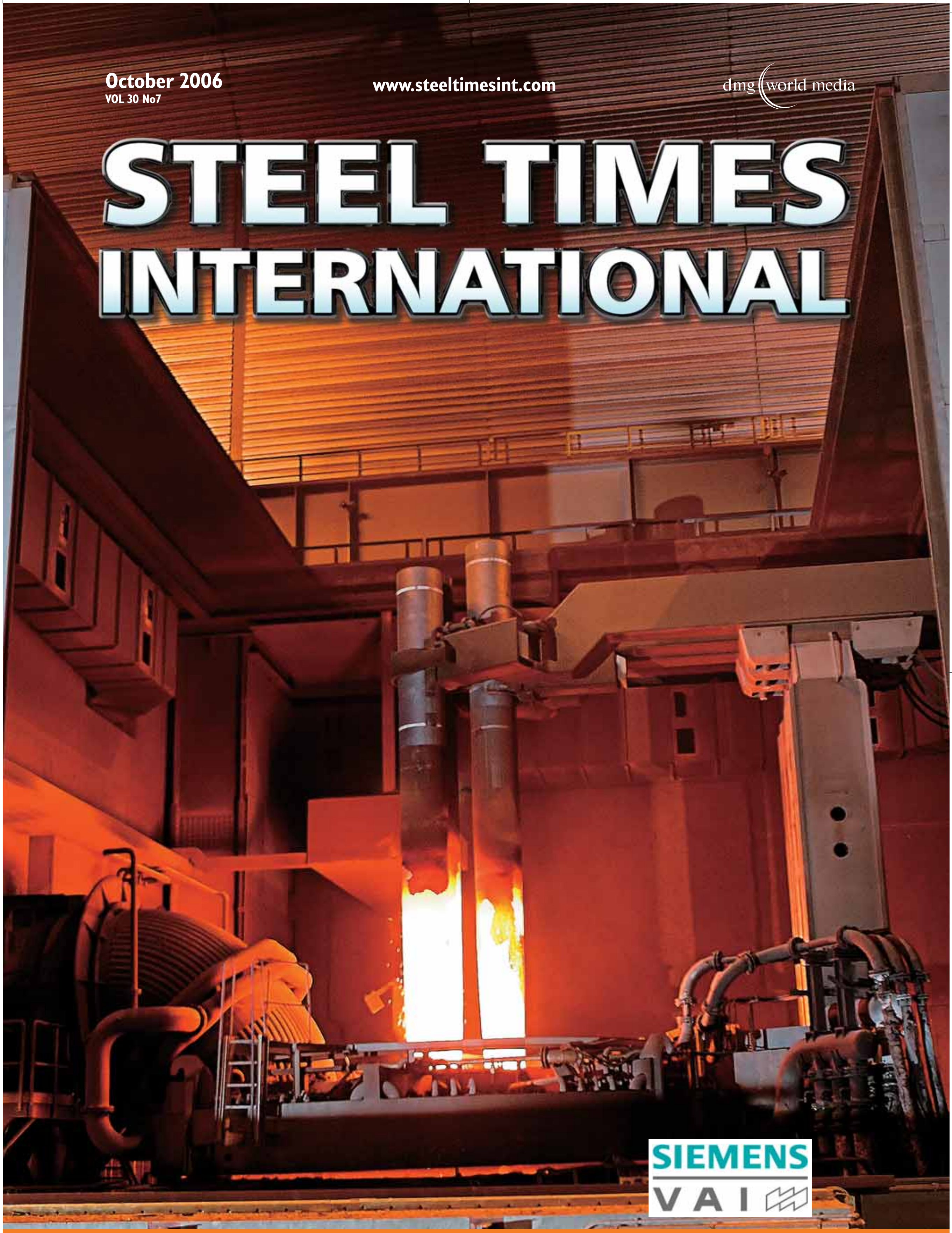

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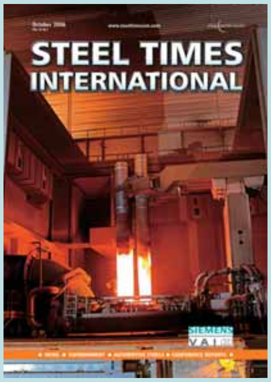

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FUTURE FEATURES 2006/2007

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IN BRIEF

DGCX to launch steel futures in 2007

Dubai Gold and Commodities Exchange (DGCX) will launch a steel futures contract, early next year. The company's CEO said the launch of steel futures would give the company two innovative products (the other is a fuel oil contract, to be launched on October 30).

TK sells minority shareholding in Wickeder Westfalenstahl

Wickeder Westfalenstahl GmbH, based in Wickede (Ruhr, Germany), has bought back the 25.1% share in its capital held by ThyssenKrupp Steel AG.

Wickeder is an SME focussed on the production of cold-rolled strip, clad materials and components for CRT monitors – not a core activity for ThyssenKrupp Steel.

However, the companies' long-standing business partnership for starting material supplies and intensive exchange of know-how will continue.

www.thyssenkrupp-steel.de

Maverick/Tenaris merger approved

The Colombian Superintendence of Industry and Commerce has completed its review and has cleared the proposed merger without conditions; the Colombian condition precedent in the merger agreement with Tenaris is now satisfied. The proposed merger has now been cleared by competition authorities in all those jurisdictions in which it was a prerequisite. Maverick's special meeting of stockholders – to vote on the proposed merger – was scheduled for October 2, 2006 (see page 18).

New Chinese contracts for Danieli

Danieli Wean United recently signed a contract for a new continuous hot dip galvanising line for the Tianjin Tiantie Metallurgical Steel Plate Co Ltd and another with the Changshu Everbright Material Technology Co, Ltd (China) for two new continuous hot dip galvanising lines.

Posco to start construction of India plant in April

Following delays in land acquisition for Posco's proposed steel plant in Orissa, India, the company has changed its plans and hopes to begin construction work from April 2007.

The company has decided to begin construction with partial acquisition of land; of a total 4000 acres, around 3500 acres is Government-owned, the rest is tribal land.

Posco India's chairman/managing director, Mr Cho Soung-Sik said recently that there had been resistance to the project, particularly on land acquisition. "There were 6000 objections of which around 2500 have been heard with another 3,500 objections due to be heard in the next two months. After that, negotiations for compensation can start."

Regarding the Orissa government's proposal that Posco use Paradip port to meet its requirements instead of setting up a captive port of its own, Mr Cho said there were two points: "Orissa definitely needs more ports. So why object. Secondly, all the top steel plants have their own ports – it is necessary to be competitive."

On the issue of iron ore export, he noted that the company would be exchanging 30% of its 600Mt iron ore location. "We will send Orissan ore with 4.5% alumina content to our Korean plant and replace the same amount with 0.6% alumina content Brazilian ore. This blending is necessary for large size blast furnaces," he said.

Source: The Hindu Business Line

Arvedi, Siemens to build world's first steel ESP plant

The Italian steel producer Acciaieria Arvedi SpA (Cremona) will build the world's first Arvedi ESP (Endless Strip Production) plant which will continuously produce finished steel strip from liquid steel in an endless process. The combination of different and, till now, separate process steps in a single production process will enable the direct and continuous production of high quality steel strip and so result in significantly lower production costs. Arvedi's partner for this is Siemens VAI; they have established a joint venture company, Cremona Engineering srl, to be responsible for development and design of the new plant and to market this technology on a worldwide basis in the future. The first plant is already scheduled for start-up in 2008 in Cremona.

(A full technical article will appear in the November issue of *Steel Times International*.)

Hazira picks ABB to equip South Asia's largest plate mill

ABB has won an order from Hazira Plate Ltd, part of India's Essar Group, to support construction of the largest plate mill in South Asia.

ABB' scope of supply for the hot rolling mill includes plant design, dimensioning, supply and commissioning of low-voltage and medium-voltage motors and drive systems.

The new Hazira hot rolling mill, scheduled to begin operation in early 2008, will be the largest of its type in India and the South Asia region. ABB orders for hot rolling mill applications in India have exceeded $25M so far in 2006.

Japan asks China to reduce steel capacity

In an unusual move, during a recent visit to Beijing a senior official of Japan's Economy, Trade and Industry Ministry (METI) asked China to cut its steel production capacity.

Tetsuhiro Hosono, director general of METI's Manufacturing Industries Bureau, made the request directly to Liu Tienan, director of the Industry Department of China's National Development and Reform Commission, which is in charge of economic policy.

Liu expressed a willingness to make efforts to cut China's steel output capacity, which has expanded exponentially as the country gears up for the Beijing Olympics in 2008.

The Japanese government decided that China's crude steel output could cause steel prices to plunge across the world, adversely affecting Japan's economy. Therefore, Hosono asked the Chinese government to abolish small blast furnaces with a capacity of $300m^3$ or less. In exchange, Japan would help scrap the facilities and offer environmental protection assistance and energy-saving technologies via major Japanese steelmakers.

Sinosteel to build Indian plant

Sinosteel Corp may construct its first steel plant in India, building its planned 3Mt/y plant in the states of Orissa, Jharkhand or West Bengal, competing with ventures planned by Mittal Steel Co and Posco. The company may initially invest US$500M in the venture and is seeking rights to mine 5Mt/y of iron ore for up to two decades. it will decide on a location once its study is completed.

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click on the 'News' button to see the full list of news and features

Russian steel demand and output rising at a rapid pace

Steel consumption in the Russian Federation is growing strongly: the country's mills are cutting exports as higher prices are available in the home market.

Since it touched a low point of 14.6Mt in 1998, Russian steel consumption has increased by an average of 10% annually. However, in H1 2006, that rate of growth has more than doubled to 21%, according to preliminary estimates by the Ministry for Industry and Energy. Annual consumption of finished steel has now increased to more than 35Mt.

Gross domestic product rose by more than 6% in 2005; this year's projection is 4-5%. High global prices for fuels – Russia's largest industry by value – are promoting strong levels of investment in new installations for the production and transport of oil and gas.

Source: MEPS – European Steel Review

JFE's year end results

In the year ending March 2006, JFE Steel managed to secure a high level of earnings on the back of brisk demand in the manufacturing industry, especially in the automotive sector.

Operating results (in ¥bn) Year ending 31 March	2005	2006
Consolidated net sales	2421.7	2753.8
Consolidated operating income	456.3	513.8
Consolidated ordinary income	450.3	510.7

Consolidated crude steel output decreased to 30.15Mt as production, especially regarding thin sheet in the domestic and Asian markets, was adjusted to improve the demand/supply balance. Net sales increased to ¥2753.8bn (US$23.6bn), reflecting flexible management of production and sales according to market trends.

Ordinary income increased to ¥510.7bn (US$4.38bn) – attributed to accelerated sales of high value-added products and further reductions in costs. Its subsidiaries also did comparatively well, offsetting the impact of increased raw material prices.

The company expects demand for high end products to remain robust in the year to March 2007.

Iran's steel industry registers 5% growth in five months

Iran's steel industry has registered a 5% growth during the first five months of its current year (the Iranian year started on March 21, 2006). The industry had shown a growth of about 2.5% during the previous 16 months.

Exports of steel products increased by about 4% this year despite the fact that, due to market regulatory measures taken by the Iranian government, no semis were exported during that time.

Supplying the earthquake-stricken regions of Iran with products has meant steel plants operating at full capacity; a new steel production plant will be launched within the next four months.

Vietnam considers anti-dumping action against Chinese steel makers

Chinese steelmakers may need to be sued for dumping processed steel on the Vietnam market at excessively low prices, steel industry experts commented at recent talks, held by the Market Control Department and the Vietnam Steelmakers Association, on strengthening controls over imported steel.

Although the cost of producing steel from steel semis adds US$30-35/t to the cost of processed steel, processed steel imported from China was currently entering Vietnam at a price that failed to reflect this processing cost, said experts.

Processed steel from China was currently priced at about $400-409/t. According to the Steelmakers Association, an additional $30-35/t and a 10% import duty should be factored onto this cost.

According to the Steelmakers Association, 5kt of rolled steel were recently imported into Vietnam and about 10kt more would be imported in the near future.

The Steelmakers Association has requested that domestic steel producers cut production costs and seek lower-priced sources of semis in order to lower steel prices. Monthly demand for rolled steel in the country's northern region is around 30kt.

Source: Daily "Vietnam News"

Essar Steel faces challenges in Trinidad

Essar Steel is facing serious environmental challenges in its quest to construct a US$1.2bn steel plant in Central Trinidad.

The Pranz Village Development Community is protesting the company's decision to construct the plant, citing environmental, health and social issues. The community plans to go to court on the matter.

In response, the company has proposed a green belt with trees as high as 30' (9.14m). 'The plant would have gas extraction mechanisms to collect and recycle gases back into the processing system,' the company said in a statement.

It also said that it would import iron ore, which will be transported from the Point Lisas Port, adding that the company was subject to a certificate of environmental clearance.

IN BRIEF

Resita Works renamed

At an Extraordinary general shareholders meeting of SC CSR SA (Resita, Romania), a subsidiary of Russian steelmaker TMK, a decision was adopted to rename the plant SC TMK-Resita SA. The decision was adopted to strengthen the single TMK corporate brand, following TMK's acquisition in March 2006 of Sinara Handel GmbH, which owned the controlling stake in two Romanian companies SC TMK-Artrom SA Pipe Plant (Slatina) and SC TMK-Resita SA Metallurgical Works (Resita).

While TMK-Artrom specialises in the production of seamless pipes, the Resita works has 500kt/y capacity for EAF steel and 700kt/y capacity for rolled steel.

Novolipetsk Steel profit to rise to $3.7bn/y by 2011

Novolipetsk Steel expects its average operating income to increase to $3.7bn/y by 2011.

Operating income in H1 2006 fell 16% to US$925.3M.

Novolipetsk, one of Russia's biggest steel and rolled stock producers, plans to raise steel output by 40% to 12.4Mt/y and rolled stock production to 9.5Mt/y, including 3.5Mt to be produced abroad.

It also said its purchase of the Urals-based private steel maker VIZ-stal in August 2006 has already produced savings of $180M.

BlueScope moves to block Smorgon merger

According to various reports, BlueScope Steel, the largest steel company in Australia, acquired a 19.9% block of shares in Smorgon Steel to ensure that the pending OneSteel/Smorgon merger could not proceed in its currently proposed form. BlueScope expressed its concern that the combination of the two companies would create competition problems. It does not plan to increase its stake prior to any merger.

Gerdau steel production up 10.4%

Gerdau investments for Q1 2006 totalled US$1.1bn, of which $697M was devoted to acquisitions and $392M to expansion and upgrades of existing installations. Of this sum, $3.8bn (60.8%) was derived from the international market, through exports from Brazil and the performance of Gerdau units in Argentina, Canada, Chile, Colombia, Spain, the United States and Uruguay.

The company's consolidated steel production grew 10.4% to 7.7Mt, while production of rolled products was up 17.4% to 6.3Mt.

Sales revenue from the Brazilian domestic market was up 3.4% over H1 2005, totalling $2.4bn or 39.2%. Sales volume was up 12.1% to 2Mt, chiefly due to a recovery in demand from civil construction and continued consumption by industry.

In the same period, part of the volume normally exported from Brazil was redirected to meet increasing domestic demand. Shipments abroad were down 12.9% to 1.4Mt, including sales to Gerdau Group companies in a number of countries. Revenues from these shipments totalled $533.4M. Of this, the Brazil units produced 3.6Mt of steel (up 1.8%) and 2.3Mt of rolled products (up 15.9%).

North American sales were up 9.5% totalling 3.5Mt (or 47.3% of the Group's total sales). To meet increased demand, North American mills produced 3.5Mt of steel (up 7.3%) and 3.3Mt of rolled products (up 4.4%). Revenue for the region was stable at $2.7bn – representing 43.0% of the consolidated total.

Incorporation of the Sidelpa and Diaco units in Colombia plus the increased holdings in Sipar (Argentina) from 38.5% to 74.4% had a positive effect on results for the region. In total, sales from operations in Argentina, Chile, Colombia and Uruguay were up 115.5% from 316kt to 681kt. For the first time, Gerdau Group sales revenue for South America (excluding Brazil) exceeded $510M, up 76.6% on Q1 2005. Steel production in the region was up 114.2% to 489kt, with rolled product production up 135.9% to 587kt.

Q1 2006 also saw consolidation of the 40% stake in Corporación Sidenor (Spain), which added $198.1M in revenue and 157kt in physical sales. Production totalled 166kt of steel and 143kt of rolled products.

Its consolidated profit for Q1 2006 was $800M, up 6.2% on the same period in 2005.

IPSCO and Newport Steel – where next?

According to Canadian buyer IPSCO, it may increase job numbers at NS Group's Newport Steel plant (Wilder, Kentucky, USA). Certainly the existing 250 jobs appear to be secure as its customers are demanding the type of steel pipe made there and the company may even need to boost production.

IPSCO, which already produces the same kind of pipe at six other factories in the US and Canada, has made a $1.46bn offer to buy Newport Steel, indicating it needs further capacity to meet customer demand so its plan is to ramp up production to full capacity. IPSCO produced 3.2Mt of steel last year.

Demand for the pipe made by both companies has grown rapidly as energy prices have skyrocketed in recent years, stimulating oil and natural gas exploration that depend on the pipes and casings that are used in drilling operations. The Wilder plant, which can produce 520kt/y of pipe, is currently running at 40-50% capacity and operated at just 39% capacity in 2005. It can produce pipe up to 16" in diameter, which is larger than those manufactured at IPSCO's three US pipe factories in Blytheville (Arkansas), Camanche (Iowa) and Geneva (Wisconsin).

Corus of approval for Boll filters

International metal company, Corus, recently installed a new continuous slab caster at Port Talbot in South Wales, UK. The No 3 caster has increased its annual slab output by 25%, with a overall production capability of nearly 5Mt/y.

As part of its major investment programme, the company installed a number of Boll filters at the site to filter both the raw water supply and plant cooling water: automatic self-cleaning systems filter raw water from the internal works reservoir feeding the three slab casters to remove contaminants, as well as in-line cooling water for the slab casting and torch cutting process. Another automatic filter removes particulates from the cooling tower serving the re-cooling system, and coarse air strainers have been fitted to filter the compressed air system.

The Boll 6.18 automatic water filters feature a unique backflush process that enables them to operate without regular cleaning or maintenance – making them ideal for continuous manufacturing processes such as steelmaking

www.bollfilter.co.uk

Two Boll automatic self-cleaning systems that filter raw water from the internal works reservoir at Corus, Port Talbot.

Avtron supplier contracts

Steel Dynamics, Inc (SDI) recently awarded Morgan Engineering/Alliance Crane an order for new ladle and charge cranes at its Columbia City (Indiana, USA) mill. The ladle crane has a 75' span, is rated at 250/50/15t and consists of a main hoist, auxiliary hoist, trolley and bridge. An 85' span charge crane was also ordered with a 150/50/15/15 ton rating with main hoist, auxiliary hoist, second auxiliary hoist, trolley and bridge.

The hoist drives will use Avtron's proven ADDvantage-32 DC drive technology and the travel motions will use the ACCel500 AC family of drives. Ethernet communication will tie all of the equipment together and to an Avtron DriveWin diagnostic system. DriveWin will present maintenance and operating personnel with real-time data on the crane along with fault and support information. A remote connection will be provided to a ground station so that both cranes can be monitored without physically climbing up to them.

In addition, Avtron's Industrial Automation Division with its India System Integration partner, Nelco, has received two contracts for Tata Iron and Steel Company (TISCO) at Jamshedpur, India.

Another contract in India is to upgrade the stacker system on the Jamshedpur hot shearing line.

www.avtron.com

Revision to E 45 inclusion content standard

ASTM International Committee E04 on Metallography has concluded an extensive revision of an important standard, E 45 (*Test methods for determining the inclusion content of steel*). Because of this revision, manual and automated image analysis (IA) test methods for obtaining JK nonmetallic inclusion ratings for steel are now defined within one document.

The new version of the standard, approved in November 2005, incorporates large elements of standard, E 1122 (*Practice for obtaining JK inclusion ratings using automatic image analysis*) which has now been withdrawn.

ASTM International standards are available from service@astm.org or ***www.astm.org***

Sustainability indicators at Thyssen Krupp Steel

	2001/02	2002/03	2003/04	2004/05
Effectiveness				
Sales (€M)	6861	7448	8387	9291
Efficiency				
Productivity (t/man-year)	585	627	634	636
Resources				
Training (days/employee)	2.7	3.6	2.7	2.8
Health promotion (%sick absence rate)	5.4	5.2	5.1	4.9
Energy consumption (M GJ)	237.1	233.7	238.9	237.6
Water consumption (Mm^3/y)	54.1	60.9	57.4	57.2
Impact				
Dust emissions (t)	4756	4706	44611	4473
Carbon dioxide emissions (Mt)	19.5	18.2	16.3	15.8
Accidents (per 1M hrs worked)	11.4	9.9	8.3	8.5
Solidarity				
Proportion of appentices in the workforce (%)	5.1	5.2	5.4	5.5
Justice				
Local value added (Procurement volume of its site in 100km radius in %)	49.6	46.8	51.9	53.1

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Siemens ladle furnace & billet casters to Dneprovsky

Ukrainian steel producer OJSC Dneprovsky Iron and Steel Integrated Works has ordered a new 250t ladle furnace and two 7-strand billet casters from the Siemens Group Industrial Solutions and Services. With the completion of this project, Dneprovsky Iron and Steel Integrated Works will be able to substantially replace its existing ingot-casting route with continuous casting, lowering production costs, improving steel quality and increasing product yield. The ladle furnace and the first of the two billet casters are scheduled for start-up in May 2007. Start-up of the second billet caster will follow in early 2008.

Dneprovsky Iron and Steel Works (DMKD) produces more than 3Mt of foundry pig iron and steel each year, mainly sold to customers in the Ukraine.

www.industry.siemens.com

US$1bn investment in Dung Quat steelworks

The Vietnamese Ministry of Planning and Investment (MPI) has licensed Tycoons Worldwide Steel Vietnam (Tycoons) to invest US$1bn in a steelworks factory in the Dung Quat Industrial Zone in the central province of Quang Ngai.

The company will build a steel and rolling mill with 5Mt/y capacity for steel semis to be totally completed by 2013. It is currently operating a cold rolling plant in My Xuan A2 Industrial Zone within the Ba Ria-Vung Tau province. TWSV received its licence on September 18.

Tycoons will invest $539M to build a mill by 2009 to produce 2Mt/y of semis. The 2009-2013 second stage will need another $500M to expand the plant's capacity by another 3Mt/y. Once fully operational in 2013, the plant should help revitalise Vietnam's ailing steel sector, according to the Vietnam Steel Association (VSA).

As much as 70% of the new facility's total output has been earmarked for the domestic market. Vietnamese steel mills are expected to produce 3.8Mt of construction-grade steel in 2006, 3.5Mt of which is to be sold on the domestic market.

Canam's Structal $40M for Yankee Stadium

Canam Group's Structal subsidiary has won a $40M contract to supply structural steel for the new Yankee Stadium in New York. Structal Heavy Steel Construction was awarded the C$900M contract by builder Koch Skanska. The new ballpark is expected to open in the spring of 2009. Fabrication of the structural steel components will begin in December 2006, mainly at the St-Gedeon (Quebec, Canada) and Point of Rocks plants, and last about one year.

Earlier this year, Canam also won a $70M contract to fabricate steel for the New York Mets' new stadium.

Mittal Steel moving fast in India

Mittal Steel has reportedly identified four potential sites for its Orissa plant out of seven possible sites proposed by the Orissa government. While its plans for Jharkhand are still unclear, Mittal is likely to sign an agreement with the Orissa government within the next two months for setting up a $7bn, 12Mt steel plant. Government sources also indicated that Gopalpur is more likely to be its chosen port rather than Bhambra.

The company and its promoters are in the process of complying with the state's additional statutory formalities and approvals are expected shortly. The MoU will be formally signed once Mittal Steel has acquired the 3 000 acres of land it is seeking from the government.

For further news stories and updates visit
www.steeltimesint.com
click on the 'News' button to see the full list of news and features

Heavy-duty weighing

In the steel-producing industry, most diverse materials and masses are gravimetrically-controlled, mixed, melted, alloyed, rolled, cut and prepared for shipment in many process steps. In the severe environment of a steel plant, proper weighing technology is a critical issue. Consistent steel quality that is stable, safe and versatile requires a perfect mesh of all process steps using a high-quality weighing solution.

Schenck Process' versatile weighing systems can offer proven solutions for multiple applications. Its products can endure temperatures up to 200°C in the sensor area as well as heavy shock loads and contamination.

In addition to proven standard transducers like RTN load cells, DWB weighbeams and DMA measuring eyes, the company also offers custom-engineered DRA radial load transducers and MAC measuring axles; it offers steel plants and outfitters a single source for complete design, data processing and engineering with guaranteed accuracy of load transducers plus long-term adherence to specified system accuracy in any configuration.

Canada extends dumping ruling

Canadian steel firms Algoma, Dofasco and Ipsco are hailing an August Canadian International Trade Tribunal decision to continue hot-rolled steel sheet dumping findings against Brazil, China, Chinese Taipei, India, South Africa and the Ukraine, and to continue subsidy finding against India.

The trade tribunal originally ruled in 2001 that the countries have injured Canadian producers by selling dumped – sold at prices cheaper than production costs – and subsidised hot-rolled steel sheet into Canada. The August 16 continuation extends the ruling until 2011. Under the ruling, hot-rolled steel sheet exported to Canada from these countries will be required to be at monitored values.

August 2006 Crude Steel Production

World crude steel production for the 62 countries reporting to the International Iron and Steel Institute (IISI) was 101.6Mt in August - 11.0% higher than for the same month of 2005. The figures suggest that China currently accounts for 36% of world crude steel production compared to 34% for the same period last year. Excluding China, world production rose 7.9% compared to August 2005.

China produced 36.7Mt of crude steel in August, an increase of 17.0% year-on-year (y-o-y). Japan produced 9.6Mt in August, up 4.1% y-o-y. South Korea produced 4.0Mt of crude steel, an increase of 5.7% y-o-y.

Germany was again the largest producer of crude steel in the European Union with total production of 3.9Mt in August - 16.7% higher y-o-y. August production in Italy was 1.8Mt, up 13.9% y-o-y. As the largest crude steel producers in Eastern Europe, Russia and the Ukraine posted crude steel production figures of 6.0Mt and 3.5Mt respectively, up 9% and 14.1% over the same period last year.

Brazil produced 2.8Mt (6.6% higher) while in North America, Canada produced 1.3Mt (up 12.6% y-o-y).

http://www.worldsteel.org/index.php?action=stats&type=steel&period=latest&month=8&year=2006

For online statistics table visit http://www.worldsteel.org/csm_table.php

MIDDLE EAST STEEL FORUM – Conference Programme

14 – 15 November 2006, InterContinental Citystars, Cairo

The *Steel Times International* Middle East Steel forum has a confirmed programme of 21 speakers for its two day conference and exhibition. To view the Conference Programme visit www.steeltimesint.com and click on the 'Exhibitions' tab.

Presentations include: Arab Iron and Steel Union, UNCTAD, EZDK, Midrex, Techint-HYL, Siemens VAI, Danieli and SMS Meer and more. The forum's conference and exhibition covers all aspects of the Middle East steel industry. There is an optional plant visit to the EZZ Flats product minimill at Ain Sukhana, Suez on the third day. Delegate cost is £300; to register, please visit www.steeltimesint.com and click on the 'sphinx' banner on the right hand column or, if you wish to view the exhibitor brochure, click on the banner at the head of the page.

The Middle East Steel Forum enjoys the full support of EZDK Group, one of the leading steel manufacturers in the region.

International Events Diary

November

06-07 Surface quality of continuously cast semis
London, UK.
Tel +44 (0) 20 7451 7303
Fax +44 (0) 20 7839 1702
casting@iom3.org
www.iom3.org

06-08 2nd Annual world scrap metal congress, Shanghai, China.
Tel +65 6322 2795
Fax +65 6226 3264
kinsum.kong@terrapinn.com
www.terrapinn.com/2006/wsm_ch

07-09 16th Rolling conference, San Nicolas, Argentina.
Tel +54 3461 460803
Fax +54 3461 462989
genzano@siderrurgia.org.ar

09-09 Vibration in rolling mills, London, UK.
Tel +44 (0) 20 7451 7302
Fax (0) 20 789 1702 email
lisa.bromley@iom3.org
www.iom3.org

09-10 Stahl 2006, Düsseldorf, Germany.
Tel +49 (0) 211 6707 533/534
Fax +49 (0) 211 6767 670
www.vdeh.de

09-12 8th Ankiros/7th Annofer/Turkcast, Istambul, Turkey.
Tel +49 (0) 511 89 0Fax +49 (0) 511 89 32626 info@messe.de
www.messe.de

14-15 November
Middle East steel forum,
Intercontinental Citystars, Cairo, Egypt.
Tel +44 (0) 1737 768611
Fax +44 (0) 1737 855469
Contact
steel@uk.dmgworldmedia.com
www.steeltimesint.com

14-17 12th Metal-expo, Moscow, Russia.
Tel/Fax +7 (095) 901 99 66
info@metal-expo.ru
www.metal-expo.com

22-23 Measurement & control technology for hostile environments in the metals industry, 1 Carlton House Terrace, London, UK.
instrumentation@iom3.org
www.iom3.org

26-30 4th International congress on the science and technology of ironmaking, Osaka, Japan.
Tel +81 6 6312 0461
Fax +81 6 6312 0462
cf4m-nsmr@asahi-net.or.jp

December

● **03-04 China steelmaking raw materials & finished products conference,** Beijing, China.
Tel +44 20 7903 2056
www.cru-china-steel-conference.crugroup.com

14-15 27th ATS international conference, Paris, France.
Tel+33 1 41 25 58 00
Fax +33 1 41 25 58 58
www.ats-ffa.org

March

● **03-05 4th Steel success strategies europe conference,** Amsterdam, The Netherlands.
www.metalbulletin.com/mbevents/conference.asp?id=142&cat=3

● **04-06 CRU's 13th world steel conference,** Bonn, Germany.
Tel +44 20 7903 2056 Fax +44 20 7903 2172
www.cruevents.com

● denotes new events

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MC-CCPIT events

The Metallurgical Council of China – Council for the Promotion of International Trade (MC-CCPIT) is a promotional organisation which facilitates foreign economic and trade cooperation in the metallurgical industry in China. This government-approved organisation is in charge of exhibitions events both at home and abroad and provides a window onto the steel industry in China. It plays an active role in various economic and trade cooperation and technical exchanges, participates in top exhibition and conference events, organises overseas delegations and assists with visa applications, surveys and industry investigations. It also holds a series of training and professional events, provides a useful information service and encourages Chinese enterprises to increase their exports to the international market.

Among the events it organises are:

- China International Metallurgical Industry Exhibition. Founded in 1987 it is now the second largest show in the world for the metallurgical industry. It is held every two years regularly in China. The latest show was in Beijing in April 2006.
- China METALSFAIR. Jointly organised by CNSIA and CNIA, this show was founded in 2003 to cover eight topics spanning steel to non-ferrous metals manufacture. The next one will be in Guang Zhou in 18-20 May 2007.
- China International Steel Structure Exhibition. Founded in 2001 by the Ministry of Construction, this promotes steel structure technology all over China to meet the increasing demand for steel structures in industrial and civilian construction and urban infrastructure. The 6th exhibition will be held in Beijing in October 2007.

Protectionism raises its ugly head

Asked whether US steel manufacturers will again cry 'wolf' a New York-based analyst quips "They've already begun to …", referring to the unease felt in the US steel industry over the latest data on rising imports of foreign steel and the pressure on the US administration to crack down on what is perceived as dumping.

Using the latest statistics as ammunition, the steel industry has warned that, if current trends continue, the US could shatter its previous record in steel imports in a single year. This ominous forecast was reinforced by the American Iron and Steel Institute (AISI), a Washington DC-based interest group representing the US steel industry, which is also campaigning against dumping.

During the first six months of the year, overall steel imports rose by 33% while finished steel product imports were up by 32% over the previous year. However, in June the US imported some 3.4Mt net of steel, including 2.9Mt net of finished steel, which meant a decline of 14.4% and 9.2% respectively compared to May.

CALLS FOR TIGHTER ENFORCEMENT

Two major products which recorded a substantial jump in imports in June over the previous month were tin plate steel (+53%) and wire rods (+50%).

As expected, the AISI reacted strongly to this 'unprecedented rise' and called for tighter enforcement of trade laws. The US steel industry has rejected the belief, widespread amongst US steel consumer industries, that steel manufacturing in the US will become more efficient and competitive if steel imports are allowed; the US steel manufacturers argue that imports are cheaper only because of the massive state subsidies provided by foreign governments.

China is often cited as a classic case where manipulated currency and massive subsidies make it possible for that country's suppliers to ship products at prices lower than the production costs – which meets the criteria of 'dumping'. Indeed, there is a strong underlying fear in the US industry that, once China's domestic needs are satisfied, it will begin to dump the excess steel production onto the world markets, particularly the US.

Voicing these concerns, the AISI chairman Louis Schorsch (Mittal Steel USA), issued a statement linking the increased imports in the first half of the year to continued state support for the massive expansion of steel capacity in China and the rest of Asia. "A revitalised, globally-competitive American steel industry urges continued close vigilance of imports and strong trade law enforcement to ensure market-based outcomes," he said.

US steel executives have been meeting to devise a strategy that will ward off 'dumping' by foreign suppliers, though many see China as the main culprit which is not adhering to what is referred to as 'fair trade practices'. However, these same executives know that the US administration received a black eye when it last imposed restrictions on steel imports, with the WTO ruling that such restrictions violated the tenets of free trade. While the steel industry will try to push for restrictions on Chinese steel imports, the US administration will be wary of such initiatives. Most experts say that, if pressurised, the administration will probably search for a 'middle path solution' between an outright stoppage and unrestricted imports. STI

Changes at Mittal

The reorganisation at Mittal Steel's plant in Weirton caused some initial unease amongst the trade unions but the Independent Steelworkers Union (ISU) leaders expressed confidence in the Weirton plant's future, though it said that was waiting to hear more about the strategy of the new VP of operations and CEO.

According to an announcement by the company, Mike Rippey will replace Louis Schorsch as president and CEO; Schorsch will take over as CEO of flat products for the Americas, and will take charge of streamlining management for CST and Vega do Sol in Brazil, Mittal Steel Lazaro Cardenas in Mexico, Mittal Steel USA and the flat-rolled operations of Mittal Steel Canada.

However, Weirton's future with Mittal will be decided by the US Justice Department, which has a consent decree with the company to avoid an anti-trust action on the tin-mill capacity in the eastern region of the United States. The Department is closely scrutinising the Mittal/Arcelor merger because Mittal would have developed an overcapacity for tin, due to Arcelor's Dofasco unit in Canada, plus Mittal's mills at Weirton and Sparrows Point Maryland.

US analysts maintain that the consent decree requires Mittal to make its 'best efforts' to sell Dofosco and, if it does not want or cannot sell it, the Justice Department may ask Mittal to put either the Maryland or Weirton plant up for disposal. STI

BY MANIK MEHTA, NEW YORK

Esmark wants to make its mark at Wheeling-Pitt

Esmark, the steel service centre company, has recruited steel industry veteran V John Goodwill who, experts say, could play an important role if the company achieves its hostile takeover of integrated steelmaker Wheeling-Pittsburgh. Indeed, Goodwin, now 62, is tipped to become Esmark's vice president of mill operations of the steel facilities it would acquire from Wheeling-Pitt, if the takeover is successful.

Goodwin has more than 40 years experience in the steel industry, and last served as chief operating officer of International Steel Group until April 2005 when the company was acquired by Mittal Steel. Prior to that he held senior positions with US Steel, National Steel Corp, Betal Steel and Steel Consultants.

Esmark is trying to convince Wheeling-Pitt shareholders to elect its proposed slate of directors to the steel company's board; if successful, the new board would be asked to approve the service centre group's acquisition of the Wheeling, West Virginia-based company. Esmark has argued that, as Wheeling-Pitt has not been making adequate operating profit, a merger with Esmark would allow the steel company to reduce its operating costs and, in effect, raise its profitability. Wheeling-Pitt, on the other hand, is looking to merge with Brazilian steelmaker Companhia Siderurgica Nacional (CSN). STI

Kenwal SC for SeverCorr mini

Kenwal Steel, a Dearborn, Michigan-based group of companies providing flat rolled steel products and services from processing facilities in the Midwest and Canada, announced that it is building a $15M state-of-the-art processing and distribution facility next to the SeverCorr minimill now under construction near Columbus, Mississippi.

The mill is a jv between Russia's Severstal (80%) and former Nucor CEO John Correnti; it will use SMS flat product casting-rolling technology (see *STI NovDec 05, pp22-23*). Kenwal's service capabilities will include a light gauge slitting system with surface critical technology that will focus on cold rolled, and coated materials from 0.010" (0.254mm) to 0.060" (1.524mm) thick in widths up to 72" (1829mm) wide; a heavier gauge system tailored to run unexposed materials like hot-rolled black and pickled and oiled from 0.055" (1.397mm) to 0.375" (9.525mm) thick in widths up to 72" (1829mm); an automated packaging line will complement the slitters to accommodate specific customer needs on all slit coil requirements; rail and truck shipping and receiving docks will be supported by 44t cranes to handle SeverCorr's large coil capability. Kenwal expects the ground breaking ceremony to be held in October while the launch should take place in late spring 2006. STI

A world centre of leading factories – Japan

Having continuing historically high levels of profits, many Japanese manufacturing companies are now becoming more confident than ever about their businesses and are ready to make positive investments and developments in order to take the initiative in global competition.

BY NOBUHISA IWASE*

Most Japanese globally-competitive companies are not only keen to increase production capacity abroad, particularly in such growing countries as BRICs (Brazil, Russia, India and China), but are now also eager to strengthen their development and production capabilities at home. While the move is spearheaded by automobile companies such as Toyota and Honda, other manufacturers – in electrical machinery, electronics, chemicals and other material-related sectors including steel – are no exception to the trend. Although China continues to increase its importance as a central factory in the world, Japan's importance as a centre of leading technologies and state-of-the-art production facilities will not dwindle and is likely to increase further.

NEW PLANTS FOR TOYOTA

Toyota has a medium-term plan to increase its worldwide sales units to 10.3M in 2010 from the current 7.27M. Most of the capacity increase will be realised at its foreign production bases. Just after its recent start-up of the new Guangzhou assembly plant for the Camry model for 100 000/y units in China, the company revealed it intends to increase its Chinese assembly capacity to almost one million units a year in 2010 from 240 000/y in 2005, including an additional 100 000/y in Guangzhou. The company is also about to start operation of new assembly plants in Texas, USA (2007) and Canada (2008). It plans to start US production of the Prius, its flagship 'hybrid car', with a production plan for 1M hybrid cars worldwide. It is also strengthening its development and production capabilities in Japan, making maximum use of qualified labour and strong supplier networks.

Toyota recently invested US$300M opening a major engine production plant in northern Kyushu – the fourth in Japan, but the first-ever engine plant outside the Aichi prefecture, the company's production centre in central Japan. The plant's capacity is 220 000/y units, most of which is supplied to its neighbouring assembly facility for the Lexus model. The company sees Kyushu as its major production center after Aichi as, in northern Kyushu, the combined assembling capacity for passenger cars now amounts to almost 1M/y by Toyota, Nissan and Daihatsu.

Apart from the 'big three', auto parts and components manufacturers have gathered in the area to make up an 'automotive cluster' almost equidistant (1000km) from Shanghai, Tianjin, and Tokyo. Ulsan of Korea, one of the key industrial cities in the automobile and shipbuilding sectors, is located only 250km away from northern Kyushu at the opposite side of the Sea of Japan. Actually many auto parts and components companies in northern Kyushu actively trade with Korea and China According to a survey, 28 automotive component manufacturers export to China, 14 to Korea and 29 to ASEAN countries. Given globally-connected supply chains, particularly in Asia, the importance of development and production capabilities inside Japan, especially for high-end products and components, has again increased.

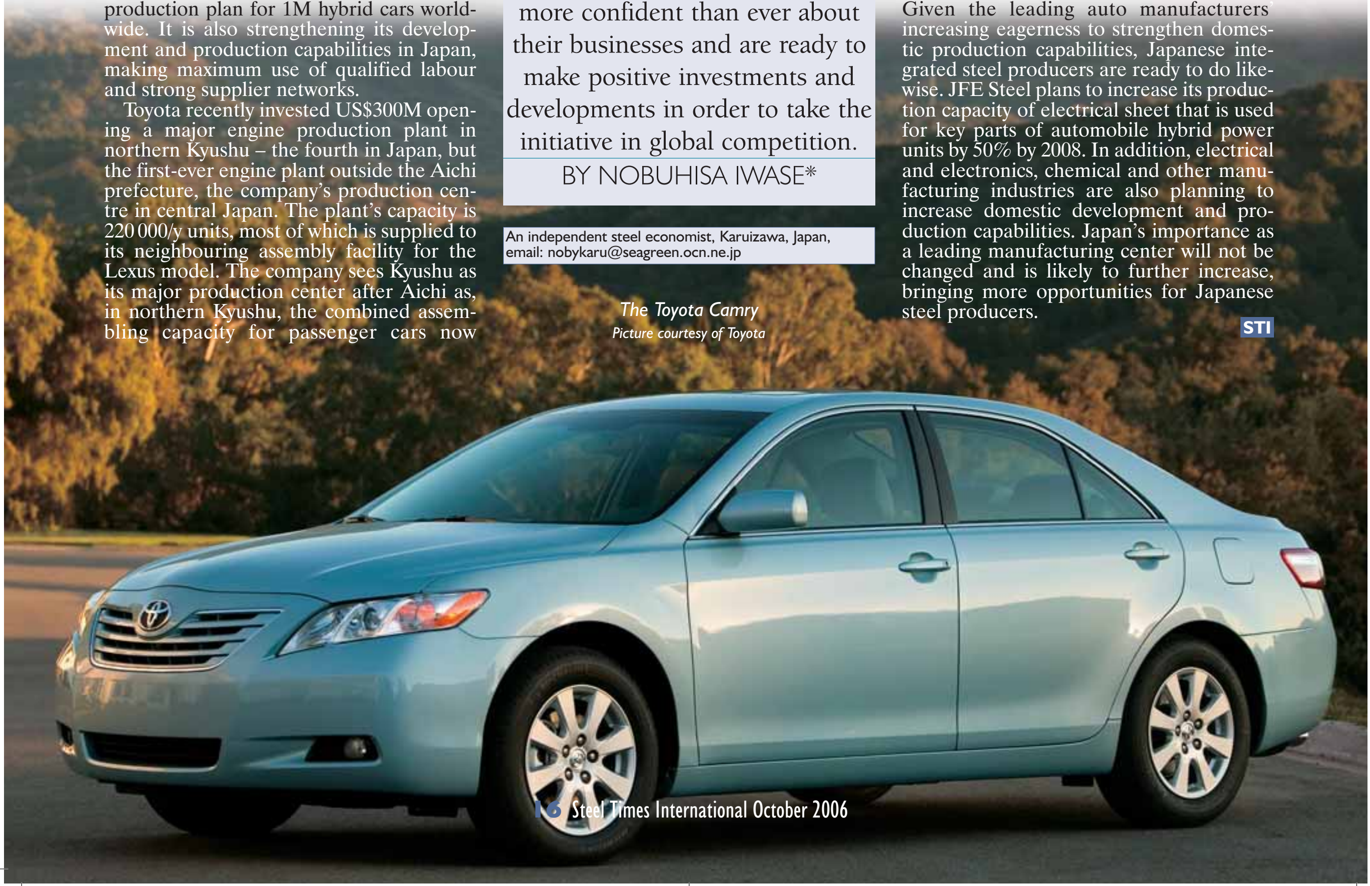
HONDA'S AGGRESSIVE STRATEGIC PLAN

In May, Honda revealed its very aggressive strategic plan that included almost 20 new investments and developments worldwide under its new global sales target of 4.5M/y units for 2010. The company plans to invest US$600M to construct a new passenger car assembly plant in northern Tokyo by that date. The new 200 000/y unit capacity facility will be the first new assembly plant in Japan for the company for the past 30 years. Apart from its home market, Honda intends to construct an additional US$400M assembly plant in the US with 150 000/y unit capacity by 2008; it also intends to invest US$140M in constructing a new 200 000/y unit capacity engine manufacturing plant in Canada by 2008. However, its central efforts will focus on strengthening its national development and production capabilities, particularly for hybrid cars. The company plans to build a new 200 000/y unit capacity plant for electric motor production for hybrid cars, four times more than current capacity, in its central production center at Suzuka in the Mie prefecture. Major parts and components for hybrid cars are technically and strategically the most important for the leading competitive auto manufacturers, so the company will increase production capacities of those key parts at its home production bases in order to prepare for future expansion of hybrid car production both at home and abroad. Honda also revealed a plan to establish a new US$150M research and development facility north of Tokyo by 2009. Having recorded five consecutive years of historically high net profits, the Honda group has accumulated US$6.5bn of retained earnings. With this increased financial capability, it has regained its appetite both for expansion and for increasing production volumes.

OTHERS QUICK TO FOLLOW SUIT

Given the leading auto manufacturers' increasing eagerness to strengthen domestic production capabilities, Japanese integrated steel producers are ready to do likewise. JFE Steel plans to increase its production capacity of electrical sheet that is used for key parts of automobile hybrid power units by 50% by 2008. In addition, electrical and electronics, chemical and other manufacturing industries are also planning to increase domestic development and production capabilities. Japan's importance as a leading manufacturing center will not be changed and is likely to further increase, bringing more opportunities for Japanese steel producers.

STI



The Toyota Camry

Picture courtesy of Toyota

An independent steel economist, Karuizawa, Japan, email: nobykaru@seagreen.ocn.ne.jp

Maverick's acquisition: Tenaris expands again

The deal by Tenaris to buy Maverick will surpass last year's $2.25bn transaction between Hylsamex and Ternium (both controlled by the Techint Group).

In the internationalisation of Latin American steel companies, Tenaris has played a prominent role in many dimensions. In terms of geographic distribution, no other Latin America firm as definitively controls productive assets in so many countries and continents – Argentina, Mexico, Italy, Brazil, Canada, Venezuela, and Romania.

Now, as a consequence of the Maverick transaction, it has finally gained a foothold in the United States, a long-held goal for the company. Maverick has also plants in Canada and Colombia.

Maverick is a leading North American producer of welded oil country tubular goods (OCTG), line pipe and coiled tubing for use in oil and natural gas wells. Its electrical products division produces welded pipes for electrical conduits. In real terms, it is a relatively new company since it began operations in 1978; at that time, it was dedicated to manufacturing mechanical tubing. Two years later, it entered the energy market, producing its first OCTG and went public via an IPO in 1991.

The company has experienced a considerable growth during the past decade. In 2000, it merged with Prudential Steel, a Canadian tubemaker based in Calgary, Alberta. In 2002, it purchased five pipe mills from the former LTV Tube division while last year, it acquired both Tubos del Caribe, a Colombian manufacturer of OCTG and line pipe and Colmena, a Colombian manufacturer of steel electrical conduit and other pipe and tube products.

On the other hand, also in 2005, Maverick sold its hollow structural sections (HSS) business to Atlas, a market segment in which the company had been engaged since 1994. In 2006, the company decided to shut its Elyria, Ohio plant, which had been its only mechanical tubing production facility, thereby exiting this market segment too.

After all this restructuring, Maverick has a combined annual capacity of 1.8Mt/y of steel pipes with a size range from one-quarter inch to 16 inches. Last year, it shipped approximately 1.2Mt of welded pipes. Maverick's revenues totalled $1.8bn in 2005, of which 82% came from its energy products division. Its EBITDA margin was equivalent to 16%.

Tenaris and Maverick expect the transaction to close late Q3 2006 or early Q4 2006, pending regulatory approvals. The Colombian Superintendence of Industry and Commerce has completed its review and has cleared the proposed merger without conditions; the Colombian condition precedent in the merger agreement with Tenaris is now satisfied. The proposed merger has now been cleared by competition authorities in all jurisdictions in which such clearance is a condition precedent to the transaction. Maverick's special meeting of stockholders to vote on the proposed merger is scheduled for October 2, 2006. Assuming that the acquisition is completed, Tenaris' global rated capacity will expand to 3.3Mt/y of seamless tubes and 2.7Mt/y of welded pipes. It will also capture a 20% share of the North American (USA and Canada) OCTG market too, while taking the lead position for tubular products for the world's oil and gas industry.

Its annualised revenues will be improved to roughly $9bn, of which 30% will be in the USA and Canada. The company firmly believes that the acquisition will increase its purchasing power with steel companies and create complementary product ranges. According to the company, product offerings in North America will cover a wide range of applications from onshore shallow wells to complex deepwater applications. Its position in Colombia will complement the enterprise's assets in Venezuela and allow an expansion towards high-end product range, to include coiled tubing and umbilicals.

In the largest acquisition ever carried out by a Latin American steel company, Tenaris recently announced an agreement to purchase US tubemaker Maverick Tube Corporation, in a $3.18bn all-cash transaction (including net debt).

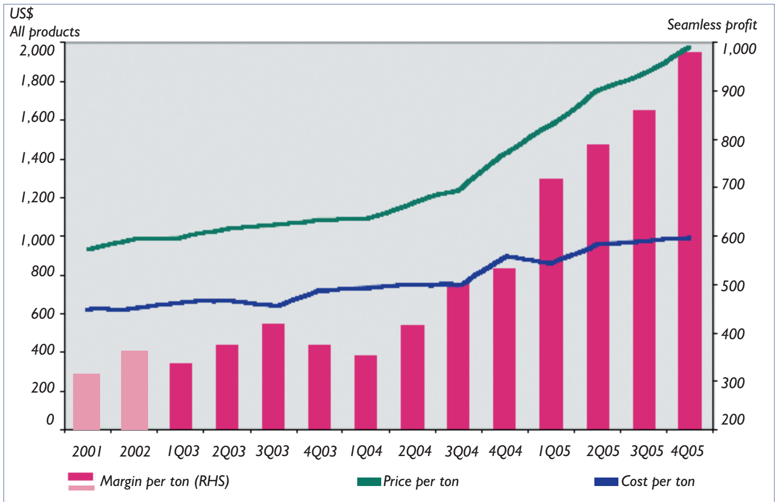
BY GERMANO MENDES DE PAULA*

It will continue to supply the USA from its other tubular operations in Canada, Mexico and Romania. Tenaris' chairman has declared that Maverick, on its own, cannot supply all Tenaris' current US customers. The purchase of Maverick will boost the proportion of welded pipes – last year, for example, 76% of Tenaris' sales were related to seamless tubes. Before Maverick's acquisition, Tenaris' welded pipe operations were restricted to Confab (Brazil) and SIAT (Argentina).

Tenaris had very little net debt at December 2005 – just $183M – in relation to its EBITDA ($2.2bn) and net sales ($6.7bn) and the Maverick acquisition is expected to proportionately lower its net debt against EBIDTA.

The company's results have benefited from strong global demand from the energy industry for OCTG and other seamless pipe products. Furthermore, the favourable market conditions include relatively stable prices for raw materials, plus robust demand for high-end seamless pipe products (**Fig 1**). The seamless tube profit margins have increased from $300/t in 2001 to $1000/t in the Q4 2005 (see right axis of **Fig 1**).

The combination of a fairly comfortable financial situation (low net debt), a market characterised by strong demand and increasingly high profit margins and the past record of successful acquisitions suggests that Tenaris will be continue to act as a predator in the worldwide steel industry consolidation game. **STI**



1 Tenaris' pipe profit margins, 2001-2005 ($/t)

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* Lecturer in Economics, Federal University of Uberlândia, Brazil. email: germano@ufu.br

Recycling potential of secondary mill sludge

A method of decanting secondary mill scale to reduce its oil content, followed by air drying then furnace drying, has been developed by SAIL which conducted trials that show the resulting iron rich material can be added to the sinter plant at quantities of up to 10kg/t sinter without adversely affecting sinter mechanical properties or flue gas emissions.

BY S MITRA MAZUMDER, V R DESHMUKH, G D MAHESHWARI, S BHATTACHARYA, S N TIWARI, S PRAKASH & H R MURTY

The primary mill scale collected as a coarse material in the initial settling tanks of the mill cooling circuit is fully recycled in almost all steel plants. However the very nature of secondary sludge (hydrated oily sludge) collected at a later stage makes it difficult to process. On the other hand, stringent regulations make it increasingly difficult to dump oily waste in landfill sites. Since the iron content of the sludge is significant (generally > 55%) the material has a high potential for recycling. As this kind of recycling is not widely practiced and sparingly reported in the literature, a pilot study was undertaken to study some aspects of recycling this sludge with the ultimate aim of developing a suitable process to use the material.

SECONDARY MILL SLUDGE

Oily wastes from mills contain lubricating oil and hydraulic pressure fluids that are usually emulsified. There are other oil interfaces too; for example, during pickling of hot strip, the strip is pre-oiled to prevent scratching as it is uncoiled. Mill rolls are also often sprayed with an emulsion of water and soluble oil. The emulsions, or more precisely the base oils, contain anti-oxygen or algaecide additives. During the process of surface cleaning, scale becomes mixed with these emulsions.

After settling, primary scales remain relatively oil free and are readily usable in the sinter plant. However, secondary sludge remains a problem since it not only contains oil but also has significant moisture content even after separation of the oil water emulsion through skimming and natural drying.

SECONDARY SLUDGE USE

The main alternative recycling possibilities reported in the literature for recycling of oily mill scale within an integrated iron and steel works are:

- Spraying of oily mill scale onto the sinter belt (Bethlehem Steel);
- Injecting into the blast furnace through a tuyere;
- Adding oily mill scales onto the sinter strand using a top-layer sintering process;
- Biologically de-oiling prior to using.

Looking at some techniques in detail:

Spraying of oily mill scale in the sinter plant: The Burns Harbor division of Bethlehem Steel developed and patented an innovative technology for recycling oily mill scales and sludge to the sinter plant without opacity problems in the sinter plant stack emissions or adverse sinter quality problems. The process involves spraying the sludge directly onto the sinter bed immediately after ignition using high-pressure spray nozzles to form a fine mist which is then drawn down through the flame front of the sinter bed. However, the process required the oil content to be moderately low.

Mill sludge as blast furnace feed: To explore the possibility of using mill sludge as a substitute for iron ore in blast furnace feed, briquetting tests were conducted. For these tests briquettes were made with sludge using different percentages of molasses and hydrated lime as binders. Reportedly, the main problems arising from the procedure are related to fine mill scale becoming trapped in the filters and settling tanks.

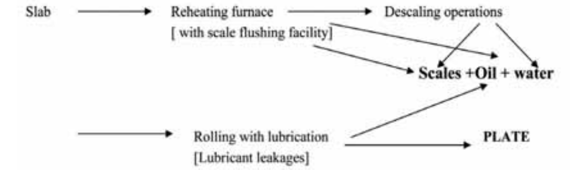
Top-layer sintering process: In the top layer sintering process developed by VAI, organic-bearing reverts are charged onto the surface of the existing sinter bed, forming a second layer with a thickness ranging between 20 to 50mm. This layer is separately and intensively ignited and converted to sinter. During this phase most of the organics are combusted or at least cracked.

Biologically de-oiling: Bethlehem Steel's test to 'compost' sludge at Burns Harbor, (Indiana) and Sparrows Point (Maryland) showed that naturally occurring micro-organisms could be used to achieve reduction in the oil content sludge. However, since the process is quite slow it can be used as one part of a multi-stage process.

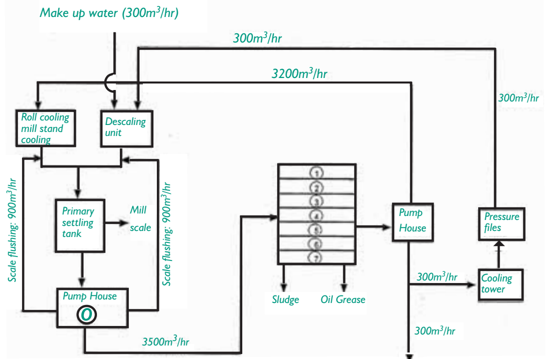
All the processes reported in the literature need strong process interventions which is often discouraging for 'process owners' as this may cause disruption in existing operation. The pilot study was aimed to study the potential of using the sludge through a non-invasive manner. Towards this end, secondary sludge generated at the plate mill of Bhilai Steel plant (BSP) was taken up for experimental purpose.

PLATE MILL SLUDGE

In BSP's plate mill, larger-sized mill scale generated from process operations is already collected from the primary settling tank and fully recycled to the sinter plant. However, secondary sludge collected from the secondary settling tank consists of fine



1 Flow chart for generation of oily sludge



2 Secondary sludge settling tank zone

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Raw Materials	Fe	SiO_2	Al_2O_3	CaO	MgO	LOI
Iron ore, Dalli	63.28	4.35	2.52	-	-	2.5
Iron ore, Rajhara	63.0	4.41	2.65	-	-	3.0
Blend one	63.22	4.362	2.546	-		2.6
Mixed flux	-	5.53	2.525	33.80	10.425	42.425
Mill scale	71.44	1.26				
Coke Breeze (Ash = 19.08%)	9.78	50.36	24.45	3.76	1.25	

Table 1 Chemical analysis of sinter raw materials (%)

Sl No	Iron Ore (Rajhara)	Mixed flux	Mill scale	Coke breeze	Sludge
1	749.16	416.02	15.0	90.0	0 (Base)
2	742.11	419.87	15.0	90.0	5
3	733.95	426.08	15.0	90.0	10

Table 2 Specific raw material consumption (kg/t)

Sl No	Sludge kg/t	Fe	SiO_2	Al_2O_3	CaO	MgO
1	0	48.59	6.440	3.360	14.12	4.35
2	5	48.41	6.456	3.387	14.25	4.40
3	10	48.17	6.486	3.570	14.46	4.46

Table 3 Target chemical analysis of sinter (%)

mill scale, oil and water and is consequently not recycled.

Fig 1 shows a simple line flow chart of the process steps leading to generation of this oily sludge.

The whole waste containing oil and water goes to the primary settling tank from where the coarser sized mill scale is withdrawn and put in the scale pit; from here the material is recycled to the sinter plant as mill scale. The finer-sized fraction goes to the secondary settling tank. A block diagram of the settling tank zone is presented in **Fig 2**. This secondary settling tank sludge, which is pasty in nature, consists of fine mill scales, oil and water. The average quantity of this secondary sludge produced each year is approximately 3 000t containing up to 10% oil.

EXPERIMENTAL

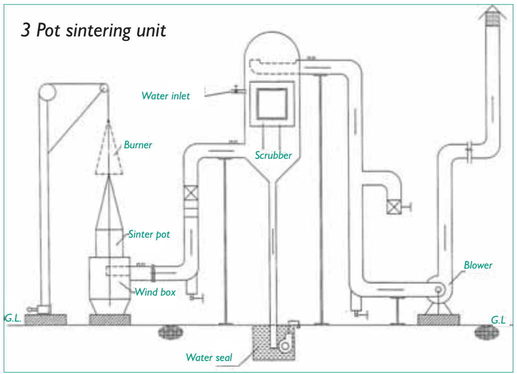
A major stumbling block in using the secondary sludge is its sticky nature. The literature survey had revealed that all the conventional methods of removing the oil would be cost-ineffective. Therefore an unconventional method was tried. Since it is difficult to remove oil from an *in-situ* air-dried sludge, fresh secondary sludge was slurried and decanted to separate the emulsion to partially remove oil. The decanted material was first air-dried and thereafter the main thrust of the trials was to find a suitable heating process to render it free-flowing. The mill sludge was then heated in a muffle furnace to prepare it for sintering. Since the material had to be ultimately treated on a plant-scale, heating was carried out in an idled heating furnace in a nearby shop using the experimental conditions:

Weight of sludge	1.5t
Size of furnace	2m x 3m
Heating material used	iron plate
Gas used	coke oven gas
Temperature	1600°C
Duration	8 hrs

Component	Wt%
Fe_2O_3	77.45
SiO_2	5.77
Al_2O_3	1.20
CaO	0.14
MgO	2.31
Na_2O	0.12
K_2O	0.023
P_2O_5	0.42
S	0.27
MnO	1.18
Oil content	5.8

Table 4 Chemical composition of sludge after pre-treatment

3 Pot sintering unit



POT SINTERING INVESTIGATION

A pot sintering investigation was undertaken to study the effect of using the treated mill sludge on sintering parameters ie, strength index, productivity, reduction degradation index, reducibility index and melt-down characteristics. A line sketch of the pot sintering unit is given in **Fig 3**. The sintering process parameters of Sinter Plant II at BSP are:

- Bed height = 450mm
- Suction =700mmwc
- Ignition time = 2min
- Mixing and balling time = 3min
- Moisture content of sinter mix = 6.2%
- Specific coke consumption = 90kg/t
- Degree of stabilisation for calculation of yield = 5 drops from 2m height
- Percentage sinter return including BF sinter = 30%,
- Mill scale = 15kg/t

The ore blend used in the sinter plant is 80:20 Dalli:Rajhara mine products. Since a mixed flux was supplied the MgO content of the sinter could not be maintained constant (**Table 1**). The chemistry of the raw materials, specific consumption and the target chemistry for the sinter is given in **Tables 1-3**.

After carrying out base parameter studies charge calculations were repeated with treated sludge added in proportions up to 10kg per tonne of sinter to find out its impact on the sinter plant environment and the properties of the sinter. Sintering experiments were carried out with the charge consisting of ore fines, fluxes, ferruginous wastes and coke breeze in the desired proportions, to achieve the required basicity, SiO_2 and MgO contents in the sinter. Ignition of the bed was performed by spreading a layer of about 650g of charcoal on top of the charge bed and igniting it under a low suction of 500mmwc for a duration of 1-2 minutes.

DROP & SHATTER TESTS

All the trial sinters were produced using this technique and then subjected to shatter and tumbler tests. The sinter produced from the pot grate furnace is tested by dropping it five times from a height of 2m onto a steel plate and the resultant material sieved and the +5.6mm fraction measured as usable sinter while smaller particles are returned to the sinter plant.

20kg of 10-40mm sinter was taken for the shatter test; the material was allowed to fall four times from a height of 2m onto a steel plate and the amount of +10mm fraction surviving is reported as the shatter index.

TUMBLER TEST

15kg of 10-40mm size sinter was taken for the tumbler test. The material was subjected to tumbling in a drum of 1 000mm diameter and 500mm barrel length. The drum was provided with two lifters, each 50mm high at opposite sides of the internal circumference. The drum was rotated at 25rpm for 8 minutes. The +6.3mm fraction was reported as the tumbler index (TI).

ENVIRONMENTAL STUDIES

Environmental studies were carried out using a porthole at the flue gas outlet pipe

▶28

Sludge (kg/t)	TI (+6.3),mm%	Y+5%	P+5(t/m²hr)
Base (0)	73.1	73.10	1.14
5	73.3	76.62	1.24
10	72.67	78.68	1.27

Y +5 = Yield of +5 mm sinter after subjecting to 5 no. of drops
BD = Bulk density (t/m^3), TI (Tumbler Index +6.3 min), %
P +5 = Productivity, $t/m^2/hr$

Table 5 Experimental results of sintering tests

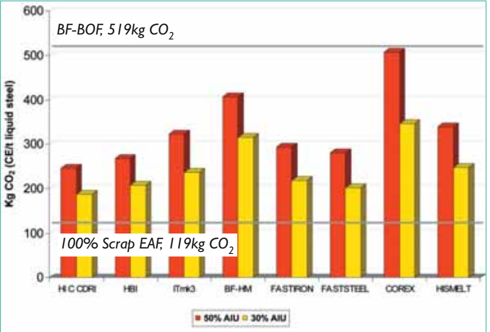
Steelmaking slag as a permanent sequestration sink for carbon dioxide

A new process to react steelmaking slag with the off-gas from steelmaking has the potential of capturing 6-11% of the CO_2 emissions from integrated mills and 35-45% from scrap-based steelmaking.

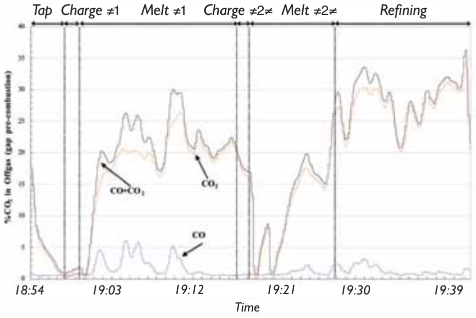
BY C H RAWLINS, VON L RICHARDS, K D PEASLEE, & S N LEKAKH

Carbon dioxide is generated directly from the furnaces in iron and steel production, or indirectly through support systems such as coal burning power plants providing electric power to the plant. Steelmaking CO_2 emissions vary based on the geographic region and the technologies used for manufacturing. Integrated steel mills generate more CO_2 per tonne than mini-mills due to coke making and blast furnace (BF) ironmaking. In 2000, US integrated mills produced 33.5M tonnes of CO_2 carbon equivalent (CE) units, of which 64% was generated through the production and use of coke[1]. During the same year, US mini-mills generated 13.7M tonnes of CO_2 CE, of which 80% was generated at the power plant[1]. On average, the US steel industry produced 0.42 tonnes CE of CO_2 per tonne of steel shipped in 2000. **Table 1** compares the rates of CO_2 emissions in the US with several European countries and Japan. It is particularly interesting that France reports an extremely low CO_2 emission rate of 0.03 tonnes CE per tonne of steel produced by electric arc furnace (EAF) steelmaking using 100% scrap and electric power generated by nuclear energy.

Anderson *et al* compared carbon dioxide emissions and energy requirements for 30 different steelmaking routes.[10] In the study, they compared emissions from alternative steelmaking technologies with two common baseline technologies: basic oxygen furnace (BOF) steel produced from 89% BF hot metal and 11% scrap (519kg CE per tonne of steel); and EAF steelmaking using 100% scrap (119kg CE per tonne of steel). **Fig 1** compares the effect of replacing scrap in EAF steelmaking with 30% or 50% alternative iron units (AIU) produced by a variety of alternative technologies. Indirect sources of CO_2 are responsible for the majority of the CO_2 generated in EAF steelmaking using scrap, with the largest fraction coming from electricity generation[11,12]. EAF steelmaking using 100% scrap in the US, Canada, and France resulted in CO_2 generation (per tonne of liquid steel) of 140kg CE, 89kg CE, and 46kg CE, respectively, based on the difference in the amount of electricity generated by hydrocarbon combustion. The US relies on 69% of the electricity from hydrocarbon combustion, Canada is lower at 32%, and France is even lower at 5%.



1 Carbon equivalent tonnes of CO_2 emitted per tonne of liquid steel for EAF steelmaking with 30% and 50% addition of alternative iron units (AIU) to scrap. Data from Anderson et al 2002[10]



2 Composition profile of the offgas collection system, during the progress of a heat, from a northeastern US EAF shop. The CO_2 and CO concentrations (vol %) are from the 4th hole gap prior to combustion

Region	Year reported	Amount (t CE/t steel)	Reference
Russia	1998	1.4	Afonin[2]
France	1989	0.42	Birat et al.[3-6]
France	1994	0.40	Birat et al.[3-6]
France	1994	0.03 (EAF/100% scrap)	Birat et al.[3-6]
Finland	1994	0.53	Holappa[7]
Japan	2005	0.46	Emi and Gielen[8,9]
United States	2000	0.42	Stubbles[1]

Table 1 Comparison of CO_2 emissions from integrated steelmaking by geographic region

OFFGAS COMPOSITION IN STEELMAKING

Offgas composition fluctuations during the stages of a steelmaking heat complicates the offgas treatment. **Fig 2** illustrates the variation in offgas composition from the fourth-hole after the combustion gap (but before combustion) in a typical EAF heat. During the melt, CO_2 concentration averaged 20-25% from the combustion of natural gas in the oxy-fuel burners and other sources of carbon in the charge. The CO_2 concentration reached its highest peak of 30-35% during the oxygen blow from the combustion of dissolved carbon and carbon injected into the slag. The average CO_2 concentration across the entire heat is about 18%, which corresponds well with the values shown by Evenson[13] (23% average for 30 heats of an EAF shop) and Grant[14] (15% for average of 15 heats from an EAF shop). A similar study of 10 heats showed similar trends with the peak CO_2 concentration averaging 30-35% and an overall average throughout the heats of 18-20%.

Combining the composition data from **Fig 2** with the temperature and flow profile of the offgas system yields the estimated CO_2 concentration at the discharge stack (after the baghouse). The offgas combustion zone operates at 1760°C, which is cooled to 450°C after air dilution. Assuming full combustion of CO to CO_2, the peak carbon dioxide concentration drops to 14-15% with an average of 6-7%. Further air dilution and water quenching drops the offgas temperature to 90°C allowing discharge through the baghouse. The carbon dioxide concentration in the stack discharge peaks at 10-11% with a 4-5% average. A furnace offgas CO_2 capture and sequestration system will most likely be installed after the baghouse to prevent dust contamination. Therefore, the technology developed should be able to treat offgas averaging 4-5% CO_2.

SEQUESTRATION POTENTIAL OF STEELMAKING SLAG

Sequestration technologies that allow direct capture of CO_2 from offgas are effective as source point mitigation when source reduction through lower energy use cannot be made. This project seeks to develop a feasible sequestration technology using slag to permanently capture carbon dioxide. A parallel benefit of slag-based CO_2 sequestration is chemical stabilisation of the slag minerals. The slag is thus rendered immune to end-use swelling or leaching, eliminating stockpile aging required prior to commercial use, and opening up more markets and value for steelmaking slag.

The potential of steelmaking slag to react with CO_2 to form permanent carbonate minerals (sequestration) is derived from slag's high concentration of alkaline earth metal oxides. Two alkaline earth metal oxides in sufficient concentration to economically sequester CO_2 are CaO and MgO. **Table 1** shows the concentration of key sequestration compounds from several industrial slags produced by North American steelmakers. A total of six steelmaking sites representing multiple steelmaking processes were sampled. All LMF slags shown were collected from EAF sites. The average of each slag type is compared with the National Slag Association (NSA) average for general steelmaking.

The sequestration potential of a slag can be determined from the amount of slag produced and the respective carbonate reactions. The National Slag Association estimates that BOF steelmakers produce 75-150kg of slag per tonne of steel compared to 65-80kg of slag per tonne of steel for EAF steelmakers[16]. Both CaO and MgO readily form carbonates upon reaction with CO_2, while the other major compounds (SiO_2, FeO/Fe_2O_3, Al_2O_3, and MnO) are inert to spontaneous reactions with carbon dioxide and are precluded from the sequestration potential. Potassium and sodium oxide readily form carbonates, but neither is present in sufficient quantities to be of value. Calcium and magnesium oxide react with CO_2 in a 1:1 molar combination to form $CaCO_3$ and $MgCO_3$, respectively. Using the average composition values for CaO and MgO from **Table 2**, the amount of slag produced per tonne of steel and the carbon emission values emitted per tonne of liquid steel from Anderson *et al* (BF-BOF: 187 kg CE and EAF: 24kg CE) allows for calculation of the effective sequestration potential. The slag produced per tonne of steel has the potential of sequestering 5-10% of the BF-BOF carbon dioxide emissions and 28-34% of EAF carbon dioxide emissions. In addition, the estimated 15-20kg of LMF slag produced per tonne of steel has the potential of capturing an additional 1.0-1.3% of BOF and 7.8-10.4% of EAF CO_2 emissions. Thus the total sequestration potential for steelmaking slag is 6-11% of the CO_2 emitted from integrated mills and 35-45% from scrap-based steelmakers.

OFFGAS CO_2 CAPTURE SYSTEM USING SLAG

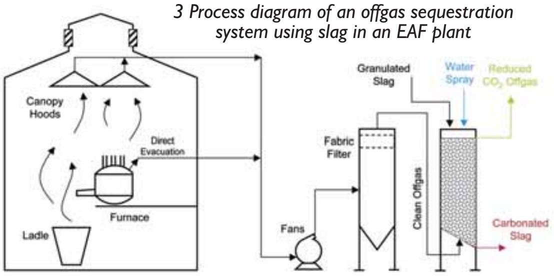
The current North American slag practice involves ground-based stockpiling to cool and stabilise the slag before it is sold for construction applications. The slag may go through several processing steps, such as crushing, screening, and magnetic separation to recover the metallic fraction, however further processing is minimal. A slag sequestration system must be simple and robust to allow for minimal cost impact to slag handling. A reactor to contact slag and CO_2 will most likely be installed after a gas cleaning system such as baghouse or electrostatic precipitator to prevent contamination with dust. The discharge gas will typically be at 90-150°C with 4-5% CO_2.

Two different design concepts are proposed for a reactor to contact slag and offgas. The first concept is a solid-gas reactor utilising either a plug flow or rotary design. A schematic of this type of system is shown in **Fig 3** where the stack offgas is directed through an atmospheric vessel containing slag particles. The sensible heat of the offgas provides heat into the system which increases the carbonation kinetics. In addition, water spray may be added as gas humidification also increases the CO_2 reaction kinetics. After reaching CO_2 saturation, slag is removed and fresh slag input to repeat the process. To allow continuous operation, either two parallel vessels would be required to allow one to dump/load while the other is reacting or a rotary vessel would be designed to flow slag particles countercurrent to the offgas.

A second design concept is to mix the slag with water to form a slurry through which offgas is bubbled. A slurry reactor requires continuous stirring and may be modeled after a mechanical flotation cell. While a slurry reactor adds the step of water handling to operation, the increase in reaction rate achieved may be critical for operation. Both design bases are being investigated in this project through bench-scale testing.

Lab-scale testing with hi-cal lime has shown a dramatic effect of temperature and gas humidification on reaction rate. Tests are conducted in a thermogravimetric analyser to measure weight change as a function of time in a furnace. An increase in temperature from 100°C to 500°C results in eight times the reaction rate. Raising the temperature proportionally changes the CO_2 diffusivity into the lime particle thus increasing the overall reaction rate. Humidification of the CO_2 gas increases the reaction rate at the same temperature by approximately 25%. Humidification has a catalytic effect by allowing the lime to enter solution in a surface gel that greatly speeds up the reaction between CO_2 and CaO. Work is continuing at the University of Missouri – Rolla on a range of industrial EAF, BOF, and LMF slags. Refinements of the operating conditions as affected by slag chemistry and phase analysis, as well as temperature, CO_2 content, and humidification, are ongoing in an effort to design a suitable full-scale system.

In addition to the positive environmental impact of this new technology, the resulting slag product will have better properties, increasing its sustainable value through the rapid conversion of CaO and MgO to carbonates. This will open up new markets for slag products and eliminate the current storage time and space requirements. **STI**


3 Process diagram of an offgas sequestration system using slag in an EAF plant

Source	EAF	LMF	BOF	NSA[15]
# Samples	8	3	2	-
	Average Concentration (Wt %)			
CaO	32.4	49.4	40.7	42.9
MgO	11.2	6.2	12.9	8.1
SiO_2	13.9	13.0	11.7	14.9
FeO/Fe_2O_3	26.9	5.6	21.7	25.0
Al_2O_3	8.3	21.3	5.9	5.0
MnO	5.4	1.1	4.6	5.0
K_2O	<0.01	<0.01	<0.01	NR
Na_2O	<0.01	<0.01	<0.01	NR

Table 2 Concentration of key sequestration compounds in steelmaking slags
NSA = National Slag Association average

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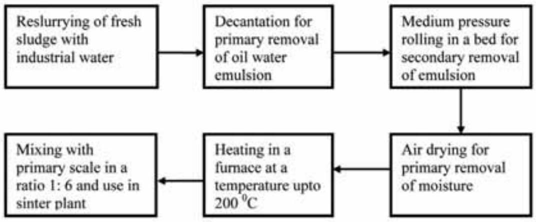
24▶Recycling potential of secondary mill sludge...

Mill sludge (kg/t)	CO	CO_2	O_2	NO_2	SO_2	H_2S	NO
Base(0)	1850	0.3	20.9	90	130	180	90
5	2050	0.3	20.9	100	136	200	100
10	> 3000	0.4	20.9	105	239	110	22

Table 6 Typical stack monitoring results at start of sintering (in ppm max)



4 A non-invasive method of oily sludge pre-treatment and use

of the pot sintering unit. Simultaneously, the flue gases generated during the sintering process were monitored to assess the concentration of CO, SO_2, NO, H_2S and NO_2. A stack gas analyser was used to study the emission levels. Although the gas monitor shows results on a continuous basis, the peak value of each parameter during the whole process stage is recorded as this takes care of the worst-case scenario.

RESULTS

A remarkable improvement was observed in the flowability characteristics of the sludge after air drying and medium-high temperature heating of the secondary decanted sludge. Fresh sludge contained approximately 40% moisture and 10% oil. The chemical characteristics of the sludge after pre-treatment are given in **table 4**.

It has been found that the use of this dried sludge does not adversely impact the sintering process.

For high additions (10kg/t sinter), a marginal decrease in the strength of the sinter was observed. For medium additions (5kg/t) the strength of the sinter increased (**Table 5**).

The specific productivity of sintering increases at all levels of sludge addition and the material helps in slightly reducing the time for sintering. In addition, the resultant sinter is richer in iron content.

Environmental studies on stack emissions showed a notable initial increase in carbon monoxide (CO) content as the quantity of treated sludge was increased in the sinter; it were more than doubled when 10kg/t were added. It was observed that the CO content was initially high, reaching a level of 3 200ppm when 10kg of treated sludge was used, which is nearly double that obtained from untreated sinter (**Table 6**). At this time, the concentration of other constituents remained low. Some time after the metallurgical reaction had started, the CO concentration reduced to a level of below 200ppm. The concentration of H_2S, SO_2, NO and NO_2 also reduced to less than 10ppm at this stage. Addition of up to 5kg/t of sinter had no pronounced effect on the emitted flue gas. Other parameters show little or no variation.

AVAILABLE MILL SCALE

The total quantity of mill scale generated in the plant is, on average, 80t/y; of that, the contribution of plate mill primary scale is around 10t/y or around 12%. The quantity of secondary scale deposited in the plate mill settling tank as sludge is approximately 3t/y, of which one can expect to recover about 50% (ie 1.5t/y). This figure has been arrived at by taking into account the high moisture content of the sludge and also the fact that any method of utilisation would result in some handling losses. Therefore, if the primary scale is mixed with treated secondary sludge in a ratio primary: secondary of 6:1, the impact of using secondary sludge will further be reduced. However on transportation and logistics grounds, such ideal mixing is not always practical. As a worst-case scenario, for experimental purposes, the dried material was used up to 10kg/t (a primary:secondary ratio of 3:2) of sinter to find out its impact on environment and sinter quality.

As a result of these studies, it was concluded that if primary scale and pre-treated secondary sludge were mixed in a ration of 3:1 (ie 5kg/t of secondary of sinter) it would improve the sinter quality.

No norms were available for CO emission in the sinter plant. However, based on CO emission in coke ovens (ie 3kg/t of coke produced as reference), the measured values of CO in the sinter flue gas were much lower than those of blast furnace operation and it was likely to fall further once this was mixed with primary mill scale after processing. Therefore the use of treated mill sludge in the sinter line would have no pronounced effect on the environment.

Such re-use of the sludge generated would not only reduce the requirement to dump it but would also save, although in a small way, in reducing specific consumption of basic raw materials. In view of the results obtained and considering the simplicity of the operation, a sludge pre-treatment and utilisation scheme where treated sludge can be added at up to 5kg/t of sinter is recommended (**Fig 4**).

FURTHER WORK

Since hardly any prior study was available on a simple and straightforward solution to the problem, the current study was aimed at finding a simple solution to the problem. Further work is being carried out in the R&D centre of SAIL to study the impact of various unit operations on removal of oil; the objective is to develop a comprehensive pre-treatment method to reduce both oil and moisture content in the sludge to render the material fully recyclable in the same way as primary scale. **STI**

Above: Glass, tyres and fluids are removed prior to shredding

Left: Cars awaiting depollution at an authorised treatment facility (ATF)

Meeting EU legislation on recycling automobiles

Tom Bird, managing director of Sims Group UK, part of one of the world's leading steel recyclers, explains a little more about the automotive steels recycling process – and some of the legislative and market issues currently driving the industry.

One thing is certain in the world of steel – and that is the uncertainty of raw material prices. Like oil or any other critical ingredient to the global industrial process, its market value moves with the fluctuating international economic winds. However, one constant that does remain the same is that a significant proportion of 'new' steel comes from ferrous material reclaimed from disused cars, otherwise known as ELVs, or end of life vehicles. And SIMS Group is one of the world's leading steel recyclers.

As a society, we recycle many types of goods in the UK. With legislation emanating from the EU such as the ELV Directive, which states that every nation must recycle 85% of an ELV by weight and also the WEEE Directive, which stipulates that every electrical product which reaches the end of its life must be recycled, the amount that we recycle is set to increase significantly. With such a reliance on landfill in this country, that is an extremely positive step forward.

However, for many years, the EU has been recovering and recycling ELVs and turning them into high quality materials for re-use. Yet with the changing nature of products and evolving legislation, there is continuing pressure on the industry to increase recovery and recycling rates.

Steel is the most important by-product of the ELV. To take the process back to when an ELV arrives at an authorised treatment facility (ATF), it is prepared for depollution, with all fluids removed, as well as tyres, batteries and other hazardous items. The ELV is then taken for shredding, where it is initially flattened, before being reduced in size by shredding hammers. The resultant material then passes through a series of wind turbines, which suck out lighter materials such as foam and cloth, leaving heavier materials such as the ferrous and non-ferrous metals to continue along the process.

The product then passes under a series of 'overband' magnets, which separates the ferrous metal from other materials. The ferrous product then goes through a picking process, where any remaining non metallic pieces, and armatures, are removed by hand, leaving the clean ferrous metal.

Sims' large shredder and processing sites are located strategically near to rail, road or sea port links so as to ease transportation. Using these links, the processed ferrous metal is transported by rail, road or sea to Sims' customers, both in the UK and across the world.The metals recycling process is an extremely effective and efficient one - and one that is environmentally-responsible, given that it is part-driven by the arising of ELVs. However, there are key political and market drivers that have an extremely significant impact on the marketplace - and these need to be looked at in order for the complete recycled automotive steel picture to be understood.

Political and legislative drivers play a crucial role in the recycled automotive steels marketplace – and in some respects are an obstacle to us, as a nation, being even more efficient in the amount of steel that we recycle. One of the biggest obstacles to greater recycling is that the system, as it stands at the moment in the EU and particularly in the UK, is not capturing all vehicles at the end of their lives. Many are being dumped illegally, or are going through the hands of illegal operators, rather than an authorised treatment facility (ATF).

The ELV Directive prescribes for the issuing of a Certificate of Destruction (CoD) when a vehicle is delivered by its last owner to an ATF to be scrapped. It is the ATFs in the UK that process and depollute ELVs – and only ATFs are allowed to issue CoDs. In the UK, however, final owners of ELVs have no need to obtain a CoD because there is no penalty if they do not; they therefore have no incentive to deliver their vehicle to an ATF.

Whilst most law abiding final owners will indeed ensure that this happens, this lack of a robust system actually encourages the unscrupulous final owner to take their ELV to an illegal operator to be scrapped. This is because an accredited ATF has facilities to de-pollute ELVs, properly, while indirectly undertaking to assist the UK in achieving the prescribed recycling targets. These activities, however, come at a bigger cost than with the illegal operator, who has no intention of incurring the cost of the required infrastructure to de-pollute the vehicle or attempt to reach the recycling targets.

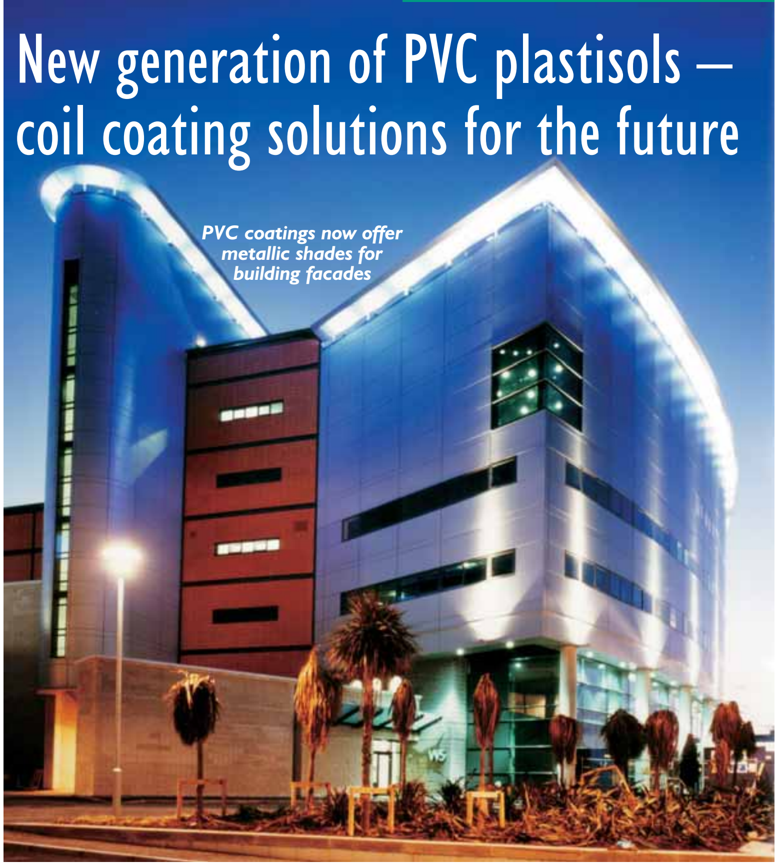
The only way that the ELV Regulations can be made to work effectively is through the adoption of a robust licensing system that ensures every car is registered to its legitimate owner and that a financial penalty is applied to the final owner of the vehicle should they fail to obtain a CoD from an ATF.

In that way, a greater proportion of vehicles reaching the end of their lives will be captured by the system. And that means fewer vehicles being dumped or ending up in landfill – and more ELVs entering the recycling process. The DVLA is looking into the matter but, until there is a continuous licensing system in the UK, this will continue to be a problem.

Legislative change has a huge impact on the amount of recycled automotive steel coming back through the system. For society, this is a positive step forwards – but it is vital, from an environmental perspective, that we do not stop there.

We must continue to push for ever greater levels of automotive steel recycling and this will only happen if the industry produces the highest quality recycled steel that the primary steel manufacturers want to buy. This means that the demand for recycled steel – and its price – lies very much in our, the recyclers own hands, in terms of the product that we, as an industry, offer.

New generation of PVC plastisols – coil coating solutions for the future



PVC coatings now offer metallic shades for building facades

Following a period when PVC coatings were recognised as environmentally unfriendly, new formulations have not only removed the heavy metal filler content but are also striving towards production based on renewable organic oils as the raw starting material.

For more than 30 years, PVC plastisols have played an important role in the automotive, flooring and coating industries; but what about the future? Numerous people within the market repeatedly forecast the end of PVC plastisols, but all predictions have proved incorrect: the PVC business is still going strong. In 2005, for example, the ECCA posted sales of PVC at 19.2% by volume. What are the reasons for this? On the one hand, PVC-plastisol products for coil coating are broadly accepted to be the best for rough outdoor conditions. When asking about an effective protection of steel buildings against wet weather conditions and UV influence, there is no qualitatively equivalent alternative.

In recent times, noteworthy new developments have come to market which optimise the environmental impact of these products with improved longevity. Today we can speak of a new generation of PVC plastisols – but there is still room for further development.

Beginning in 2000, the entire PVC industry – and BASF Coatings in particular – have made great efforts to meet the requirements of individual governments and environmental pressure groups. The Vinyl 2010 group was founded – as an independently audited group – aimed at minimising waste and evaluating the real impact of PVCs on the environment.

BASF Coatings has always been a leader in this process, for example with the substitution of heavy metal stabilisers. Within the coil coating industry, its implementation of stabiliser systems with a lower environmental impact has been ahead of the wider industry. The widespread use of lead and barium-cadmium systems ended almost 20 years ago, with tin-based systems becoming popular. In recent years barium-zinc and calcium-zinc technologies have been proven to give excellent physical properties and strong weathering characteristics.

As far as the use of controversial substances like diethyl heptyl phthalate, diiso decyl phthalates and butyl benzyl phthalate is concerned, the coil coating industry has progressed beyond the political discussions currently being held in the EU.

Today the use of non-phthalate systems has become the norm at BASF Coatings. Certain alternative plasticisers, such as monomeric or polymeric adipates, are used to replace phthalate systems, killing two birds with one stone: phthalates were replaced and, at the same time, the new generation systems feature improved physical properties, particularly at lower curing temperatures and greatly improved UV resistance. Since their market launch, phthalate-free plastisols have asserted themselves on a wide front.

Over the medium term, BASF Coatings expects the complete replacement of phthalate-containing PVC-plastisols.

In addition to improved performance and reduced environmental impact, the high film build provided by modern plastisol systems results in a very robust finish that can withstand severe stress during assembly at a construction site. These systems meet the highest requirements in terms of outdoor properties, as defined for Great Britain and Scandinavia.

The latest innovations also bring sustained benefits in processing. The use of new technologies in the PVC production process gives great production control. This allows either lower curing temperatures or faster line speeds by providing perfect control of rheology. Another trend is that buildings are becoming more colourful. For example: Corus and BASF Coatings worked together closely to develop new colours for the construction industry. One specific solution resulted in metallic shades for building facades realised with coil coatings.

The Swansea Liberty building

The next generation of PVC plastisols will use organic-based stabiliser systems rather than the calcium zinc or barium zinc used at present. These systems will avoid the use of any metal stabilisers, further reducing any perceived environmental effects.

Currently, most plastisers use natural oils as their base raw material. BASF's research activities go far beyond this considering the use of renewable resources such as sunflower oils. The development of such systems would mean that, in the near future, PVC plastisols could reach a renewable resource content of up to 80%.

Considering the product benefits and sequential improvements in terms of eco-efficiency, PVC plastisols are expected to remain a talking point for many years. STI

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Can Poland ever be like the West of us?

To fully appreciate the transformation made in Poland and the subsequent changes in its society, economy and steel industry, it is essential to look back at what there was before and contrast this with what is happening now and where the country is heading. As issues arising from overcapacity are solved, supply dips closer to demand and the price of finished products approaches market value, helping to make Polish producers profitable. 2005 and 2006 witnessed production of the Polish steel industry creep ever-closer to a market-based rather than volume-based philosophy.

BY ELOUISA DALLI & OLIVER CAMPBELL*

Hindsight is seldom forgiving when it scrutinises communism, but to fully appreciate the transformation made in Poland and the subsequent changes in its society, economy and steel industry today, looking back is essential. Ernesto 'Che' Guevara is now a T-shirt design, Chairman Mao is now officially 30% wrong, and the wall that would never fall, fell. Those 'recovering' from communism tend to avoid looking back. Would McCarthy have ever feared 'the Red menace' had he known Eastern Europe's particular brand of communism would be as inherently suicidal as it was sadistic?

From the alleys and squares in picturesque cities such as Krakow, to the Lego-like structures in the planned industrial zones of Nowa Huta, it is clear that today's (unemployed or underemployed) Polish youth has more in common with its American, British or even Japanese counterparts than with its own parents: Poland is suffering from social schizophrenia. Before Google, MTV or 'just doing it' were fashionable in Eastern Europe, a wall divided an already divided German city, students were cut down in Beijing's 'Gate of Heavenly Peace' and an iron curtain provided Poland with shade from many of the activities, information and choices that its youth now takes for granted: it is hard to remember the merits of communism in Poland.

POLAND TODAY

The success of today's steel industry is therefore despite rather than because of the communist era. By looking at the situation within each sector of Poland's steel industry today, we can get a better idea of where it is headed. After good results in 2004, 2005 was more a year of good intentions. Several issues arising from overcapacity were solved through rigorous structural changes and further international consolidation, allowing international supply to dip closer to demand. The prices of finished products began to correspond to market value, helping to make Polish producers profitable for another year. 2005 and 2006 are witnessing the production output of the Polish steel industry creep ever closer to a market-based orientation rather than volume-based. Romuald Talarek, chairman of the Polish steel association Hutnicza Izba Przemyslowo-Handlowa (HIPH) believes that, "owing to investment, improvements and the closure of certain projects over recent years, we are not diverging from international standards, practices or environmental controls."

	1990	2005	Remarks
Supply/demand	S ≤ D	S ≈ D	Strong capacity reduction – more than 50%
Ownership	State	Private owners	
Main end-users	Military industry + infrastructure	Like in the EU	
Production structure	Long 70% Flat 30	Long 60 Flat 40	Objective: Flat 60% total
Steelworks	Majority: open hearth furnaces	Only BOF + EAF	

Table 1 Carbon steel – main differences in 1990-2005

Source HIPH

Poland's domestic supply today is dominated (over 60%) by long products. Talarek believes that "thin flats supplies coming from captive manufacturing processes are not sufficient" and that "domestic consumers have a complete product range to offer". In terms of Poland's trading partners, EU steel imports account for 85% of total imports; exports to EU countries account for over 67% of the total figure. The trade balance, as Talarek notes "is not alas positive for Poland".

In terms of the sustainability of an industry that, as recently as six years ago, looked as if it might have breathed its last, Poland is now looking at the creation of longer term value, with new steel mill owners continuing investments into downstream processes. Mittal Steel Poland's construction of a new hot strip mill in Krakow suggests that the country's strip range will drastically improve.

Productivity rates across the steel industry, while still below those in Western European countries, are rapidly improving. The arrival of new, private, foreign owners means that the operations and philosophies of the Polish mills have changed for good – 'now economics come first' as Talarek explains.

Poland's recent steel consumption floats between 7.5-8.5Mt/y. Talarek acknowledges that this figure is expected to increase substantially as public and private sector investments into construction and infrastructure projects, particularly as predicted by Poland's government, will 'substantially boost steel consumption in Poland."

One part of restructuring, which was essential if the Polish steel industry was to truly shed its communist skin, has been cuts in employment. Consequently productivity levels have increased whilst relative labour costs are falling; the net effect on Polish society has been a drop in employment. This, coupled with the increased flow of labour towards Western Europe (specifically the UK) after 2004's EU accession has left some or the older, die-hard industry members telling the younger Polish generation: "Will the last one to leave turn out the lights!"

Foreign owners, working with EU directives and the Polish government, have provided not so much a 'stay of execution' but rather have taken Poland's steel industry off Death Row and transformed it into a productive, efficient, attractive and responsible member of the international steel community.

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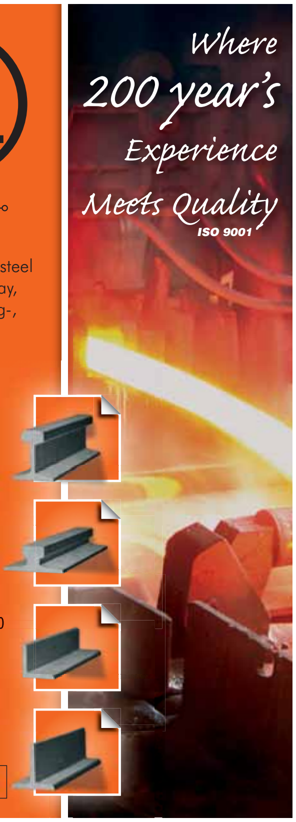
AN IRONIC TURN – IRON CURTAIN RESTRUCTURED

What westerners call ‘steelworks’, the Czechs call ‘hut’, the Germans call ‘hütte’, the Poles call ‘huta’. The construction of Nowa Huta (New Steelworks), showed that Poland could add some much needed carbon to its iron curtain. Nowa Huta today, can only be described as a city that would bring George Orwell to tears. The concept of Nowa Huta began in 1949 as a separate town near Kraków on terrain repossessed by the Communist Government from the former villages of Mogila, Pleszów and Krzeslawice. It was planned as a huge centre of heavy industry. The town itself was to become an ideal town for the communist authorities, populated mainly with industry workers. In 1951 it was joined with Kraków as a separate district and the following year tramway communication was started. World War II presented a particularly busy period for Polish steel production. The establishment of the People’s Republic of Poland (as it became known after 1952) and the emergence of Krakow as a city relatively unscathed by the war (excluding the fact that Auschwitz is a stone’s throw away) was a cause of certain jealousy from other areas of the Republic. The Communist authorities decided that the substantial resistance presented to its regime from middle-class Krakovians could be ‘corrected’. To "correct the class imbalance", the authorities commenced the building of this satellite industrial town to attract people from lower socio-economic backgrounds to the region, such as peasants and the working classes.

Thanks to a series of political and economic changes made from the end of the 1980’s until now; streets formerly named after Lenin and the Cuban Revolution have been renamed to honour Pope John Paul II and exiled leader Wladys Law Anders. In 2004 Plac Centralny, Nowa Huta's central square which once was home to a giant statue of Lenin, was renamed Ronald Reagan Square (Plac Reagana). Today Nowa Huta is seen as much as a tourist destination to see the ‘novelty’ of steel production and manufacturing under Communism as much as anything else. STI



Krakow's old town

POLAND

Steel's making progress

To merely say that Poland today is a different country to the place it was 20 years ago would be to do its economic and social progress an immense disservice. If we look at several indicators of economic transformation over the past 16 years we can see almost polar changes.

In considering the recent developments that management and ownership changes have forced on the Polish iron and steel making industries, we see that 2004 was actually a very good year for Poland. 2005 saw Polish iron and steel turn out 21.2% less steel compared with the same time the previous year. Output figures dropped in all steel ranges except pipes and tubes – the major attributable reasons being the overall domestic cooling of the Polish economy combined with a drop in the quantity of steel consumed. The effects of both of these factors were compounded by changes in foreign exchange rates which began to favour imports, making life that bit harder for Polish steel producers. According to HIPH, 2005 saw, as in 2004, positive after-tax profits; which were however five times lower than those in 2004.

All of these actions count for nothing without results. So what are the signs that Poland's steel industry is progressing and is having positive effects on the economy, society and environment without draining funds from elsewhere? As Romuald Talarek of HIPH explained, "Poland is no longer a polluter. Steel in Poland is no longer the unwanted industry. Of course employment is down, but the awareness has changed: the role of the manufacturer is not just to provide jobs, but to produce." This reflects some of the harder actions and decisions that the mills had to make and take. Huta Krolweska and its GM Marian Banach explain; "We halted production of a small section mill last year, mainly due to the fact that the competition in Poland increased. This mill was not as productive or effective as our competitors', so we decided to close it down. These specific structural changes were made due to the fact that economically, the small section mill was not competitive on the market and was closed. We had to reduce (our labour force) by some 120 people in order to save the whole outfit and to make it economically stronger." This 'cruel to be kind' attitude is understood across Poland as a necessary measure that will secure the long-term future of the industry. As such, relations with the government and unions has actually become stronger, "The cooperation between us and the Unions is very good due to the fact that they understand that this is an old mill, and that we have to make some cuts in order to lower costs. We meet with the Unions once a week. We have a very good relationship and as far back as I can remember there has never been a conflict that could not be resolved."It is easy for Talarek to be optimistic about the current and future situation of Poland's industry when he compares it with where it was as recently as six years ago, "Given what has happened, we now have investors who have enabled the restructuring of the sector and averted the bankruptcy of the industry, which was a real threat at the beginning of the century." He elaborated on the shift in focus throughout the industry: "The problem with logistics was cured by consolidation as there was no duplication or overlapping of production. Everyone is now aware that they produce for the sake of the market and not for the sake of production." This is certainly reflected in recent figures: in 2005 the steel mills – as beneficiaries of such state aid as is permitted under the restructuring programmes – turned out 62.7% of total crude steel made in Poland. Those mills specifically contributed volumes to overall sector shipments which were down from 62.2% in 2004 to 57.9% in 2005. Shipments themselves were lower by 21.2% in value terms when compared to 2004.

IMAGE PROBLEM?

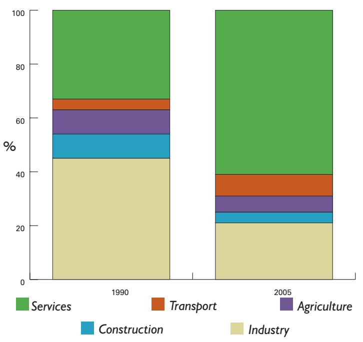
To merely say that Poland today is a different country to the place it was 20 years ago would be to do its economic and social progress an immense disservice. If we look at several indicators of economic transformation over the past 16 years we can see almost polar changes, but these figures alone do not demonstrate sufficiently the effects of this progress on day to day life in Poland, let alone the extent and rate of change that its steel industry has had to undergo.

Poland's population has barely changed during this period and remains at around 38.5M. Poland's GDP however has increased from US$59bn in 1990 to $286bn today.

Through consolidation and responsible planning, crude steel production has dropped from 18.6Mt/y to 9.6Mt/y while apparent consumption (AC) has risen from 7.3Mt/y to 8.6Mt/y in 2006. Steel consumption per capita has increased from 190kg in 1990 to 210kg in 2006; some optimistic estimates suggest that, given another 15 years and pending the success of various proposed infrastructure plans, this could climb as high as 300-400kg.

Between 1990 and 2004, a future for the steel industry was by no means guaranteed. Looking back as recently as 2001, Poland's steel industry was described by the *Warsaw Voice* as, "fragmented, ineptly restructured, burdened with depreciated assets and [with] its debt snowballing." Deputy Economy Minister at the time, Edward Nowak explained that, "The financial liquidity of Poland's steel mills is deteriorating, and they are rapidly losing their markets". He prophetically elaborated, "Privatisation and consolidation may be the last chance for Poland's steel mills."

Back at the turn of the century, Poland was itself trying to consolidate its fragmented industry and bundle it into packages that would entice the foreign investor. Czeslaw Zabinski of Huta Katowice Walcownia Blach, looking back explains, "From a general point of view what happened was a crisis in the Polish steel working and metallurgical industries. The ownership of the mills had to undergo some changes. Back then most of the steel producing mills used to belong to the government, who at that time didn't have the means to invest sufficiently in the sector."Tearing off the band-aid of communism has caused some pain in a transformation that is mainly attributable to this turbo-charged 'healing' process. STI



1 Structure of Poland's GDP *Source: HIPH*

	1990	2005	Remarks
Steel distribution (SSC+SSH)	Organised by state entreprise	Direct sale to end users and via distributors	
Ecology/Environment	Secondary	Became important	Strong emission reduction
Economy	Volumes over profits	Profit and cash flow	

Table 1 Poland – Main differences in 1990 and 2005 *Source HIPH*

Foreign owners – saviours of Polish steel?

Transition, transformation, restructuring or 'perestroika' as the Soviet's called it represented the end of what had been a dark period, not just for its steel industry, but for Poland as a whole. The Polish steel industry can be best seen as a jigsaw puzzle that was hastily assembled under a Communist regime; the sweeping reforms of the early 1990s split this puzzle into hundreds of pieces and now foreign investors have been reassembling this complex picture into something much more manageable, with far fewer pieces.

Steel in Poland today is still considered to be very much an important sector within the country; a fact that is reflected and emphasised by the degree of employment in the sector as well as the added value created by Poland's steel producers. The past ten years have seen a significant restructuring of the Polish steel industry, perhaps better described as an 'overhaul'. During this period a large number of fatally under-invested and consequently non-viable facilities were permanently closed, whilst those that showed even the faintest glimmer of life were modernised and upgraded so as to enable the production of steel to the grades and quality expected by international markets.

The ownership structure of the mills would also witness a radical change: "It was clear that the public and the government were not the best owners" – Czeslaw Zabinski of Huta Katowice Walcownia Blach

The changes in the management structures, encouraged by the arrival of foreign investors and owners, have taken place simultaneously with continuing privatisation and the concentration process. By looking at the improvements in the financial and output statistics of Poland's steel producers, the shift from a product-orientated to a market-orientated industry is clear to see.

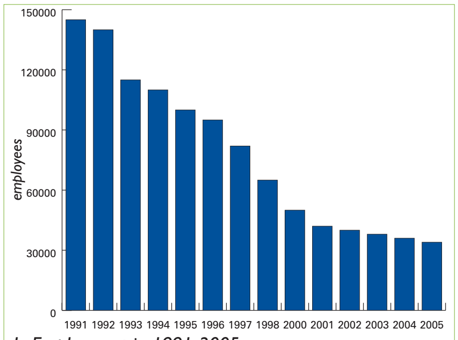
Certainly one of the universal characteristics of this restructuring period was a notable reduction in manpower (**Fig 1**); this gave rise to a significant increase in the levels of productivity (**Fig 2**). The drop in employment in this sector has forced the industry to look towards the implementation of strong social measures in order to reduce the impact of this restructuring on Polish society.

Other technical restructuring measures have helped the sclerotic mills in Poland to not only reduce the input costs but also to cut emissions otherwise detrimental to the environment (**Fig 3**).

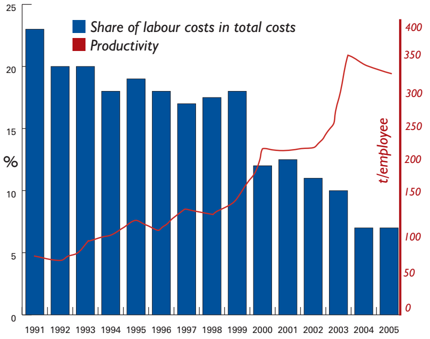
FOREIGN OWNERS TO THE RESCUE?

Despite these specific initiatives to revitalise Poland's steel production, some argue that there is still further scope for improvement and consolidation. Certainly Mittal Steel Poland, which rode into town with the acquisition of Polskie Huta Stali (PHS), has grand ambitions for its operations here, operations which already constitute some 70% of Polish steel output. Today, it is clear that the mills, a majority of which are now under foreign ownership and control, have for the most part reached levels of viability and efficiency which allow them to remain competitive under normal market conditions. 'Viability', until fairly recently, required large amounts of money from the state; a scenario by no means unique to Poland and mirrored amongst its neighbours. This state aid was heavily questioned at several stages and regulating it became essential as a part of Poland's EU accession.

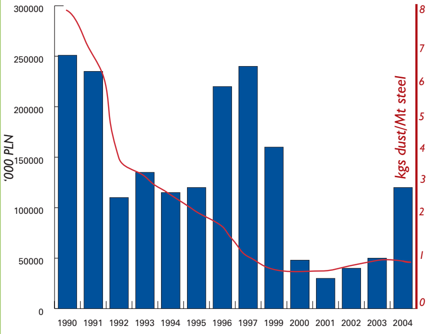
As Adam Zolnowski, CEO of PAIiIZ explains, "The EU was forcing us to stop supporting the steel industry with state money; yet at that time the steel industry was not profitable at all. It was a real bone of contention in terms of the negotiation process with the EU." The state-aid was regulated by the financial projections of the National Restructuring Programmes which were adopted by the governments of the EU applicants (including Poland) and verified by the Commission during 2002 and 2003. Exemption from these EU rules was laid out during the accession talk negotiations between Poland and the EU and are governed by a series of protocols relevant to the accession of the new members of 2004.



1 Employment in 1991-2005



2 Share of labour costs in total cost and productivity in 1991-2005



3 Environmental expenditures in 1990-2004

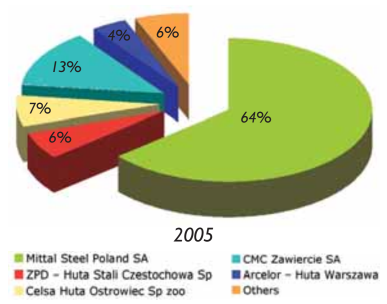
Protocols 2 and 8 are specific to Poland and the restructuring of its steel industry began in 1993 when it entered into the Europe Agreement with the EC. Protocol 2 contained a framework of bi-lateral agreements for a steady relationship until accession and related directly to the elimination of trade restrictions and to competition. These provided a transition period for the restructuring of the sector. The Polish National Restructuring Programme was adopted in March 2003. Protocol 8 of the Accession Treaty also outlined specific conditions for steel restructuring up to 2006. Outside of these protocols, it became clear that any additional state aid to the steel sector would be in breach of EU accession regulations. The call for a change in the state-owned PHS was answered by Mittal.

BUYING OUT STATE OWNERSHIP

Something had to be done to turn around a centrally-planned industry and rapidly develop its ageing mills and the osteoporosis of its distribution network. It was obvious that the Polish government was always going to be limited in the support that it could offer its geriatric steel industry, given the stiff regulations issued in its EU accession bid. As Novak had said, "Privatisation and consolidation may be the last chance for Poland's steel mills." Talarek, even today shares this view, "Consolidation is very important to us. We have consolidated in terms of the ownership structure, then we began to sub-consolidate for investors. This further consolidation was to some extent forced by the market, insofar as the investors are responsible and they themselves have to respond to the markets."

Time has shown that this solution has been the most clinical yet organic answer in terms of saving Poland's steel industry. Whether or not such a strategic resource as steel is best left in the hands of private foreign owners, has not gone unquestioned, however (**Fig 4**).

Vijay Bhatnagar, CEO of Mittal Steel Poland, explains Mittal's interest and experiences since arriving in Poland and what it means to be a foreign investor in the Polish steel industry. "I think that this was a very tough acquisition. [It] included 13 entities who took up the first bid, as offered by the Polish government for PHS (Polskie Huty Stali) as it was then known; of those 13, only three



4 Current ownership in Polish steel industry

responded – Mittal Steel, US Steel and Arcelor. Out of these, only two ultimately came to the contest – US Steel and Mittal. Obviously Mittal’s offer was the better value for money.”

Bhatnagar explains Mittal’s initial interest in Poland, “Mittal’s interest goes back to a Central and Eastern European strategy, that began sometime in the year 2000.” It is more than just fortuitous timing that, whilst Novak was calling for privatisation and foreign investors, companies such as Arcelor, US Steel and Mittal in its current guise, truly foresaw the potential in Poland, both in terms of its facilities, its market and its economy.

Bhatnagar placed Mittal’s interest in Poland and its plans for Central and Eastern Europe in context: “The first target of that strategy was Romania, then the Czech Republic and then Poland, all part of that Central and Eastern Europe strategy. Central and Eastern Europe was identified quite early on to be given high priority because these countries were on the cusp of joining the European Union”.

Thanks to two successive baby booms, which many attribute to successive periods of martial law and curfews in the second half of the 20th Century, Poland has an unusual demographic that provides an excellent, sustainable platform for economic and industrial growth. Poland itself, with an educated workforce of which over 50% are under 35 years old, stands out amongst these Central and Eastern European republics as a country with a huge economic potential as well as a geography and demography to reinforce the sustainability of that potential.

Bhatnagar adds, “So a confluence of factors (represented our interest): a good, skilled labour force that is competitive with costs and proximity to some of the upstream ores, either coal or iron ore. These countries also had high potential in themselves because countries like Poland have a comparatively large population, which needs a lot of potential to grow.”

Talarek explains how market forces provide sufficient controls and barriers within which foreign investors are obliged to operate. In this way, the privatisation of Poland’s steel cannot be seen as a negative activity but rather as a necessary activity.

“It’s a hygienic solution which prevents the steel producers from setting prices as they like. 85% of products on sale in Poland originate in EU countries. Its exports to other EU countries are 66% of all of its exports. Prior to the transformation, industry contributed around 60% of GDP – today, the situation is very different as services now make up a higher proportion. When we tried to downsize our capacity, we had to bear in mind that similar things had happened in many other sectors too – that’s why industry in Poland today is responsible for a much smaller part of GDP. The Polish economy is adapting to the general situation, which means it is changing the orientation of the industry of a whole; therefore it is continually adapting, so consequently is playing a lesser role than previously.”

SHEETS, BARS, RODS BUT NO POLES

Given the conditions and obligations placed upon Mittal as part of its acquisition of PHS, its success and ambitions in Poland are to be commended. While some Poles feel that steel is far too important a sector to be left entirely in the hands of foreign entities, the argument is entirely academic. Talarek notes, “We have lost some of the national character of the industry; because we now have global companies, some nationalism is lost. We have to develop mentally, domestically, regionally and internationally. We have to find our path.”

Bhatnagar himself when asked the extent to which he thought foreign investors were seen as the ‘saviours of Polish steel’ is as diplomatic as he is pragmatic: “I suppose it depends on who you ask. Different people have different ideas. Generally a layman will think privatisation is bad – that these sectors are national assets; that person would obviously respond in light of that view. Those involved more closely in the industry will believe that privatisation and globalisation bring a different kind of perspective to the industry that ultimately benefits the countries.” This much is clearly true; Mittal’s hopes for Poland, whether born out of a genuine desire to catalyse the development of its host nation, or whether to capitalise on a large, new EU member who is still squinting its eyes in the harsh light of capitalism, is entirely immaterial. The consequences of the acquisition of PHS by Mittal can only be seen as benevolent and the motives irrelevant. Bhatnagar explains that, given time, people will come to appreciate the role of the foreign investor in Poland: “Employers start to realise that a loss-making company is not good for anybody; it won’t pay its employees on time, it won’t generate any tax revenue for the country, it can’t protect the environment and it is no good for the community at large as it can not help anybody. But it takes time for people to realise that.”

Explaining that Mittal has provided a future where before there was only uncertainty, Bhatnagar says: “PHS was making an immense loss and had no money to invest; this created uncertainty about its future. Today, with a new investor, people know it has a future: Mittal has the will and the wherewithal to provide investment, secure the future of the company and the future of the people is secure.”

One Polish individual heavily involved in upstream steel production shows strong nationalistic feeling, despite all that foreign investors have done for the Polish industry. Maintaining that keeping some Polish aspects will be essential, he says: “I believe it is very important for Polish steel to maintain some Polish characteristics and ownership. Polish owners have a better understanding of the Polish mentality.” In a globalised world where the international steel industry is, in a very real sense, getting smaller and more familiar by the minute, these sentiments may very well be irrelevant.

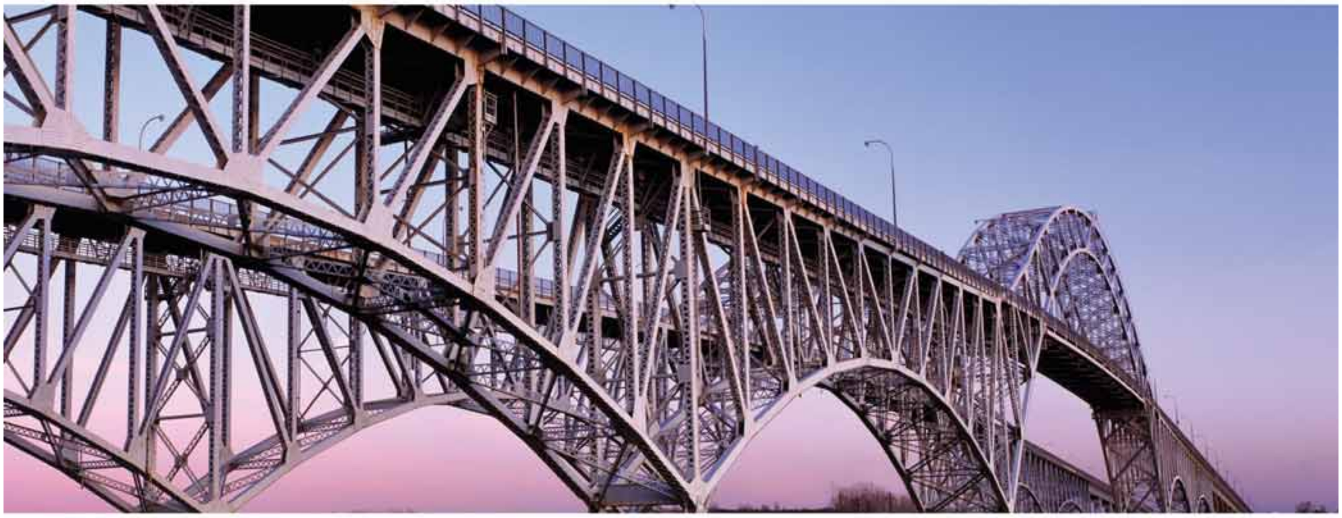
The drop in upstream output has certainly made some of those servicing the industry think about their operations. Zaklady Ropcyze, a manufacturer of refractory products explains what happened when the successful consolidation took place; “The high demand for overseas refractory material) was due to the fact that steel production in Poland was almost twice what it is today. When Polish steel output was cut, it represented a difficult time for us. On top of that, consumption of refractory material per one tonne of steel produced dropped.” Mr Józef Siwiec President of the Management board and Mr Marek Tymkiewicz, VP of management board at Ropczyce explain how their focus has shifted, “It is a competitive global market; consumption for refractory materials is much lower. This, of course is all connected with much higher efficiencies and in Poland certainly the 50% drop in steel output (has affected us).” They both see themselves in Poland as having a much more international perspective now, “We think that the exports will increase relatively over the next year because although the Polish market is a big one, the Ukrainian for instance just over the border is massive! We can help steelworks in Ukraine update from older technology to a newer one.” Ropczyce are just one example of a Polish company who are not letting this paradigm shift stand in their way and are adamant that despite the arrival of foreign owners and a decrease in output, their future and that of Poland is to be assured, “If you look at Polish business and society we are very open, we have been travelling and trading for ages. We, in terms of location are right in the centre of Europe at the cross roads of any trading. After joining Europe, these characteristics can now be exploited very easily.”

Within Poland, Zlomrex is a good example of a company that is maintaining a very Polish feel. Established in 1990, Zlomrex’s initial activity included only small-scale trade with scrap metals. As the firm systematically developed, the range and scale of its activities were extended. Nowadays it operates as a joint stock company and is the leader of a group of production facilities and distribution centres. Having been more recently established, the company has not been part of the heavy-handed way in which the steel industry was controlled in the second half of the 20th century; perhaps this has given it more ambition and clear-sightedness than its colleagues. Certainly its investment plans reflect a true belief both in Poland and the industry: “Our main investment will be in the steel melting shop. We have just completed investment into production intensification. By using the hyper-oxy burners, these changes should increase our capacity by 15%” explains Henri Odoj, president of Ferrostal, part of Zlomrex Group.

“We are now thinking about improving billet quality and adding further liquid steel degassing stations; we are also thinking about what we can do with the rolling mill - this should go in the direction of changing product, not just improving the line, which is a relatively small line compared to CMC, Celsa or Mittal.”

Mr Walarowski of Zlomrex puts Zlomrex’s investment plans into context of its general strategy: “2006 will witness further development and investment. Over the next three years, we have planned a US$400M investment. It consists of three segments: scrap collecting; modernisation and acquisition in steel production; and acquisitions within the distribution network.

“We have a new slogan: ‘Three times a million’ – representing targets of 1Mt of scrap, 1Mt of steel production and 1Mt of distribution.”



The appeal of Poland on the international stage

Above: Landscape of steel plant in Dabrowa Gornicza, Mittal Steel Poland

Industry figures explain why Poland is an attractive target to external investors and the impact of inward investment on the Polish steel industry.

The first stage of continuous casting in Dabrowa Gornicza steel plant, Mittal Steel Poland

Vijay Kumar Bhatnagar – chairman, CEO of Mittal Steel Poland

There is a widespread belief within Poland that the future holds great promise for the country – a hope shared by Polish suppliers, distributor organisations as well as the new foreign owners who have forged a place for themselves in this country's fast moving market.

MITTAL'S PERSPECTIVE

Vijay Bhatnagar and Mittal Steel Poland share these hopes from a mill perspective: "Polish consumption per capita is probably close to 230/240kg/y and this could definitely move to around 400kg/y.

"It is at that part of the development cycle where steel consumption growth is very directly linked to the GDP. With Poland's GDP growth at around 5% it depends on how the economy is managed. It is a good market with good potential."

Bhatnagar is clear that his goals for Poland will remain the same despite Mittel's merger with Arcelor, "On a micro level in Poland, it's about the investments and what we are supposed to deliver in terms of capacity, introducing value-added products into the market and developing a new customer base. We need to improve significantly on how we really look after the customer in terms of: delivery, quality and cost. This will be a significant challenge.

"On a micro level, in Poland we have a very different IT platform. There were four differently owned and run companies that were simply put together. Obviously these systems do not 'talk' to each other. Therefore, right now we have just completed the implantation of phase 1 of SAP across all units. We shall be completing phase 2 sometime by the middle of next year. We have spent close to €10M to put this one unit on a common platform.

"A third challenge is that we need to improve our productivity to the levels in the European business plan, which is roughly a 60% improvement over the current level of production." In Poland this represents not a case of 'never being satisfied' but more a case of always being challenged. Mittal's plans for this country show that it is doing more than merely riding the crest of a wave, it is in fact making the waves in this industry.

BENEFITS TO HOME GROWN COMPANIES

Mittal's plans will benefit many others in Poland too, from downstream producers, to those servicing the industry and the retail market itself. Pedmo, for example, which was founded more than 50 years ago has noticed the changes in this rapidly expanding environment. The company supplies components for the metallurgical, cast steel and cast iron, non-ferrous metals founding and metal industries. Pedmo's president Edward Aponiuk puts in plain words how privatisation has affected Pedmo: "After the process of privatising the steel industry in Poland, relationships between companies such as Pedmo and the big steel companies are much better. They are now based upon economic terms." He went on to explain how consolidation and privatisation in Poland had helped Pedmo stretch itself across other parts of Europe, "Now after privatisation we have very simple and open rules: money comes in on time, deliveries are made on time. We cooperate with Mittal steel all over Eastern Europe." One aspect where Pedmo has reacted slightly differently from many Polish industry colleagues has been its lack of focus on organisational change after EU accession and privatisation. "The structure of the company did not change much since privatisation; one focus that was shifted was onto research. We are much more focused on this and as a result, we can offer very new products for our customers." This is from a company that has truly experienced some of the most varied times in Poland's business history, and is coming to terms quickly with what it means to operate in a free market. "We are producing auxiliary materials for the steel industry, foundry industry, aluminium and copper industry also refining and insulation. We have partners and customers all over Europe but at the time of privatisation Pedmo was only operating in Poland." Pedmo must surely be evidence of how the privatisation of the upstream industries has helped provide a future for those who service this industry and has also helped, in a short space of time, to explain the possibilities for export into this global-town and European-village.

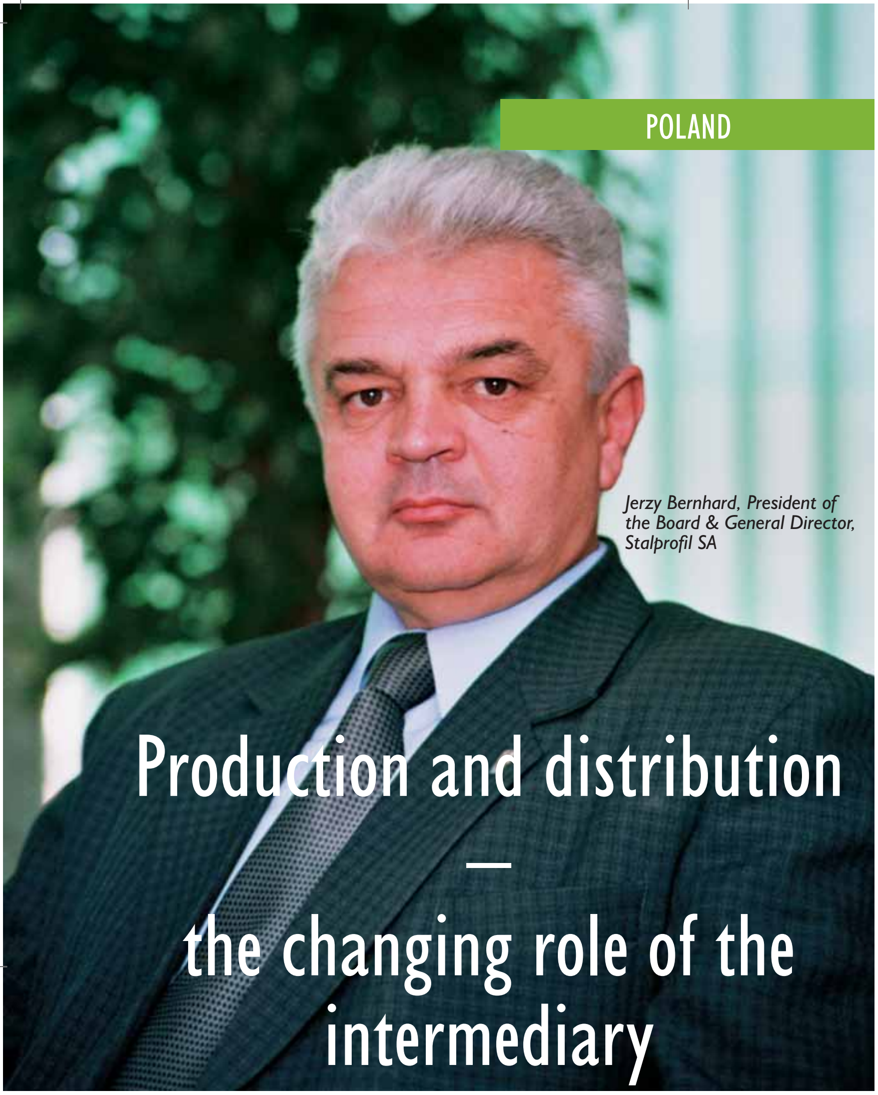
COMING TO TERMS WITH COMPETITION

Bipromet is another organisation, like Pedmo, which has a long and intertwined history with Poland's steel industry. Bipromet has seen decades of central planning and has had to very quickly come to terms with competition, an ailing industry and the necessity for marketing. Tadeusz Baj explains, "The first 40 years Bipromet was a state owned design office, employing up to 1300 people designing the whole Polish non ferrous metal industry. I think it is no exaggeration to say that all Polish copper, zinc, lead, aluminium smelters and processing plants were designed by Bipromet specialists."

Baj is another industry individual who acknowledges the benefits of privatisation and EU accession and elaborates as to how it has obliged a change of focus on organisational change and reliance on markets: "The accession of Poland to EU just made it easier for Bipromet to offer its services abroad. Mainly electro filters and fabrics filters are designed, delivered and assembled in many countries of the EU, the most recent filters being installed at a coke plant in Belgium. Some of the export activities worth mentioning were carried out in Thailand where converters were designed and delivered to Rayong Copper Smelter. We also approach Scandinavian and French markets; so undoubtedly, (EU accession) presented an opportunity and not a threat."

He is clear that Polish companies such as Bipromet will have the edge on competition for many years yet, thanks to lower prices, due to lower costs. "Polish engineering services are far less expensive then in western European or American markets. I think many years will pass before they reach parity. Many foreign engineering companies realise the difference, so some mergers and acquisitions have occurred by some well known corporations such as Lurgi, Fluor Daniel and many others."

Baj goes on to add, "The most competitive services that we offer are most probably electro-filters and fabric-filters-due to these European directives limiting the air polluting tolerance." He is hopeful that EU emissions directives will focus on the services offered by the likes of Bipromet. STI



Jerzy Bernhard, President of the Board & General Director, Stalprofil SA

Production and distribution – the changing role of the intermediary

In a recent conference address, Jerzey Bernhard, general director of Stalprofil, noted that where once the state-controlled Polish steel market was simple, post-1989 changes have shaken everything up to create a complex environment with privately-owned players at every stage from pre-production to post-manufacturing distribution.

The structure of the Polish steel market before 1989 was not a complicated one. The entire industry was under the control of the Ministry of Industry & Metallurgy whose influence was directly reflected in the operations, planning and output of the Polish steel mills. The steel mills would then distribute products either to the foreign trade office (Stalexport) or to the steel sales office, Centrostal.

Stalexport dealt with the exports and supply of imported material to 'big end users' while Centrostal dealt with domestic material and supply to the 'big end-users' (**Fig 1**), as well as supply to the small end-users. The general changes that took place post-1989 involved a near collapse of this old network. The phoenix that rose from the flames brought with it a host of new companies, most of whom were private. There was an increase in European stocks and the domestic distribution network became hugely fragmented.

Jerzey Bernhard explains how tough the situation between 1989 and 1990 became at times: "Polish steelworks lost their financial liquidity so, to buy steel products from them, we first had to finance resources and transport for them. At that time only about a half of our turnover came from selling steel products."

STOCKHOLDERS RAN THE INDUSTRY

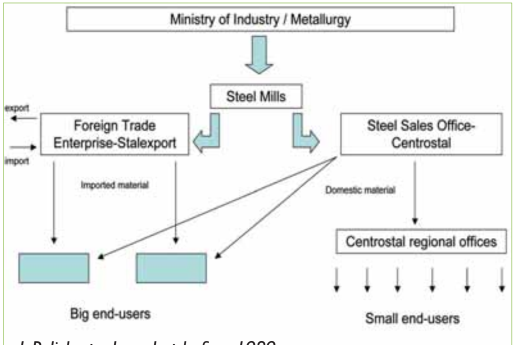
Between 1989 and 2000, the Polish steel industry was so close to extinction that words such as 'bankruptcy' were bandied around lightly. It is safe to say that, during this period, all Polish steel mills or 'Hutas' experienced payment blockades and encountered huge difficulties in obtaining capital for production financing. It was at that time that the stockholders became directly involved in financing production, which led to a system of barter that involved the trade of steel products against the delivery of raw materials for steel production. The stockholders were, in essence, acting as payers for the delivery of the raw materials. The stockholders at that time brought in capital for de-blocking payments that in turn included a compensation trade with other brands of industry (**Fig 2**).

Bernhard explains how the arrival of foreign investors helped the mills to turn around and how this changed the relationship and role of the intermediary in the Polish steel system: "In the past, Polish steelworks suffered from a permanent lack of cash. This gave distributors the opportunity to gain advantage from the organisation of deliveries of resources in barter transactions. Thanks to foreign investors, the steelworks recovered their financial liquidity and limited the role of distributors to steel trading. This is a new challenge for them as now they have to search for a competitive advantage through identification of end-receivers' needs and fulfilling them with an adequate trade offer."

For Bernhard's own Stalprofil, the end of this barter system changed the way transactions were made, "Concentrating only on selling steel products obviously caused a decline in sales volume but it also improved our financial liquidity. The elimination of barter transactions unleashed considerable financial means; this is why today we can settle accounts with our suppliers in cash without any problems." Bernhard does not miss the bad old days and is very bullish about the future of not only the upstream industries but also of distribution and what that means for intermediaries too: "The Polish steel distribution market is becoming more and more similar to the western markets. The many foreign companies investing in Poland has speeded up this process. Today, low costs are the main advantage that Polish companies have in the EU market; however, this is expected to change as the economic development of Poland progresses. Better customer service will become a competitive necessity then."

OUT WITH THE OLD, IN WITH THE NEW INVESTORS

2004 ushered in several fundamental differences – these represented more of a step-change than an alteration of an



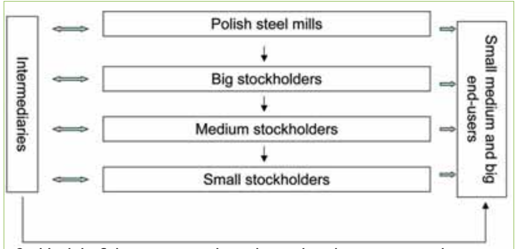
1 Polish steel market before 1989

unsustainable system. After the arrival of foreign investors into the upstream industry – namely Mittal Steel, CMC, Celsa and Arcelor – it became clear that the old network was not going to be suitable for, or compatible with, the newcomers.

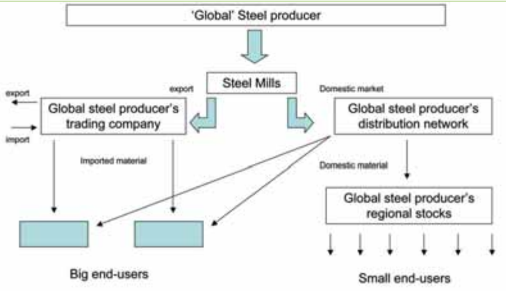
Post-2004, there was a growing market share of steel stockholders and a limited market share of intermediaries and other enterprises treating steel as a method of recovering the debts of the mills. The role of the standard intermediary continues to decrease as steel mills can now pay cash for raw materials and deliveries are purchased directly from the producers. Cash is now the demanded payment for steel products.

At present, however, Polish producers still do not have either their own distribution network or, according to Bernhard a ‘clear-cut concept of how it should be organised in the future.” As intermediaries search for supplements to their core activities, adding value en route to the customer (in the guise of service centres or an initial processing of steel products), it becomes clear that the future distribution model is in the hands of the main producers (**Fig 3**).

In Bernhard’s prediction for distributors, he sees a growing role of big stocks and service centres: “Companies providing added services (like steel products’ initial processing) and with adequate financial potential and trade infrastructure are the future of the Polish steel distribution market. Small intermediaries will gradually disappear [from it].” He adds, “Distributors without suitable trade infrastructure will gradually disappear from the Polish market. Thanks to the investments made many years before, Stalprofil now has large and modern steel depots [Its capacity reaches 80kt] providing competitive advantage to the company. Complex customer service is our objective and we want to achieve it by providing an extensive assortment and by adding value to steel products’ initial processing. Our exporting experience and strong position in the EU market are notable reasons for our success. Today Stalprofil sells to about 60 companies from 20 European countries. We gained the ‘Bull and Bear’ prize for the best-managed company on the Warsaw Stock Exchange. With the strength of a bull, we constantly try to improve our competitiveness.” **STI**



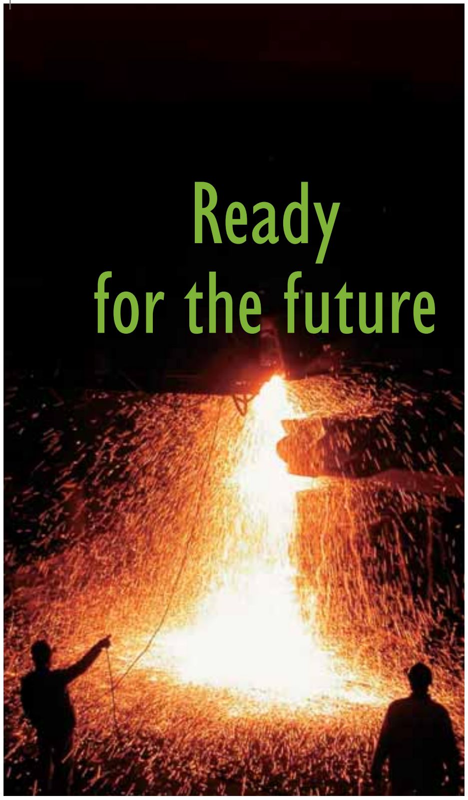
2 Model of domestic steel products distribution network before 2004



It already was once, wasn’t it? (but it collapsed – Polish market pre-1989)

3 Future steel market?

Fig 1, 2 and 3 are:"Information extracted from Jerzy Bernhard’s SBB Steel Markets Europe 2006 speech"



Ready for the future

Poland has done all in its power to drag its steel industry kicking and screaming into the 21st century. It has dropped down in the world rankings of international steel producers because of the emphasis placed not only on responsible production and the elimination of cycles but also because of the implications of being a market rather than a production-based economy. This has meant an obligation to invite foreign investors and owners to come and take a look around. Far from the mills being seen as a second-hand car or jumble sale antique, these facilities, when combined with the investments made by foreign owners and the young, low-cost labour; are showing themselves to be true powerhouses.

The efforts made to increase the grade and varieties of steel produced have helped the development of all parts of the industry. Distribution networks have been upgraded as has the relationships between the producers and the intermediaries. The intermediaries are having to find new ways to process, initially and subsequently, the steel to maintain some place between the producer and the customer. With mills in Poland trying to get ever-closer to the customers, and with investments focusing on downstream production; the space between producer and end user is closing in. Companies such as Stalprofil focus on large stocks and service centres as well as citing the oft-used phrase, "one stop shop" to guarantee that its presence is well deserved. The shift from a production orientation to a market orientation has taken place at a breakneck pace; the evidence in the value created by steel in Poland is clear in the changes in manufacturing and service industries, as a component of GDP: Value, value, value.

All acknowledge that GDP growth is a huge indicator and factor in steel consumption, hopes that steel consumption could one day rise to 400kg are optimistic. But then so were hopes in 2000 that several foreign companies could come and give this industry the adrenalin shot it needed. As the global steel industry becomes more and more familiar and gets closer and closer to the living rooms (Mittal Steel welcome you to Balice Airport in Krakow), the advantages of having an educated, ambitious, populous, low-cost European nation as a manufacturing base, as well as a valuable sourcing destination become ever-clearer. STI

HIPH

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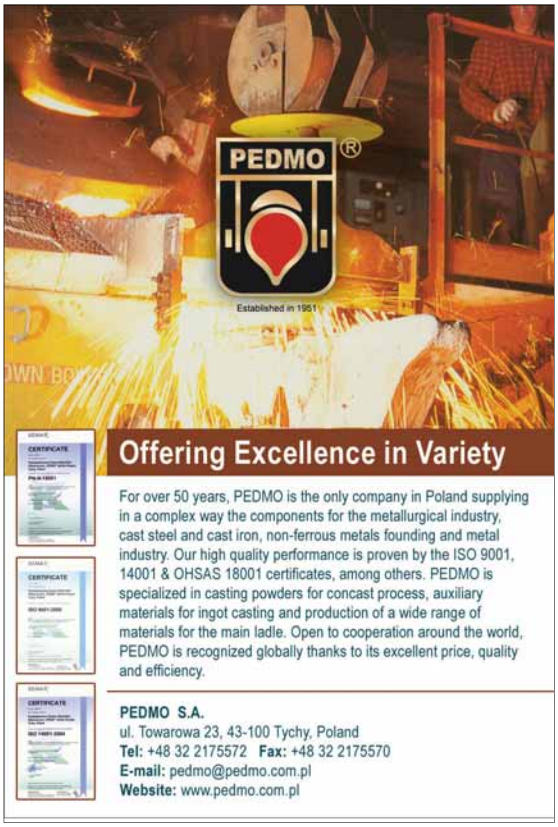
HIPH – The Polish Steel Association Tel +48 32 788 7777 www.hiph.com.pl



Market challenges in the US automotive market

Higher fuel prices and an aging customer base are driving customers in the USA towards smaller vehicles to the advantage of 'new domestic' (transplant) producers who are expanding production and domestic content while the 'Big Three' are cutting output and increasingly sourcing materials outside the USA.

BY MYRA PINKHAM – NEW YORK

Despite the well publicised economic problems of the Big Three automakers, North American automotive production is expected to be flat or only slightly down this year. This is largely due to the growing output of 'New Domestic' (formerly known as transplant), automakers, who are adding new assembly plants at the same time as traditional producers are closing manufacturing facilities. The end result is fairly steady steel consumption for domestic steelmakers who supply both groups of automakers.

Perhaps of greater concern to steelmakers is that high gasoline prices and other factors are causing North American consumers to downsize the vehicles they are driving, in some cases causing them to buy passenger cars instead of higher steel-content sport utility vehicles (SUVs) and light trucks. Light trucks use approximately 50-100% more steel than passenger cars, with the largest differential being in special bar quality (SBQ) steel, says Christopher Plummer, managing director for Metal Strategies Inc, West Chester, Pa.

During the first half of the year, according to Mark Cornelius, president of Morgan & Co (West Olive, Mich), a total of 8.26M vehicles was produced in North America, which were up 1.9% from auto output for the first six months of 2005, when 8.11M vehicles were produced. This is despite the fact that both General Motors Corp and Ford Motor Co have announced significant programmes to decrease their production capacity in North America.

"Auto demand actually has been okay," says Bob Dicianni, marketing representative for Mittal Steel USA (East Chicago, Ind). "You always hear about how bad the Big Three are doing, but the New Domestics are picking up production and as a result it is averaging out to be an okay year – close to last year or maybe just a little lower."

In fact, Roy Platz, Mittal USA's marketing director, observes that July production was quite strong – a seasonally adjusted, annualised 17.2M units, which makes it the second best month of the year. He admits that in July the Big Three automakers did announce some steep year on year sales declines, "But that was principally because of the incentives that were in place last year. Early indications are that August will also be a good production month and that 2006 as a whole will be a decent year – not a blow out, but a decent year."

Mike Jackson, director of North American vehicle forecasts for CSM Automotive (Farmington Hills, Mich), says that it is likely that by the end of the year, auto production should be somewhere between 15.5M and 15.8M vehicles this year and there could be as many as 16.1M produced in 2007, depending on how the economy holds up. From a sales perspective, George Pipas, sales analysis manager for Ford, says, "We are on focus for 17.2M cars and trucks this year versus 17.4M last year, which is a modest decline, but nothing dramatic."

Ronald P Krupitzer, vice president of automotive applications for the Washington-based American Iron and Steel Institute agrees, stating, "We are continuing to see auto production move at a steady clip," which has been good news to domestic steel makers given that about 64% of the weight of the average light vehicle is steel. In fact, he says that over a third of all steel goes into some kind of automotive application, which is second only to construction.

There are definitely downward pressures in the marketplace. "Rising interest rates and stock market uncertainty has given consumers reasons to pause and re-evaluate their household budget and look for ways to make adjustments," admits Kevin L McCormick, manager of global sales and service communications for DaimlerChrysler Corp, (Auburn Hills, Mich). Pipas agrees, stating, "Next year it is safe to say that, if interest rates continue to increase there could be another decline in sales."

The traditional Big Three automakers are particularly feeling the pinch financially. One reason, according to Plummer is that the Big Three, much like the integrated steelmakers, are saddled with higher labour and legacy costs. "The New Domestics have come into the market similar to how the minimills came into the steel industry with new equipment and no legacy cost. The big difference is that steel is steel and with automotive you also get into consumer preference."

And consumer preference has also helped contribute to the inroads that the New Domestics have made in the North American market. "The Big three do not have as fresh of a product line as the New Domestics," says Cornelius.

"We have been able to update our product line in a meaningful way, in a way that represents consumers' wants and needs and they have been responding to that," maintains Ernest Bastien, vice president of vehicle operations for Toyota Motor Sales USA Inc (Torrance, Calif), one of the New Domestic companies that has been growing recently.

NEW CAPACITY

Currently, Bastien says, Toyota's North American productions capacity is full, restricting how many vehicles it can make here. To alleviate that, Toyota is in the midst of several expansion projects. A greenfield assembly plant in San Antonio, Texas, is to start operations at the end of this year and will be producing 200 000 vehicles a year – the new Tundra pickup – by early next year. The company is also building an assembly plant in Woodstock, Ontario, to produce its Rav 4 'crossover' (truck chassis with a car frame) vehicles. It will produce 150 000 vehicles a year when it comes on line in 2008. In addition, Toyota, through its joint

SUV's are losing market share to 'crossovers' and passenger cars

GM's ChevySilverado

Toyota's Baja plant in Mexico

Manufacturer	Model	,000	Start up
Toyota	Tundra	200	2007
Toyota	Rav 4	150	2008
Toyota/Subaru	Camry	100	2007
Hyunda	Sonata & Santa Fe	300	2006
Kia		300	
2009Honda	'entry level'	200	2009

Table 1 New output by New Domestics

venture with Subaru will be producing about 100 000 Camrys at Subaru's Lafayette, Ind, facility starting in the spring of 2007 and plans to start making the Camry hybrid – its first North American hybrid production – in its Georgetown, Ky, plant.

Several other New Domestics have either recently added North American production capacity or have plans to do so including Hyundai, which in May opened its first North American production plant in Montgomery, Ala, where it currently makes Sonata sedans and will begin making Santa Fe SUVs there a well. That facility has the capacity to produce 300 000 vehicles a year. Honda is currently building a new facility in Greensburg, Ind, which is its sixth plant in North America, where it will produce about 200 000 four-cylinder, entry level vehicles starting in 2009. Kia has announced plans to produce 300 000 vehicles a year in West Point, Ga, also starting in 2009.

BIG THREE OVERCAPACITY

This all comes at a time when the Big Three are in an overcapacity situation and have announced plans to shutter facilities, with the most recent announcement coming from Ford stating it would be reducing Q3 and Q4 production and closing 14 plants by 2012. Late last year GM announced that it would be reducing its North American assembly capacity by about 1M units by the end of 2008.

One reason for this disparity, Dicianni says, is the perception, whether true or not, that New Domestic vehicles, especially Hondas and Toyotas, are higher quality than those produced by the Big Three. "The Big Three's vehicles are better than they were several years ago, but the decline is being driven by the sins of the past. It takes a while for perception to catch up with reality. Consumers don't trust the Big Three as far as value while they do like what the New Domestics have to offer."

Compounding that, he says, is the fact that the Big Three have been heavily relying on SUVs and light trucks, which are 'gas guzzlers' and have been hard hit now that gasoline prices for much of the country are over $3 a gallon. "With consumers believing that high gasoline prices are here to stay, they have been discouraged from buying these vehicles.

Cornelius notes that in July light truck sales were down 10.7% from a year ago while passenger car sales are up 22%, adding, that it is likely that car sales could actually exceed truck sales within the next few months, something that hasn't occurred since May 2002. Plummer says that the truck percentage of all North American light vehicles is expected to fall to 55.6% this year, down from 58.6% in 2005 and 59.7% in 2004.

Years	Cars		Trucks		Total	
		%		%		%
2005	2257	52.2	1629	22.6	3886	33.7
2000	1872	33.8	854	12.5	2726	22.0

Source: Metal Strategies Inc

Table 2 US Transplant Auto Production (000 Units)

		Actual 2002	Actual 2003	Actual 2004	Actual 2005	Forecast 2010
North American	Total	16 713 689	16 246 128	16 254 346	16 349 262	16 965 000
Europe Total	Total	19 955 141	20 405 050	21 301 265	21 157 190	22 575 000
Asia / Pacific Total	Total	20 300 408	21 833 444	23 690 810	25 395 974	30 750 000
South America	Total	1 999 667	1 996 214	2 470 464	2 848 055	3 350 000
Global Grand Total	**Total**	**58 968 905**	**60 480 836**	**63 716 885**	**65 750 481**	**73 640 000**

North America includes Commercial Medium/Heavy Trucks

Sources 2005: Morgan & Company ACEA JAMA KAMA. Sources 2002-2004: Morgan & Company Wards Automotive News

Table 3 Global vehicle production

It is not, however, that there has been a wholesale shift in consumer tastes from large vehicles to smaller ones, McCormick points out. John McDonald, a spokesperson for GM, agrees, stating, "People need and use vehicles for a lot of different reasons. Because of that we are seeing a lot of strength in full-sized pickups and large, luxury SUVs. People who have the money to buy these vehicles tend not to be as worried about inflated gasoline prices or higher interest rates."

"What are really getting killed are mid-sized SUVs," observes Dennis DesRosiers, analyst for DesRosiers Automotive Consultants Inc (Richmond Hill, Ontario). Cornelius observes that during H1 2006, sales of midsize SUVs were down 32.3% compared with H1 2005 while large and luxury SUVs were down only 18.4% and small SUVs were only down 7.4%. He cautioned that the year on year comparison looks worse because in 2005 the Big Three's employee pricing incentive plan was in force, which was not the case this year.

By comparison luxury cars were up 0.8%, large cars were up 10.9%, midsized cars were down 0.3% and small cars were up 5%. Small crossover vehicles were up 42.7%, midsized crossovers up 1.5% and luxury crossovers up 2.2%. Generally speaking, says GM's McDonald, consumers are just shifting down one segment. He adds that the move away from midsized SUVs is actually not a new phenomenon started by fuel prices and interest rates. "They have been seeing a decline for the past five years."

Part of it is also due to a demographics shift. "The baby boomers are getting older," explains Ford's Pipas. "The first of the baby boomers turn 60 this year and you drive different vehicles in your 60s than when you are 40 or 50. Also their households aren't as big. There is an increasing number of empty nesters. They like vehicles that are easy to get in and out of and they want the ride and handling to be more comfortable, more car-like," he says. Crossovers allow consumers to have the same or similar utility and functionality as SUVs but are better suited to this new demographic.

Demographics are also at least partly responsible for the growing popularity of subcompact, or entry level, passenger cars, given that, Mittal's Platz notes, the peak of 'Generation Y' is just turning 21, and, according to Cornelius, these affordable vehicles are aimed at people who just graduated from college and are getting their first job. Sales of these vehicles, which include such models as the Chevrolet Aveo, Honda Fit, Toyota Yaras, Nissan Versa and Kia Rio, are up over 40% from a year ago, he says.

These trends are not necessarily good news to metal producers. "Obviously it takes less metal to build a Focus than an F-series pickup truck, so there will be somewhat lower volumes of steel used" Ford's Pipas admits. However, Bill Gair, spokesperson for Dofasco Inc, Hamilton, Ontario, says that order volumes from automotive customers are about the same despite the product shifts. And in the case of crossovers, Mittal's Dicianni says that while there is some reduction in the steel used per vehicle, it uses more coated steel and advanced high strength steels, so there really isn't that much reduction in demand.

Much of the impact on the steelmaker, CSM's Jackson observes, has to do who they do business with. The good news he says is that, as the New Domestics expand, their domestic supply base also expands. Currently, Plummer says, the New Domestics have a very comparable and, in some cases, even higher domestic content as the Big Three since they have been increasing their domestic content while, in some cases, the Big Three are outsourcing parts.

"Our growing presence in North America enables us to increase our domestic content as it provides us with new marketing opportunities with North American suppliers," says Toyota's Bastien, adding that the automaker is especially able to increase domestic content as it produces new models here. "For example, our new generation Tundra will meet a new high level of domestic content."

Plummer says that in 2005 New Domestic vehicles had an average of 58.2% domestic content, up from 42.4% in 1995, while the traditional Big Three vehicles had 78.5% domestic content, down from 85.4% in 1995.

With fuel prices up, you would think that automakers would be taking a more serious look at lighter-weight materials, such as aluminium, but it appears that steel has been holding its own. "Aluminium has made some inroads, but at a slow pace since the changeover cost is so prohibitively expensive and there are a lot of other barriers to displacing steel," Plummer declares. Also, AISI Krupitzer observes, "Steel itself can be used to lightweight a vehicle, especially advanced high strength steels, which can provide 25% or more weight savings." Platz says that the steel industry has been very successful in developing new materials that compete with alternative materials, noting that over 50% of the steel specified today wasn't available 10 years ago.

New Domestics have come into the market similar to the way in which the minimills came into the steel industry with new equipment and no legacy cost

Toyota Motor Manufacturing (TMM), plant in Indiana

"Steel has some very good properties. It is a very good material for safety and light weight," says Nick Twork, a Ford technology spokesman. Chris Naughton, spokesperson for American Honda Motor Co Inc (Torrance, Calif), agrees, stating that as cars are redesigned Honda is using more high strength steels, as it allows for a strong, lightweight unibody structure. "We use a lot of aluminium as well," says Twork. "It depends on which material offers the best solution and the best cost for any given application. Ford F-150's lower control arm is made from aluminium. Meanwhile the new Mustang has a stamped steel control arm that is actually lighter than if it was made from aluminium."

While there are certain aluminium intensive vehicles being produced in Europe, including by Ford's Jaguar subsidiary and by Audi, Twork says that is not occurring in North America.

Also, Krupitzer notes that the steel industry has been working to win back certain auto applications that have been taken by aluminium and other competing materials including wheels and fuel tanks. "Industry trends are driving steel to seek new solutions, but we are technologically in good shape to develop the products needed for future needs." Dicianni agrees, stating, "The long term fundamentals for the auto industry are very good. The North American market should be strong for the next 20 years. STI

Corus helps Ford optimise material selection

Corus has been working closely with Ford to help the carmaker develop and implement the latest grades of high strength steels into several key applications on the new Galaxy model range.

Today, the demand for high strength steels, including the latest dual-phase materials, by vehicle manufacturers is increasing because of the overall blend of structural, crash performance and weight benefits they offer. The attraction of these steels is that they offer vehicle engineers a good balance between strength and formability. However, they do behave differently to traditional steel grades and require significant expertise to implement successfully.

The collaborative work has seen Corus combine its material expertise and computer simulation techniques to help Ford identify areas where material selection can be optimised for a number of key parts for the rear structure of the new Ford Galaxy. Importantly, improved application of high strength steels during the early design and engineering phase of the new Galaxy has provided opportunities to reduce development time and costs as well as improve vehicle crash performance.

Working closely with Ford engineers at Merkenich, collaborative projects undertaken by Corus on the new Galaxy included forming feasibility studies on the rear-floor, rear-cross member and the heel-kick panels. The study on the rear-floor panel looked at opportunities to reduce the gauge and, therefore, the weight of the panel, whilst ensuring that the complex panel shape was feasible to press. With the growing use of high-tech steels in today's automotive press shops, it is increasingly important for carmakers to fully understand how a material will deform and flow during the pressing process in order to ensure capability, quality and performance of the finished component.

Corus was also involved in a detailed parts integration study of the rear-floor panel. In this study, Corus showed that it was possible to use just one part for the floor panel instead of the originally planned two, allowing Ford to save on tooling, process and manufacturing costs.

For the heel-kick and rear-cross member panels, Corus again demonstrated that it was possible to down-gauge in order to reduce weight, replacing High Strength Low Alloy steels with dual-phase material whilst retaining the same impact performance for these panels.

As part of its collaborative work, Corus also employed its unique materials analysis simulation technique called *Forming to Crash* or F2C® to help Ford engineers evaluate the crash performance of key parts such as the rear longitudinals made from its dual-phase material. By using computer crash analysis techniques, Ford engineers were able to optimise the design of these parts during the Galaxy's development process. STI

The Ford Galaxy

Corus Automotive – investment and innovation

Corus is the third largest steel producer for the automotive sector in Europe. It has recently announced a £153M investment in a new cold mill and galvanising line to process a new generation of steels for the sector, the Advanced High Strength Steels.

Anglo Dutch company Corus earlier this year announced a major investment of £153M at IJmuiden in The Netherlands to further expand its product range for the automotive market, including production of Advanced High Strength Steels (AHSS). The investment in downstream processes will include a new galvanising line and a new cold mill. The facilities are expected to be operational in 2008.

Corus Group Plc is currently the third largest steel producer for the automotive sector in Europe, which accounts for 16% of the company's turnover.

During the week of the announcement, Corus sponsored the Automotive Design Degree Show, an annual event in which final year Masters students of UK-based Coventry University's MA in Automotive Design compete to present their ideas of the car of the future in the form of drawings and a scale model. Since the course attracts a wide range of international students, their creations often reflect their cultural background as they strive to design a car appropriate for home consumption. This year's 15 students came from China, France, Greece, India, Korea, UK and USA.

Jean-Michel Raad was awarded the 'Best Vehicle Design' accolade for his design concept *The Moov*!! because it showed pure passion, innovation and fantastic execution, said the judging panel.

Second prize was awarded to Christopher Lavelanet (USA) for his *Future New York City Taxi* and third prize to Alexis Julian Waterson (UK) for his *Space, Form and Structure*.

Sponsorship of the Coventry University Automotive MA Design Show, now in its eighth consecutive year, forms part of Corus' work in bridging the gap between advanced metal engineering and leading edge product design.

FORUM

The event, held at the Coventry Transport Museum was preceded by a forum in which a panel of experts answered questions from an audience associated with the automobile industry. Richard Jones of Corus Automotive fielded questions on material selection conceding, that in addition to weight saving, some aluminium alloys offered better crash protection than steel due to a greater ability to absorb energy. However, aluminium's higher costs and difficulty of forming, joining and in reparability, along with the success of steel in light weighting the *body in white* by using thinner gauge higher strength steels, hydroforming and laser welding, meant that steel remains the material of choice for mass production. He also highlighted advances in the joining of aluminium with steel which is enabling hybrid structures to be built to improve weight distribution – a lighter front end improving handling performance. The BMW Series 5 in which the front section of the car up to the dashboard is of aluminium construction and the remainder in steel, is an example of such a hybrid body.

Mr Jones additionally confirmed the development by Corus of an Advanced High Strength Steel with super plastic properties achieved through twinning during deformation. Such a steel has the potential to win back several applications lost to plastic components.

Other matters discussed by the forum were the importance of supply chain control, which was said to be the key not just to growth but to survival. There is currently oversupply in the automotive market and car builders have to out perform their competitors to achieve market share. The answer was to develop more common platforms but it was then the designers' responsibility to achieve sufficient differentiation between models to attract buyers. In the mass market, 80% of the platform could be common relying on 20% to differentiate models. In the elite market greater differentiation was necessary. The importance of interior design was also emphasised. Too little attention is often paid to this with most of the 'selling' being done on the exterior design.

On hybrid-powered cars, combining electric motors with the internal combustion engine, these were seen as an intermediate stage between the IC car and the fuel cell-driven car of the future. Present hybrid cars were less efficient in terms of CO_2 emissions because of the additional weight resulting from the need for two engines and additional battery capacity. However, they had a role in city driving in places of high pollution. Diesel engines were identified as the present power source of choice because of their lower specific CO_2 emissions and they also have the ability to run on bio-produced fuels thereby creating a sustainable drive system in which the CO_2 emitted during driving was captured by the fuel plant during its growth.

Safety was discussed in some detail, emphasised by a 40% greater likelihood of injury to occupants in a car rated at only 2* in the Eurocap tests compared with one rated 4*. There was also a call to design for greater pedestrian safety, as well as occupant safety. However, other factors, in particular road design and driver competence, also have a major role in reducing injuries. **STI**

AUTOMOTIVE DESIGN COURSE

The Coventry Masters programme is designed to appeal to former BA Design graduates who would like to further advance their skills or acquire new ones, especially in the use of Alias software and clay modelling.

The MA Automotive Design course is a 15 month course with emphasis on advanced concept thinking and computer-aided design.

For more information on Coventry University School of Art and Design visit: www.coventry.ac.uk/csad
For more information on Corus Automotive visit www.corusautomotive.com

Christopher Lavelanet's Future New York City Taxi took second place

Jean-Michel Raad's The Moov!! winner of the Coventry University Best Vehicle Design award

Alexis Julian Waterson took third prize with his Space, Form & Structure

The Platts' ferroalloys and steel conference

Hot on the heels of the announcement that, starting 2007, the LME was to use Platts to monitor prices for those commodity steels it plans to trade, was the second steel and ferroalloys conference organised by Platts.

REPORT BY DR HANS MUELLER*

The May 16-17 conference was organised by the Platts company, (a member of the McGraw-Hill information and news conglomerate) which tracks a large number of non-ferrous, precious and minor metals as well as ferroalloys and stainless steel scrap, publishing its prices in *Metals Week*. The company has long been in the business of organising conferences and symposia. However, this was only its second event on steel and ferroalloys, which may have been the reason why it attracted no more than 50 delegates. Platts is now in the process of systematically collecting and reviewing price data on a representative number of steel products which – as announced on the first conference day – has already attracted a prominent client, the London Metals Exchange.

Anthony Poole, managing editor of Platts Metals New York, made the opening remarks, acted as moderator throughout the event and spoke about the setting of benchmark prices.

Two sessions were scheduled for the first day, one addressing steel industry topics and the other market prospects for various non-ferrous metals (Mn, Ti, FeCr, and Mo) and scrap. The third session, held in the morning of the second day, offered presentations about the changing US automobile industry, problems of barge transportation and benchmark pricing methodology.

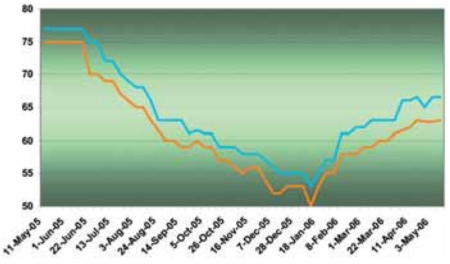
Very likely, what most delegates came to hear were the five presentations covering benchmarking and ferroalloys. The rest, though interesting in themselves, were not always well-integrated with the ferroalloys theme.

This is also the sequence that will be followed in this review: first benchmarking, then ferroalloys and last the steel-related topics, including this reviewer's own presentation.

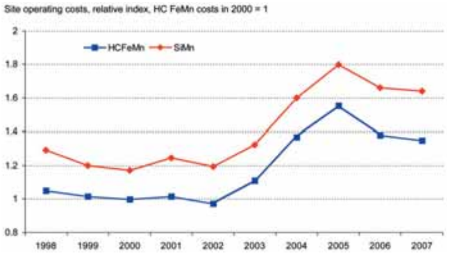
EXPERIENCE IN PRICE ASSESSMENTS

'Setting benchmark prices: the science behind the numbers' was what Poole set out to explain, relying heavily on the experience gathered by the Platts Metal Group over several decades, beginning 35 years ago with MoO_2 and FeMn and gradually encompassing many ferroalloys, metals and stainless scrap. The methodology was "an editorial process of gathering and analysing information", which depended on human experience and judgment to sort out the data obtained from telephone contacts, narrow down their range and develop a system of verification. The final assessments represented the most frequent transactions, normalised for standard terms and conditions. They were not a weighted average or index of reported data (**Fig 1**).

The methodology was regularly reviewed through internal audits to achieve maximum transparency. As an example of a company having confidence in the Platts assessments, Poole cited Carpenter Technology which uses Platts to determine its Ti surcharge on the prices of certain special steels. He also provided further details concerning the announcement that the LME had made Platts its partner for assessing the price of selected steel products, including semifinished grades, HR coils and rebars. The step was taken, he added, in response to steel producers seeking more price transparency and steel users wishing to reduce their price-risk exposure through the use of financial instruments. He attributed the LME choice to the company's experience with 'non-commoditicised' markets featuring industrial users, complex products and regional specifications/logistics.



1 Monitoring of US ferrochrome price range by Platts
A Poole, Managing editor Platts Metals New York



2 Fe-Mn and Si-Mn price index (2000 = 1)
K Golovko CRU London

	SiMn		HC FeMn		Ref FeMn	
	2000	2007	2000	2007	2000	2007
China	15	**45**	24	**37**	11	**29**
CIS	13	9	14	8	2	**4**
E. Europe	3	2	4	2	0	**2**
W. World	69	44	58	53	87	65
World demand mln tonnes	3.6	7.4	3.2	3.9	0.7	15

Table 1 China is now the world's largest consumer of ferro-alloys
K Golovko CRU London

FERROALLOYS

Manganese: Mr K Golovko of CRU looked at the role that CIS countries, Eastern Europe and China played in manganese alloys markets, specifically silico-manganese, high-carbon (HC) ferroalloys and refined ferromanganese. All three had seen prices soar in 2004 (to $1800/t for HC FeMn), fall abruptly in 2005 ($600) and then rise again in the current year ($800 May; $1050 July[1]). The most widely used, SiMn, was again moving toward a market surplus, whereas HC FeMn was in tight supply and refined FeMn in such short supply that additional price increases were inevitable (**Fig 2**).

China produced enough Mn alloys to spare some for exports, although these might soon be restricted by the central government as the country is now the world's largest consumer of ferro alloys (**Table 1**). Ukraine and Kazakhstan, the world's low-cost producers of both SiMn and HC FeMn, would remain large exporters of these alloys, Golovko predicted. Most high-cost capacity in Poland, Romania and Slovakia was idled following the '05 decline in global prices but might be restarted if warranted by higher global prices.

Titanium: Ti consumption by the commercial aerospace industry was likely to rise by leaps and bounds, Mr R Borowski of Titanium Metals Corporation told the audience. Although passenger aircraft orders would remain at present levels, Ti consumption per plane was rapidly growing. For example, whereas a Boeing 747 contained 45t of the metal, the 787 would use 91t because Ti is more compatible than aluminium with the composites widely used in the newer aircraft. Airbus models showed a similar trend, though at a less intensive pace.

Prices have been moving up, reaching $8/lb by the end of Q1 2006 for ingot chips and nearly twice as much for Ti in 'bulk weldable' form. Not surprisingly, Ti-sponge producers in many countries plan capacity expansions, especially in Russia (Avisma), Japan (Sumitomo and Toho) and the USA (Timet and ATI). Borowski looked forward to an expansion of global Ti sponge capacity from 108kt in 2005 to more than 160kt by 2010-2011 (**Table 2**).

Ferrochrome: The global stainless steel industry consumed 84% of ferrochrome, most of which is purchased as high-carbon (HC) rather than the more costly low-carbon (LC), explained Ms J Ward, owner of Pennsylvania-based metals dealer Reward Raw Materials. She noted that global FeCr demand was relatively weak last year despite a surge in China's requirements. Efforts made by major suppliers

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to restrict capacity use were inadequate to sustain the mid-’05 high price of 76 cents/lb and prices soon fell to 60 cents. By now they had recovered to 71 cents and Ward gave three reasons why she expected further increases during the next several years:

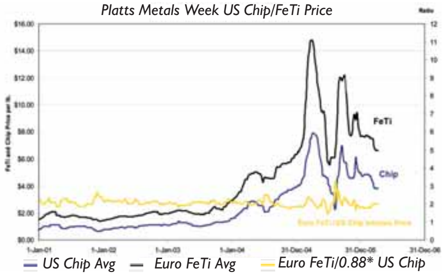
(1) estimated growth of global stainless steel consumption at 5%/y;

(2) cost pressures in South Africa, the world’s largest FeCr producer; and

(3) continuation of cross-border consolidation of the FeCr industry, which would probably be reinforced by alliances and partnerships between large producers and consumers.

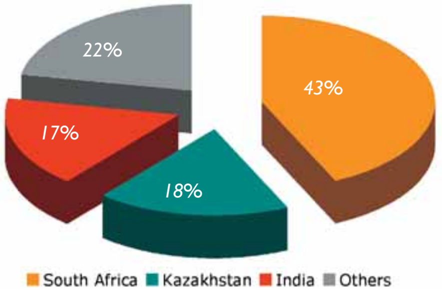
Producer	Country	2005 capacity kt/y	Future capacity kt/y	Completion Date
ATI	USA	0	3.5-5	2006-2007
AVISMA	Russia	27	44	2010
FUSHUN	China	2	5-10	2006-2010
SUMITOMO	Japan	18	24	2006
TIMET	USA	9	13	2007
TOHO	Japan	15	22	2011
UKTMK	Kazakhstan	22	22	-
ZTMK	Ukraine	8	13.5	2008
ZUNYI	China	7	10	2010
TOTAL		**108**	**157-163.5**	**+50%**

Table 2 Major producers of titanium (kt/y) *R Borowski TIMET USA*

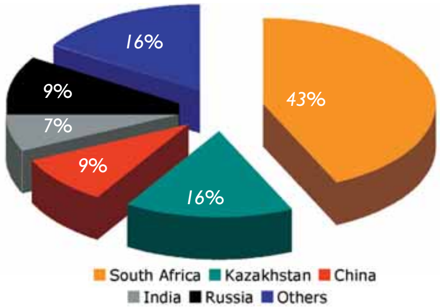


3 FeTi and Ti chip prices *R Borowski TIMET USA*

South African producers in particular would see their profits decrease due to the appreciating rand (vs the US$), rising wages, badly needed environmental and infrastructure investments, and enforcement of the black economic empowerment law requiring a 15% equity transfer to black groups by 2009 and a 26% transfer by 2014. But how much cost increases in S Africa would push up global prices was not certain considering that rivals in Kazakhstan and Russia did not experience similar cost pressures. Furthermore, global price increases would be slowed by ambitious capacity expansion plans undertaken by large producers in several countries and, in the USA, the continuing sell-off by the government’s Defense Logistics Agency of large hoards of HC and LC FeCr amassed during the Cold-War period and no longer deemed necessary (**Figs 4 & 5**).



4 Major world reserves of chrome ore
J Ward Reward Raw Materials USA



5 Production capacities of ferro-chrome
J Ward Reward Raw Materials USA

Industry consolidation began in 2003, when a relatively small company, Kermas, acquired the Russian producer Serov and in 2005 bought the Samancor Chrome division from Billiton and AngloAmerican[2]. Kermas then sold a third of Samancor Chrome to International Mineral Resources (IMR), linked to the giant Kazakhstan producer Kazchrome, which in turn is buying 50% of the Kermas share in Serov.

Molybdenum: M Magyar, of the United States Geological Survey, talked about molybdenum (Mo or Moly), how and where it was produced and its applications. Extraction from porphyry ores in the form of Molybdonite (MoS_2), often as a by-product of copper mining, was followed by beneficiation and roasting to obtain MoO_3, part of which was converted to FeMo. Worldwide, about 80% of the metal was consumed by the iron and steel industry to impart greater heat and corrosion resistance as well as hardenability to stainless, alloy and tool steels. Stainless steel and superalloys claimed 30% of the total, alloyed steels another 30%, tool steels 10% and foundries 10%, with the remainder going to industries producing catalysts, electrodes, filaments and chemicals.

Magyar noted that, before 1890, Mo was little more than a laboratory curiosity. It then served as a substitute for tungsten in the production of armour plate and now was widely used in nuclear energy plants, aircraft parts and other demanding applications. According to his data, global output in 2004 was 141kt, the USA and Chile each producing 41.5kt, followed by China with 29kt, Peru with 9.6kt and Canada with 5.7kt. He limited his discussion of prices to the US market, where MoO_3 rose sharply from $5/lb in Q3 2003 to $35 by Q2 2005, fell to $29 in Q4 and was now about $27. Hardly mentioned was international trade in MoO_3 and FeMo which must be intensive, considering that almost half of the metal was consumed in Western Europe and Japan[3] while virtually all the production occurred elsewhere.

(One disconcerting feature of this presentation was the switching of units from kilotons to million pounds for global output and from $/lb to $/kg for US price movements).

THE STEEL INDUSTRY

The remaining presentations all dealt with steel-related topics.

Consolidation: F McGrew of Morgan Joseph, a financial company, took a broad view of the steel industry and talked less about consolidation of steelmaking itself than about structural change downstream and upstream from steel, specifically the service centre and scrap industries. While the description of mergers and acquisitions (M&A) in those industries is not without interest, it was not very relevant to the main theme of that concentration in the steel industry facilitated price leadership which led to more stable prices at an elevated level, boosting the earnings of leading steelmakers and attracting the attention of financial companies. Only three rather unequal examples were given for M&A in steel: Mittal/Arcelor, (still unresolved at the time of the presentation but since completed) Arcelor/Dofasco and Steel Dynamics/Roanoke.

Mr McGrew’s prediction that vertical integration attempts would fail is hardly applicable to all sectors of the industry. Several leading steelmakers are seeking long-term access to iron ore by investing in offshore mines, slab projects in ore-rich countries, or steel companies with large mining interests (eg, Dofasco and Krivorozhstal). Steel companies have also opened new distribution and processing centers at home and abroad. Finally, McGrew’s mention of Baosteel and China Steel as examples of industry concentration in China raises a few questions.

China: J Zambelli, now heading Zambelli Technology International, emphasised how important it was for foreign entrepreneurs to foster connections, or guanxi, with private partners and government officials in China. Without such efforts, the playing field there would be anything but level.

To underscore his impression of that country’s growth momentum, Mr Zambelli noted that China graduated more PhDs and engineers than any other nation and operated 80% of the world’s construction cranes. However, his data about China’s steel industry was spotty and not always accurate. For 2005 he put steel production at 352Mt, adding that this had led to an oversupply situation. He then followed up with a consumption estimate of 402Mt for the same year. Data released by the National Statistics Bureau of China give the same 352Mt figure for output but a marginally smaller (by 120kt) figure for consumption, both in crude steel terms[4]. The IISI number for 2005 consumption of finished steel products for China is 315Mt[5]. Nevertheless, Mr Zambelli boldly predicted China’s steel consumption to reach 440Mt in the current year and 560-620Mt by 2010, again without indicating whether crude or finished steel.

India: V Kochar of Universal Steel, an exporter of stainless steel and stainless steel scrap, provided plenty of evidence that India was rapidly moving onto the global stage, attracting more foreign investment than the USA, developing a booming high-tech service industry, and – according to a Goldman Sachs study – destined to be the fastest-growing economy over the next 50 years due to its stable democracy and young population pyramid (whereas China, with its one-child policy, would become old before it got rich). Changes in government tax, tariff, monetary and fiscal policy as well as reforms of the financial and public sectors would help overcome such roadblocks as a crumbling infrastructure, a heavily-layered bureaucracy, corruption, illiteracy, over 200M people suffering from malnutrition and the economic boom so far having had little impact on two thirds of the population.

Kochar's forecast that, in 5-7 years, India's steel consumption would rise by 160Mt is far higher than even the most optimistic predictions made by Indian experts[6]. Furthermore, his observation that China covered 70% of its stainless steel needs with imports from India is obviously incorrect. China consumed about 6.3Mt of stainless products last year, 2.6Mt of which consisted of net imports. India's total stainless exports were about 0.5Mt[7], just a fraction of the volume imported by China. Finally, Kochar started out by saying that India was the world's 12th largest economy; shortly afterwards he ranked India's GDP as the 4th largest in the world. This inconsistency probably arises from the application of different measurements – exchange rates in the first instance and purchasing power parity in the second (pricing Indian goods and services as if they were sold in an advanced economy).

Steel Recycling, Transportation: J Redden of OmniSource discussed the problems facing American scrap dealers, especially in the areas of environmental rules and bulk transportation. More inspectors had to be hired to check shredded-car scrap for such non-compliance material as mercury and, to make certain its transportation needs would be met, the company was operating a private fleet of trucks, trailers and railway gondola cars. It has also invested in a de-zincing facility that yields pure zinc and 'black scrap' for remelting. Another speaker, M Wastchak of Memco Barge line, contrasted the rising demand for barge transportation with the shrinking of barge fleets and the mounting problems caused by insufficient funding of infrastructure maintenance, especially regarding the locks along the Ohio River.

Automotive industry: R Schulz, of Standard & Poor's, discussed the state of Detroit-based automakers (formerly known as 'the Big Three'), covering both US and foreign operations. In many ways, the US auto industry is dogged by the same problems as steel a few years back, especially generous pensions and health insurance for a large number of retired workers (**Figs 7 & 8**). Additionally, increased fuel prices sharply reduced the sale of trucks and SUVs (from which US companies derived most of their profits), while it accelerated sales of more fuel-efficient vehicles made by Asian competitors. GM and Ford also did poorly in Europe and only slightly better in South America. Schulz supported his well-told story of the Big Three's still unfinished struggle with a wealth of facts and tables.

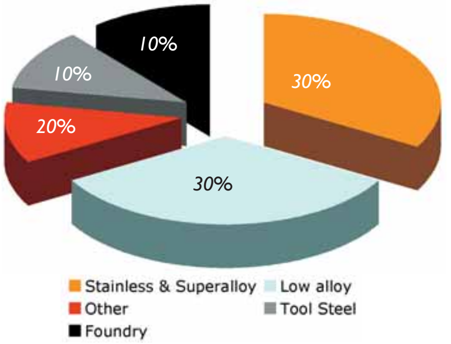
Platts had invited Dr Hans Müller to talk about the likely development of demand, supply and prices in the North American steel market. Due to a lack of adequate data regarding the NAFTA steel market, most of the discussion focused on the steel market of the USA and, where relevant, the global market.

The most outstanding feature of the US market is a domestic supply deficit fluctuating around 25% of apparent consumption, consisting of about 20Mt of finished steel mill products and 10Mt – mostly slabs plus some billets and HR band – imported directly by US steel mills and re-rollers. The irony is that the mills have claimed protection for the entire market, forcing American steel users to pay penalty tariffs on steel products that are not available from domestic suppliers.

Heavy pension and healthcare obligations for tens of thousands of retired workers, as well as the cumbersome work rules, had pushed many integrated US steelmakers to the wall by 2000. Bankruptcy allowed them to shed these costs along with most of their debt. It also motivated labour unions to give ground on work rules, wages and benefits. As a result, high-cost marginal mills were transformed into low-cost producers, which were quickly bundled into a giant new company or absorbed by other large steel producers. A sharp reduction in the number of sellers was a basic requirement for stabilising prices. However, to make this condition last over the longer term, the remaining dominant firms also had to develop a spirit of solidarity in tackling the difficult job of constantly adjusting joint sales volume to fluctuating market demand. Raising prices in lockstep during 2004 proved easy but, except for Mittal, the firms were slow to cut output in response to falling sales in the first half of 2005. Only by mid-year did they develop the solidarity of action that was crucial to achieve stable prices. In fact, they may have done their job too well, pushing US domestic prices well above European and Asian prices for the principal steel categories.

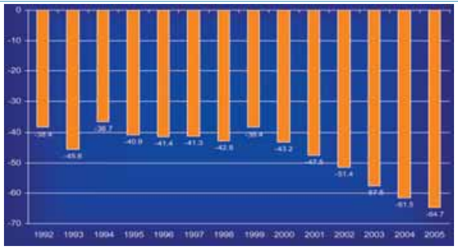
What of the future for cross-border steel industry consolidation? For instance, will a small group of 100-200Mt steel giants manage to impose price discipline on international markets by suppressing disruptive surges in trade volume? How will they react to trade cases affecting their far-flung affiliates? Will they be able to avoid getting entangled in regional protectionism? Finally, will they jointly muster sufficient clout and bargaining power to stand up to the exorbitant demands of highly-concentrated raw material suppliers?

As to the Chinese expansion, its main impact on the global steel market has been a significant boost of resource prices, particularly iron ore. As a consequence, there is a distinct shift in the comparative advantage of steel production, at least at the hot end, toward locations promising secure access to large iron ore deposits. This shift has already spawned a number of integrated slab projects in Brazil and India. **STI**



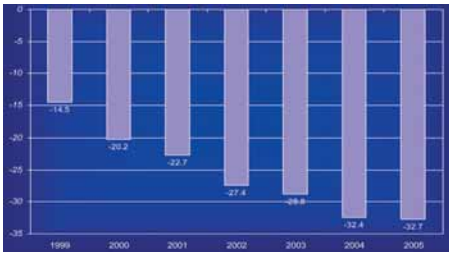
6 Uses of molybdenum

M Magyar, of the United States Geological Survey



7 GM's unfunded retiree medical liability ($bn)

R Schulz, Standard & Poor



8 Ford's unfunded retiree medical liability ($bn)

R Schulz, Standard & Poor

Footnotes

[1] Platts Metal Week, July 10, 2006, p20

[2] Mineweb, 17 Feb. 2005; see also Competition Tribunal, Republic of South Africa, cases no. 22/LM/Mar05 and 03//LMJan06.

[3] Goldman Sachs JBWere, Molybdenum Market Update, 16 Jan. 2006

[4] 4th China International Steel Congress, Beijing, April 2006, p45.

[5] IISI, World Steel in Figures 2006. P20.

[6] See eg. Steel Times International, April 2006, p41, Dr Amit Chatterjee cited in "A report on the 12th annual steel conference held in Kolkata, India" by Dr Tim Smith, STI editor.

[7] Steel Times International May/June 2006 p19, K. Prasad, "Stainless & special steel production in India". Mr Prasad's 2004 estimates were updated to 2005 from various internet websites citing H. Pariser, a stainless steel expert and Jindal executives.

76000 deliveries of new rail cars and platforms are expected in 2006

Shortage of rail, road and barges hampers US steel industry

Rail, road and waterways are all presently at a premium for shipping steel across USA, with freight companies sometimes refusing to even quote a rate until they know they have the transport available.

BY MYRA PINKHAM – NEW YORK

Railways prefer bulk commodity cargoes over steel

While all modes of transportation continue to be tight, the North American steel industry seems to be most concerned about what they see as a deterioration of service by the railroads, which includes very tight availability of rail cars – especially the gondolas cars that are used to transport both finished steel and steel raw materials – as well as skyrocketing freight rates.

Many steel companies have also questioned whether rail companies would rather have the business of other commodity sectors rather than steel. While admitting that at these times of very tight capacity they are seeking business that gives them higher rates of returns, North American railroads say this does not mean they do not value steel business. “We try to help all of our commodity groups,” says Mark Davis, spokesman for the Union Pacific Railroad.

“The American Iron and Steel Institute is aware of the rail car availability issues and is monitoring it,” says Elizabeth Vago, director of communications for the Washington-based trade association. “Many industries in the United States are experiencing severe problems with the movement of raw materials and finished products on the nation’s freight system. How to address the shortage of rolling stock, congestion on the rails and increases in shipping costs combined with diminished service has become a priority for our allied industries and has been expressed as a priority of some of our member companies.”

“Railroads have huge issues with the constraint of capacity,” says Gordy Gustafson, chief commercial office and vice president of integrated solutions for ADS Logistics LLC, Homewood, Ill. “It isn’t just a rail car supply issue,” he maintains, but also has to do with problems relating to rail infrastructure, locomotives and availability of crews. “They are in a very different position than they had been in previous years.”

The rail industry, observes Jim Ruiz, vice president of Pittsburgh Logistics Systems, Pittsburgh, has gone through many changes since the transportation industry was deregulated in the early 1980s including a round of consolidation during the mid-1990s. “After that consolidation, they began to focus more on their bottom line and rethought capacity acquisitions.”

In fact, according to David Reid, managing partner for Shackleton Partners, Malverne, Pa, that was exacerbated a few years ago when scrap metal prices jumped up a few years ago. He notes that a lot of old cars were scrapped and now that demand is so strong, the supply of cars is down.

“The market for rail transportation is very strong,” says James Schaaf, director of marketing for the Norfolk Southern Railroad, with record shipments being reported by the railroads, and by barge and truck as well. The steel industry has contributed to that rise, admits Tom Danjczek, president of the Steel Manufacturers Association, Washington, as steel shipments, which are up 7-9%. “But there has been a significant deterioration of service including a lack of availability of rail cars, particularly gondolas, due to lack in reinvestment, as well as a lack of infrastructure development,” he says, adding that this has had a very adverse effect on steelmakers, who a very dependent on the railroads. “Some companies use rail for as much as 80% of their shipments, although there are others who use it for about 30% of their volume.”

Leslie Moll, manager of logistics and external processing for Mittal Steel USA, East Chicago, Ind, agrees that while most carriers try to be responsive to the needs of shippers in the steel industry but says that the response has been slower than some companies would like, with the railroads not even quoting prices until they know they could fit the shipper in. “It is much tighter than it has been for 20 years on a sustained basis. Usually there are seasonal peaks, such as in the third quarter with the grain season, but now it is constant,” she says.

Steve Hirsch, associate counsel and director of state and local programmes for the Institute of Scrap Recycling Industries (ISRI), Washington, agrees that rail cars, while available, are very tight. “And in general it isn’t improving as many railroads have decreased their gondola fleets and are concentrating more on intermodal unit train movement. Many of our members aren’t getting the rail service that we like.” The same goes for steelmakers, Keith Busse, president and chief executive officer of Steel Dynamics Inc, Fort Wayne, Ind “Something needs to be done to change the level of service.”

NEW RAIL CARS

It is not that the railroads are not making capital investments. “They are ordering rail cars hand over fist,” says Ken Kremar, principal of the industrial practices group of Global Insight, New York. As a result, according to Peter Toja, president of Economic Planning Associates, Smithtown, NY, says there should be about 76 000 deliveries of rail cars and platforms this year, including 963 gondolas and 1240 non-intermodal flat cars, and another 73 000 car and platform deliveries in 2007. Just how many cars are being added to serve their steel and steel raw material customers varies railroad by railroad. Darrell Stanyard, director of sales, metals, for CSX Corp says the railroad has purchased 165 new gondola cars and is leasing 60 covered rail cars as well as initiating a national pool for its bulkhead flat car fleet to improve the capacity of those cars. “We currently have 22 projects in process for repairing and acquiring rail cars,” he said. Likewise, Davis said that while Union Pacific did not purchase any steel-related rail cars this year, it did acquire 600 gondolas last year.”

BOTTLENECKS

But it isn’t just the rail cars, Moll points out. “While cars is the most visible asset, there are other bottlenecks in the rail system,” she says, “Just adding more cars onto a line that already has bottlenecks will not help.”

It is for this reason, Schaaf says, that Norfolk Southern and other railroads are not just adding cars but are focusing on asset utilisation. “We are trying to minimise the dwell time of equipment – minimising delays in loading and unloading time. We’re also trying to be more selective regarding the business that we are going after, focusing on core lanes, where we are most efficient." Craig Longartner, manager of materials and transportation for Steel Dynamics' flat rolled steel division in Butler, Ind, says that while his mill, due to its location, does get a good supply of rail cars, they tend to come in bunches.

Railroads are also making considerable investments in the rail infrastructure. Davis notes that Union Pacific has invested $1.5bn on infrastructure improvements as well as adding new locomotives. Gary Sease, a spokesman for CSX, said that railroad will be spending $800M in 2006-07 in addition to what was planned for its $1bn a year capital budget to upgrade its infrastructure, particularly its Chicago to Florida and Albany, NY, to northern New Jersey corridors, to make traffic more fluid. CSX, like Norfolk Southern and others, is being more selective about the business it takes on, allocating capacity based on higher return, which has made some people in the steel industry a bit apprehensive. Jim Van Cleave, CSX's director of metals marketing, admits that if demand is more than supply there could be customers that are short, "but it is no different than what the steelmakers do when they are on allocation," he maintains.

The steel industry, however, fear that that they will be the ones left short, especially, according to Plummer, since the railroads have been burned in the past by steelmakers. "Steel has a historical track record that it needs to overcome, especially since there is a lot more profitable demand for other commodities, including coal and grain," he says. Recognising this, Danjczek says, "We are working with the railroads to show how competitive we are and that we are good customers."

Moll says there are things that the steelmakers can do to be better customers, including communicating with them more, sharing forecasts of volume, as well as being more efficient when loading and unloading dedicated equipment. But there are also certain things just in the structural nature of the metals industry that work against it, says ADS' Gustafson, including that coal and intermodal grain usually run on large unit trains while the nature of steel transportation does not lend itself to such volumes. "It is higher cost for the railroads. Either the steel industry needs to increase volumes or the railroads need to figure out a different way to deal with steel. One choice is setting up a depot where cars could dropped off or picked up.

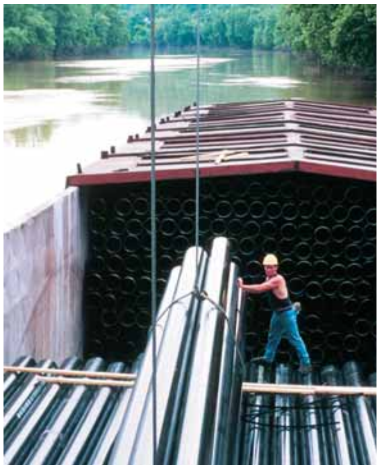
	Orders	Deliveries	Backlogs
2004 Q1	600	213	637
2004 Q2	0	37	600
2004 Q3	200	0	800
2004 Q4	720	231	1 289
2005 Q1	538	361	1 466
2005 Q2	678	367	1 777
2005 Q3	375	459	1 693
2005 Q4	475	925	1 243
2006 Q1	905	963	1 185

Table 1 Investment in rail mill Gondalas since 2004

Still, the railroads say that steel and other metals business is important to them. Davis observes, "Industrial products account for 22% of Union Pacific's business with metals and ores representing 17% of that. We try to help all of our commodity groups, but we need to look at and analyse the cost of capital."

TRUCKING ALTERNATIVE

In the light of the situation, some companies are looking to other modes of transportation, but are finding that they are tight as well. Moll says that during the first quarter her company moved some of its transportation needs to trucking and, in what is an even more extreme reaction, Hirsch says that one ISRI member started his own trucking company because of concerns about getting product to market.



1000 barges were scrapped in 2004, when scrap prices were high, but not replaced as the cost of steel to rebuild jumped 54%

(pic courtesy Ingram Barge Company)

Turning to trucking, a faster but more expensive form of transportation than rail, is not necessarily a panacea. For the last two and half years, Ruiz observes, trucking has been very tight, largely due to a shortage of drivers. He says that according to the American Trucking Association by 2012 the truck driver shortage will grow to 110 000 drivers. "Very few people want to take the long hauls. They want to be home with their families," says Toja. As a result, many would-be truck drivers are taking other jobs, such as construction jobs, which are readily available, and those that are working in trucking, are not looking for the long hauls that most steelmakers need. In an effort to get drivers home at night, "A lot of trucking companies (are) just willing to ship over a 200 mile radius. Steelmakers often service 500 mile areas," says Danjczek. This means that often steelmakers need to transfer loads from truck to rail (or barge) and back to truck.

The trucking industry will be short of 110 000 drivers by 2012

(pic courtesy Maverick Truck)

Meanwhile, according to Stephen Selig, president and chief operating officer of Maverick Transportation LLC, Little Rock, Ark, the problem of getting and keeping drivers is more pronounced for the flat bed trucks used to transport steel, as the driver needs to protect the load from weather. "It is different than the traditional driver job, where you just drop a hook. Most of our load is loaded live and it takes an hour or two to secure the load, not including wait time."

And the new hours of service rules for truck drivers exacerbate the problem, as they not only limit the hours that drivers can work in a day, but include wait time, so, according to Tom Eatinger, vice president of transportation for ADS, "If a truck sits it burns hours of service."

BARGE TRANSPORT

Barge availability is also very tight, says Christopher A Black, senior vice president and chief financial officer for American Commercial Barge Line LLC, Jeffersonville, Ind, which is not only a barge operator but also builds barges. He notes that over the last seven years dry cargo barges experienced about a 15% reduction in capacity going from 21 000 ships to about 18 000 today.

Much of that, according to Sandor Toth, publisher of River Transport News, Silver Spring, Md, is that when scrap prices went up, much like the railroads, the barge lines saw an opportunity to make good money in a short time by scrapping barges. They scrapped 1000 barges in 2004 and continued scrapping capacity at a high rate through the first few months of 2005. And even once business improved, barge operators were reluctant to order more ships. That was, he says, because there was, at least at first, a considerable amount of uncertainty whether the pickup in business of iron, coke and other steel-related raw material was "just a flash in the pan" and once they were confident that it had legs the cost of buying a barge (largely because of increased steel prices) went up from $260 000 to $400 000 or more.

Even now, says Dan Martin, senior vice president of sales and customer service for Ingram Barge Co, Nashville, Tenn, "I believe that more barges are being scrapped than replaced." He notes that industry-wide about 1000 barges are being retired annually while this year about 800 barges will be produced. "The next few years will be a challenge," he said.

"As long as the economy stays strong, we see equipment staying tight, whether it is rail, truck or barge, for at least the next year," Schaaf says. "We will continue to do the best we can with the equipment available." Meanwhile steelmakers are putting more resources into transportation issues, working with carriers, sharing information on how things could be done better, Danjczek says. "Transportation hadn't been a major area of emphasis for many companies in the past, but it is now." STI

Roll grinding developments and relationships with production of tinplate and automotive sheet

The wide ranging effects of roll quality on strip surface quality, dimensional control and overall plant throughput and yield are introduced and illustrated by the cooperation between Pomini and Dofasco in integrating modern roll grinding machines with sophisticated grinding procedures, a roll quality database, automated crack detection, and roll handling equipment.

BY S CRITCHLEY*, P GABOARDI**, G BAVESTRELLI** & C TREVISAN**

Flat rolled steel quality levels and their rate of improvement have increased every year for the past 25 years. The stunning rates of change normally associated with computer based industries have had equivalent, and in fact a related impact, on the tightening specifications of steel sheet. Thickness tolerance changes are probably the best known example.

Customer ordered tolerances have tightened radically. At the same time the published standards of ASTM and DIN for example have stayed almost unchanged since their first introduction. Can makers were the first steel users to demand a change; plus or minus 10% thickness variation was unacceptable for the production of a two piece can. Automotive manufacturers followed and moved first to using value of 'one half published tolerances', then to 'one quarter', with steel now being sold with the expectations of performance in the range of 10% of the published tolerance. This is a 1000% increase in accuracy that could not have been supported without improvements in mill equipment. In this paper we will review some of the improvements in plant performance enabled by the improvements in roll preparation.

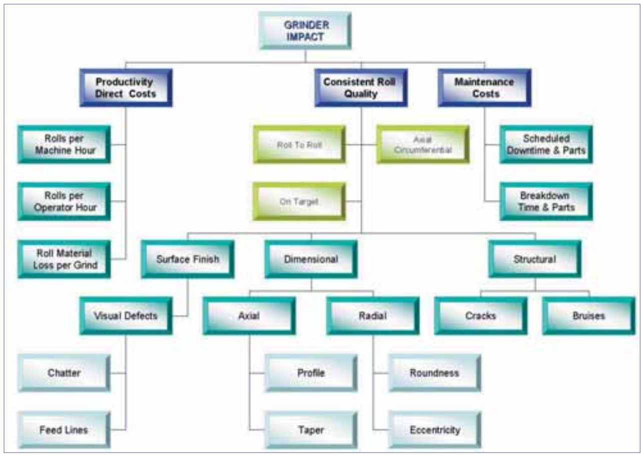
The key driver of these changes is automation of the plants consuming the sheet metal from the modern steel plant. Automatic machines make consistent product, but they in turn demand consistent inputs. 25 years ago 'traditional' minor variations in incoming material were the source of challenges to the skilled operators of the time. They would compensate for material variation by making fine adjustments in the press or other machines. Car door assemblies at the time included adjusting shims, these and other minor adjustments are not acceptable to modern automatic assembly lines.

As new machines are considered it is important to reflect not only on the impact of a roll grinding machine on the rolls and roll shop, but on the collateral benefits to overall operating costs that come with modern roll preparation.

The last decade has seen significant investment in Asia, especially China, where many new machines were sold both to existing and greenfield plants, and old machines were replaced or revamped. Major producers in Europe and the US have begun to invest in their roll shops. Mills that do not have modern rolls shops are becoming a minority, and find themselves at a competitive disadvantage.

Fig 1 shows some of the important relationships and a few examples are now described.

Flatness and thickness are limited by the dimensional accuracy of the rolls, but in this case in combination with the most complex set of roll parameters, those of its surface metrology. The flatness or shape of the strip, in turn affects the speed, productivity and yield of many subsequent operations.



1 Direct impact of roll grinder on mill operation

2 'Inspektor' ultrasound and eddy current detectors from Pomini

The surface finish of the roll directly impacts rolling mill friction. Low friction promotes the onset of mill chatter, a variation in surface continuity around the circumference of the roll usually associated with poor ground run-out can create variation in the friction, high friction consumes more energy and generates more wear particles that deposit on the strip. Hence cleanliness levels of the rolled strip are impacted by the roll shop. The surface texture and cleanliness of the strip also impact the consistency of heat treatment and coating processes. In summary a good roll shop should provide consistency around and along each roll and, equally important, from roll to roll. Roll consistency is the foundation of stability of the rolling operation. In turn, stability in the rolled product provides stability to all the downstream operations.

The value of even a 1% productivity improvement on a key processing line can be the largest contribution in the lifecycle value analysis of a roll grinding machine. While the main relationships are well known in individual areas, it is considered worthwhile to review the impact of the roll shop on the total plant. By considering first the major roll parameters, the direct impact of these roll parameters on strip production, and finally the impact of the strip quality itself on the overall plant can be determined.

ROLL QUALITY PARAMETERS

ROLL SHOP SAFETY - DEFECT MANAGEMENT

The hardness requirements for mill rolls are severe and push the capability of the roll makers. The available hardness, wear resistance and toughness of roll materials have developed over the last 25 years. Today's roll is a highly stressed piece of steel that can explode if it is not handled with care and constantly monitored for cracks and other forms of damage. The thermal strains of heat treatment leave major stresses in the roll that will result in catastrophic failure if cracks or internal casting defects are allowed to develop into cracks. Progressive mills have

*SC Support Services, Canada,
**Techint SpA, Roll Grinders Division, Italy

comprehensive safety programmes inherent in their roll management systems. Recognition and proper management of these hazards by using acoustic emission, eddy current and ultrasonic testing is an area where Dofasco has long been a pioneer. Dofasco's recent Roll Defect Management patented concepts differentiate between thermal and mechanical cracks, enabling the development of acceptance/rejection criteria and roll material removal based on grinding and mill data. A recent agreement to work with Pomini on these concepts is leading the industry toward a new level of safety.

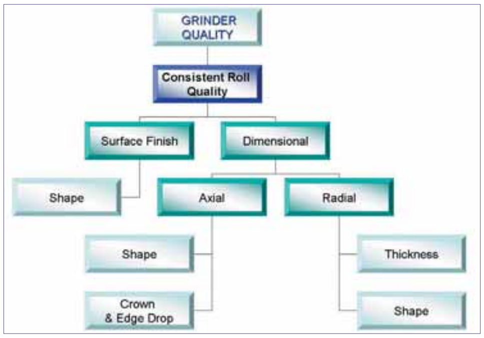
Crack detection by eddy current & ultrasound: The need to maximise safety, and to optimise costs, led to many efforts to significantly improve inspection technology. Sustaining leadership in any field of technology demands willingness to change, and flexibility in adopting new strategies, even if they sometimes involve an element of risk. This process of developing cooperation between customer and supplier started a long time ago, and it is still a work in progress. The initial Pomini project in Canada was the roll shop installation for the Dofasco Inc's first coupled pickle-line cold mill. It was also the first opportunity for Dofasco and Pomini to work together on a self contained, fully automated roll shop. The following paragraphs describe some advances in the roll shop safety that have been made by the two companies.

Ultrasound inspection: The first ultrasound inspection system '*Inspektor*^{TM}' on Pomini Roll Grinders at Dofasco was installed in 1998. The new ultrasonic sensor, combined with a new generation of digital numeric control, was integrated into the existing eddy current based diagnostic system (**Fig 2**).

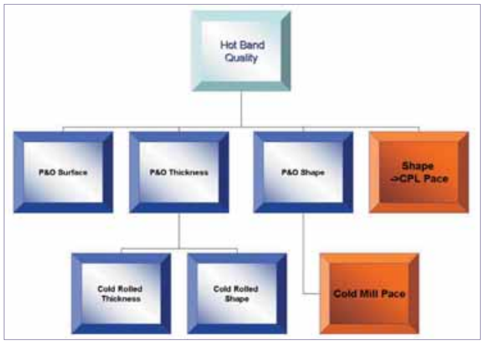
The Inspektor is controlled directly by a PC, allowing direct automation of data storage and analysis features. Hot mill work rolls are scanned by a combined ultrasonic and eddy current inspection system as part of the regrinding process.

Detection of cracks by ultrasound prevents suspect rolls from being placed in the mill, where uncontrolled crack growth can initiate serious accidents caused by the rolls breaking or catastrophically exploding. Defective rolls, isolated after the grinding cycle, should be subject to a second detailed ultrasonic scan using a more sensitive off-line system, which enables cracks to be measured and classified.

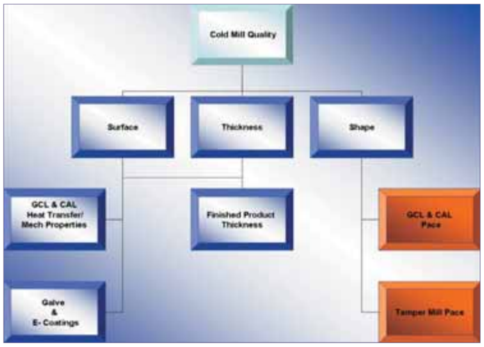
The main purpose of the ultrasonic analysis is to detect and monitor subsurface cracks. Checking for cracks in the interface between nodular/flake iron cores and spun cast/continuous pour outer roll shells is only possible with ultrasonic testing. Cold mill rolls use steels with increased levels of chrome and nickel, current air melt castings of high strength steel work rolls are still susceptible to internal defects such as non-metallics, porosity and alloy segregation. While great improvements have been made by the roll makers, it is still an area of concern and requires diligent monitoring. The high hardness possible in these rolls makes them susceptible to a type of failure where the hard shell breaks away from the core. In these cases ultrasonic scanning is a most effective method to detect and track small crack defects; enabling a safer and more cost effective roll management programme.



3 Direct impact of roll quality on strip quality



4 Indirect impact of roll quality on plant productivity and quality from hot band



5 Indirect impact of roll quality on plant productivity and quality in the cold mill

Roll Defect Classification: Automatic distinction between thermal and mechanical cracks is an example of valuable information. The decision of the optimal stock to be removed from each roll is unique. It is not ideal to react equally to all cracks by programming a fixed loss, but without knowing the type and the dimensions of the roll surface defects the application of a more advanced logic within an automated system is not possible.

Thermal cracks are perpendicular to the surface and do not tend to propagate. They can be removed to a threshold value which is a function of both the roll material and the specific use. Mechanical cracks are generally at an angle to the surface, and will propagate until roll failure. They must be completely removed.

Many roll defects are quite small, but are still able to initiate a major roll failure. A new eddy current detection head with smaller coils (2mm diameter) has been studied and developed by Pomini for Dofasco. This head is able to detect smaller defects and, at the same time, to create a detailed map of the defect area.

Newer systems are able to monitor the individual defects every time the roll returns to the grinder after a mill campaign. The ultrasound reading maps are saved in a database. They are easily compared to check if a crack is propagating, and then to provide better understanding of the conditions which can influence the crack development and of the initiation source (ie microstructure, alloy segregation, inclusions, voids etc). Defect management is not yet an exact quantitative science. However, the tracking of crack development is providing insight into the processes, allowing the steel plants to develop a better understanding and implement better operating and safety standards.

Dimensional accuracy: Dofasco has long been recognised as a market leader in thickness control, being among the first to offer improved thickness performance to its tinplate and automotive customers. Sustaining this position has been made possible by early recognition of the many relationships between the features of the mill rolls and the quality and productivity levels of flat rolled products.

The impacts of roll dimensional accuracy, concentricity and roundness on the thickness performance of both hot and cold rolling mills are well understood. However, the fact that the roll quality impacts many other facets of flat rolled product quality, yield and productivity is often overlooked.

Figs 3 to **5** show how the influence of the roll quality parameters is connected to all the important quality aspects of the full range of flat rolled products.

The links to productivity are mainly through two paths. The first is the shape of material entering continuous lines which will often cause the operators to limit the line speeds on those lines to prevent strip breaks. Modern control systems do a good job of closed loop control on thickness and shape on all the mills, hot mill, cold mill and temper mill. However the first coil after a roll change is still normally the worst performer at a downstream operation. The performance of these coils depends on the accuracy of the new rolls, compared to their ordered dimensions and surface finish specification. The shape errors on thinner products have also been linked to roll to roll and within roll surface finish differences[1].

ROLL SHOP COSTS

The cost of rolls and the associated grinding is usually second only to energy costs in a major rolling operation. The objective of roll grinding is to provide a refurbished dimensionally accurate working surface, ensuring all components of a set of parameters lie within tight specification, in the minimum time with the minimum cost.

'*Grind to Aim*' is a systematic approach to ensure a first class roll being prepared for the mill, while removing the minimum material in the minimum time.

The conventional three step process, to prepare a roll for the mill, is to:

- Remove a pre-determined depth of roll surface material;
- Inspect the roll;
- Either return to the mill or initiate a second grinding as in step 1.

This method is simple, but has major deficiencies. It can never be optimal. Either one or more cracks will remain after the first grinding programme, or time and roll material are wasted because more than the minimum material is removed. The potential risk for accidents involving personnel, product and the plant, means that having defective rolls in the work area is not an option in today's steel processing environment. Therefore methods have to be found to provide minimum stock removal, prime production and at the same time maintain the highest possible confidence that the roll is defect-free. This is best done with an independently programmable measuring carriage, on which the measuring calliper is supplemented with an eddy current inspection system. During the roll roughing stage an optimising programme determines all the salient features of the roll, and generates a map of the roll. This map or matrix of information now provides input to the grinding logic.

In the roll evaluation process three levels of crack classification are used.

- The first is the upper or 'critical threshold'. Cracks above this level are critical or very unusual and will require operator intervention. These problems should not normally be corrected in the production machines: so the grinding programme is paused and an alarm is set for the operator.
- The second classification, 'repairable', indicates that this defect can be repaired using one of the programmed sequences of the machine.
- The third threshold is the maximum acceptable level: below this level the roll is released for use at the mill. A similarcycle of checks is carried out for all detected defects.

The system first removes eventual residual magnetism that could deceive the eddy current system by indicating false positive results. If all the detected cracks are repairable, the diagnostic program locates the most severe one and the machine starts its repair phase. During this phase, the defects are removed sequentially, always working on the heaviest remaining crack. The diagnostic program monitors the reduction in defect level, and the machine keeps on grinding until all the measurements are below the minimum threshold. Then, the machine completes the normal grinding phases.

6 Moving rolls in cassettes reduces handling time by up to 85%

Recently developments of the Pomini Inspektor defect measurement system have allowed improved resolution in the defect mapping processes, which are key parts of the roll dressing logic system. At the same time the performance, size and speed of today's digital systems has increased the capability and reliability of the data management systems. One outcome of this is the ability of most recent systems to detect and respond to smaller defects. These cracks, which may actually develop during, or be uncovered by the grinding process itself, went undetected in the past.

AUTOMATIC ROLL HANDLING

A multi-purpose roll handling cassette system was developed to both increase operator safety, and to reduce manpower costs.

With the new Dofasco/Pomini roll management system the rolls are not handled one by one, but instead are grouped in cassettes holding up to six rolls. This system can reduce roll-handling time by 85%. The duty cycle on the overhead building crane is reduced by a factor of six, and interference between the crane and the roll loader becomes insignificant.

For a relatively small steel plant, it is not practical to separate and stream products in separate facilities. Fast and flexible are valuable features of the manufacturing organisation and equipment. Dofasco roll grinders must switch quickly and service several different rolling mills. The need for fast and frequent changeovers between the several roll types meant that new concepts in equipment design had to be developed for this project.

Dedicated cassettes were designed for each roll type. Rolls are transported between the mill and the roll grinder in their cassettes (**Fig 6**).

When the cassette is positioned in the roll loader, a system of detectors confirms the identity of the roll type to the roll management system.

The use of an automatic loader, fully integrated with the roll grinder, can dramatically reduce the roll loading and unloading time, and at the same time reduce the chances of handling damage. Impacts obviously can damage the rolls, but more important are the effects on the grinding machine. They not only upset the current alignment of the machine, but do incremental damage to the precision of the roll grinder components.

Multi level storage systems minimise total lifetime costs, and optimise the use of space. This is of value in both existing shops, where space is fixed and limited, and in new facilities where building costs often match the capital cost of the new equipment to be installed inside them.

The main advantage of an automatic loader integrated with the grinding machine control system is the ability to automatically organise the work sequence. In this way, starting from a programmed schedule, the integrated loader system moves the rolls and transfers the corresponding set-up and grinding data sets to and from the grinder. At the end of the grinding cycle the roll grinder requests the loader to change the roll.

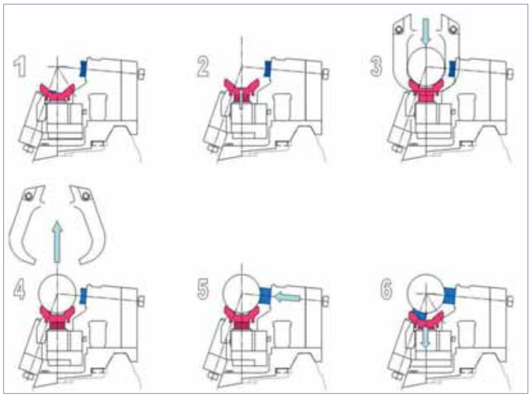
There is also the potential for the integrated system to re-match, or to re-mate work roll pairs based on the actual grinding losses. Many mills have a tight limit on the difference in diameter between the two rolls in a work roll set. There are three cases to consider:

First is the nominal case where no matching activity is required. In this case the diameter loss in both rolls maintains the matching tolerance between the two rolls.

In the second situation, the first roll of the pair is ground and sustains a diameter loss larger than expected. In this case, the mate (second roll of the pair) must have good (ie excess) material removed to keep the diameters within tolerance.

In the third case, it is the second roll that has excess loss, and the first roll of the set has to be re-loaded into the grinder to remove good material to match diameters. Time money and material are wasted by this process.

If the automation system has data on the entire roll inventory, then it is not difficult to envision a system that would automatically re-assign roll pairings to minimise total material losses.



7 Patented automatic roll neck rest to aid positioning of roll in grinder

At the cold mill roll shop each roll type requires that automation drives the loader and machine components to accurately reconfigure to a new pre-programmed geometry. The loader picks up a roll from the selected cassette; recognising its type the loader then instructs the machine to translate the neck rests and tailstock to match the selected roll. The CNC-controlled loader positions the roll over the machine and lowers it onto the roll positioners attached to the side of the Pomini patented steady rests. The bearing shoes, controlled by pneumatic motors, move to just touch the roll necks. Next the bearing shoes are clamped to hold the roll in place, then the roll positioning system retracts and the roll remains properly positioned on the neck rests in line with the machine axis. The last step in the loading process has the loader releasing the roll, leaving the grinder area, and preparing for the next series of moves (**Fig 7**).

Another challenge in grinding economically is the wide variety of rolls for the roll driving system. It has to match variations both in the position, and in the dimensions of the driving flats. To do this effectively Techint-Pomini developed and patented a new driving system which automatically matches the flats. The available configurations of interchangeable plates enable effective connection to a wide range of different drive designs.

HOW MUCH TO REMOVE?

There are several reasons to search for a comprehensive system to automatically answer the question 'How much should be ground from this roll?' Today leaving this decision to the experience of an operator is not practical. Up until the late 1980s roll and wheel technologies had lifetimes that evolved slowly over decades. The materials would evolve slowly; and operator feel and experience on manually controlled machines was a practical way to keep up with the incremental changes. Today's automatic grinders, and fast changing roll and wheel materials mean that the adjusting and compensating processes must also be automatic.

The optimal grinding programme for a particular roll depends not only on the basic roll properties, but also on the specific history of the roll. For example:

- Minor damage may be in the roll after the previous grinding operation;
- The roll may have been subjected to a strip break in the mill;
- The rolling campaign itself varies in time and severity.

Standard rules can be applied to the roll based on a combination of its rolling history and on the data collection during grinding. It is not practical for today's operators to make these decisions. Once again the two basic aims are: to reduce to a minimum the total material removed, without compromising safety, which remains the first priority, and to use human intervention only in extreme circumstances.

The first requirement is the collection of a comprehensive set of grinding data for each roll. The roll data is first assembled in a local database for immediate use, and transferred to a central location for subsequent use by the supervisory systems. Working programmes are stored on a database; where they can be easily edited, modified and downloaded to all the grinders in the shop.

This gathered data and associated experience led to further automation of the grinding operation. The Crack Management System is a recent development by Dofasco and Pomini. It is based on the Dofasco patented Roll Management Process. This system is being developed to make fully automatic decisions on how to grind a roll, based on the measured defects the automatic defect classification (thermal/mechanical), the applicable threshold (based on gathered experience), the history of the roll and its use in the mill. This system will enable consistent roll performance with improvements in roll costs, safety and mill performance.

OTHER STEPS FORWARD

In the last decade, there have been major steps forward in technology, coupled with an increasing awareness of quality. Major steps forward in internal processes for machine manufacturers has led to improved quality of the machines and surrounding systems, as documented by ISO 9001 ISO 14001 (environment) and ISO 18001 (safety).

The maintainability of the machines has been greatly improved, new software now advises operators when maintenance operations are required. This is similar to modern cars telling the drivers when they need to bring the car in for service.

Remote service is another area where technology has made big steps forward. It is now possible to connect directly to grinding machines on the other side of the world. High speed internet connections are used to drive the machine or diagnose the problems quickly, and even see how the machine is working through the use of a wireless camera, Similarly, operator training can be delivered via web-conferences with live video to explain how to change a board, to use an application or to repair mechanical damage.

Modern roll grinding machine manufacturers, such as Pomini, are also offering complete Roll Shop Management Systems to keep track of location and use of all the rolls, chocks, bearings, wheels and other items critical in the roll shop. These systems are coupled with production data from mill computer systems, so that, for example, it is possible to automatically calculate how much steel is produced per millimetre of roll wear, or to study the total history of a specific roll or chock.

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Packaging recycling in Eastern Europe

Around 60% of all steel packaging put on the European market was recycled in 2004. But in Central and Eastern Europe, according to the level of collection infrastructure in place, recycling performances ranged from 11% (metals) in Lithuania to 43% (steel) in Hungary. The best progression in metal packaging recycling was registered in the Czech Republic (37% vs 29% the year before).

At a seminar organised by APEAL, the Association of European producers of Steel for Packaging, 35 experts including steel and can manufacturers, brand owners and local packaging recovery organisations discussed the economics and performance of steel packaging recycling and shared experience on best practice in collection and consumer education. The seminar was organised in the context of the ongoing build up of packaging collection schemes initiated ten years ago in Eastern and Central Europe in order to meet the objectives introduced by the Packaging and Packaging Waste Directive. Experts including Désirée Guissard, a packaging consultant with more than 15 years experience and Christian Pürschel, Public Affairs and Recycling Manager from Rasselstein, discussed the pro's and con's of the different systems and the cost drivers and calculations for packaging collection schemes in Europe.

APEAL seminar launches ongoing cooperation In this context, the European Steel industry has made a concrete commitment to developing steel packaging markets in Eastern & Central Europe and offered cooperation to packaging recovery organisations in optimising steel packaging recovery schemes.

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The first iron works in Canada

By Fathi Habashi*

The Province of Québec is considered to be the birthplace of chemical education and metallurgy in Canada. It has its origin when Jacques Cartier landed in 1534 in Gaspé in what is known today as the Province of Québec, to take possession of the land in the name of the King of France, François I. This new empire ended in 1760 when the British defeated the French and took over the colony.

The only metallurgical operation in New France – and the first in Canada – was the Forges Saint-Maurice situated on the bank of Saint Maurice River near Trois-Rivières which is located half way between Québec City and Montréal. Saint-Maurice River is one of the largest tributaries of Saint-Lawrence River

The story of the Forges dates back to 1667 when iron ore was discovered in the neighbourhood of Trois Rivières. It was investigated by an engineer named Monsieur de la Pontardière at the request of the Intendant (colony manager) Jean Talon. Although he reported favourably, nothing was done because, at that time, the colony was under the control of the West India Company which was mainly interested in the fur trade. In 1675 the charter of the West India Company was surrendered and, in 1730, the French Canadian army doctor Michel Sarrazin examined the deposits.

The first attempt at iron production in Saint Maurice was in 1733 by François Poulin de Francheville (1692-1733), a rich French merchant from Montreal who sent three smiths to New England to collect information for building a forge. Because of the limited funds available to him he was forced to build a low furnace. This was fuelled by charcoal and blown by small bellows. The temperature was not enough to melt the iron produced and thus a bloom of wrought iron mixed with slag, was obtained. This was removed from the furnace and hammered while hot to squeeze away the slag and obtain a nearly carbon-free iron. This wrought iron was malleable and could be shaped but the iron bars produced at Saint Maurice were of low quality. The operation was short-lived as de Francheville died suddenly at the end of the first year of production. Two years later, his widow hired Pierre-François Olivier de Vézin, an iron master from France to operate the Forges.

When the new company was formed in 1736, more funds were made available by the French monarch as a subsidy and a more modern process was used. A taller furnace was constructed and larger bellows used so that the temperature in the furnace was sufficient to obtain molten iron. The furnace was 9.1m high, with an internal diameter at the hearth of 0.76m and, at the boshes, 2.1m and at the throat, 1m. The air blast was supplied through two tuyeres while a waterwheel operated the bellows. Each charge consisted of 270kg ore, 20kg limestone and 16 French bushels of charcoal (the French bushel weighed 1 kg more than the English). About 3t of ore and 1t of charcoal were required to make 1t of iron.

The iron ore in the Three Rivers District was a sedimentary deposit known as bog ore, a hydrated iron oxide or, more exactly, an oxyhydroxide FeOOH (a limonite). It was a yellow porous material that contained about 70% Fe_2O_3, 4% SiO_2, 2% Al_2O_3, 1.8% P_2O_5, and 20% loss on ignition. A sample of the iron produced was analysed later by Thomas Sterry Hunt (1826-1892), and showed about 0.03%S, 0.5% P_2O_5, 0.9% SiO_2, 1.2% Mn, and about 3% total C. To obtain a malleable product, the cast iron had to be melted again in an air stream in a finery to oxidise its carbon content. Most of the product, however, was used as cast iron. Daily production averaged 4t.

In 1741, the company went bankrupt and, as the King of France was the only financial backer, the Forges became the property of the crown. Despite the bankruptcy, the company continued to produce. War with England was a constant threat and so, for the next 20 years, production was concentrated on military equipment such as cannon and cannon balls.

In 1743, the Forges passed to the Royal domain and operations carried on for several years in the name of King Louis XV. Besides other extensive repairs, a Walloon hearth was built. Over 180 men were employed at that time, increasing to 300 in 1815. The Forges played an important role in supplying military material such as cannons and cannon balls for the King's army, as well as for manufacturing large kettles for the potash industry, kettles for evaporating maple tree syrup, stoves and, in later years, railway wheels.

With the conquest of New France in 1760, the Forge passed with other Royal properties to the British Government and was operated under military authorities. In 1767, it passed into the hands of a private company until, in 1845, owing to the dissatisfaction of settlers in the neighbourhood, the Forges was sold at public auction. In 1883, operations ceased since other furnaces had been erected in 1860 at Radnor, not far from the St Maurice Forge, where ore and fuel could be more easily obtained. As a matter of historical interest, the Forges cast shot and shell for the Americans during their siege of Québec in 1775.

The Forges operated for about a century and half. In 1973, the Government of Québec transferred administration of the site to the Federal Government so that it could be developed as a national historic park for Canada's first metallurgical operation. Immediately thereafter, archaeologists excavated the deserted region. The artefacts they unearthed were cleaned and prepared for use in interpreting the history of the Forges. A blast furnace model (complete with water wheel and air bellows operated by a water current) has been constructed to explain to visitors how iron was produced two hundred years ago.

It is now a remarkable tourist attraction. The park Forges Saint-Maurice is an intriguing spot for visits by laymen and professionals alike. It was recognised by ASM International in 1978 as a Historical Landmark and by the Canadian Institute of Mining, Metallurgy, and Petroleum in 1996 as a Canadian Industrial Heritage Landmark. On the occasion of its 250th anniversary the Royal Mint in Ottawa issued a silver dollar in 1988 and Post Canada issued a commemorative stamp. In 1998, a comprehensive fully illustrated volume was published by Laval University Press. **STI**

OPENING

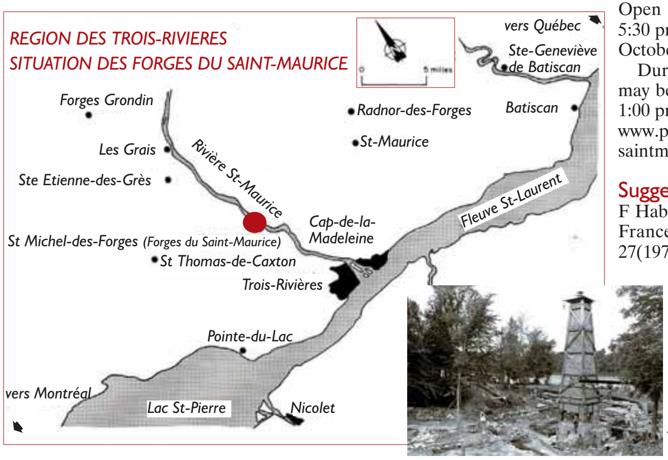
Open 2006 May 13 to October 9, 9:30 am to 5:30 pm daily (until 4:30 pm in September and October).

During the off season, site administrators may be reached from 08.00 to 12.00 and from 1:00 pm to 4:30 pm from Monday to Friday.
www.pc.gc.ca/lhn-nhs/qc/saintmaurice/index_e.asp

Suggested reading

F Habashi, 'Chemistry and Metallurgy in New France', Chemistry in Canada 27(5), 25-27(1975)

R Samson, The Forges du Saint-Maurice. Beginnings of the Iron and Steel Industry in Canada 1730-1883, Les Presses de l'Université Laval, 500 pages, Quebec City, Canada 1998. (The book is available in French and English).



A view of Forges Saint-Maurice in the 1970s and its location on the map

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Sequestration of CO_2 from Steelmaking Offgas by Carbonate Formation with Slag

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Key Words: Steelmaking Slag, Offgas, Carbon Dioxide, Sequestration, Phase Stability, Reaction Kinetics

INTRODUCTION

The alkaline earth-containing phases in steelmaking slag can form carbonates thus sequestering carbon dioxide from the surrounding atmosphere. Work has been undertaken to improve the carbonate formation kinetics, enabling steelmakers to directly remove CO_2 from furnace offgas with slag, which in turn reduces the slag stabilization time. A study of basic oxygen furnace (BOF) and electric arc furnace (EAF) slags is reported in conjunction with their carbonate formation thermodynamics and capacities, yielding an overall slag CO_2 capture potential. Preliminary results are presented from bench-top "wet" and "dry" slag carbonation tests on industrial slags using a slurry reactor and large-scale thermogravimetric analysis (TGA).

CO_2 EMISSIONS IN STEELMAKING

In response to political demands, carbon dioxide has been targeted as a key industrial emission requiring regulation and control. As a key industrial sector relying on carbonaceous material for operation, the steel industry worldwide will be affected by these regulations. The regulation of carbon dioxide as an emission in the steel industry must be based on an understanding of the sources, amounts, and variations of the generation of this gas. Control methods can be put in place to target specific sources and sized to handle the amounts and variations involved. Carbon dioxide can be generated directly through iron or steel processes (blast furnace or BOF), or through indirect means (coke ovens or coal burning power plants providing electricity to EAF). Each of these sources requires a specific means for regulation and control, which also must be viewed in relation to the entire steelmaking route. A comparison of CO_2 emissions based on geographic regions and steelmaking technologies can be made from published data.

Stubbles provides trends of U.S. domestic steel industry energy use and CO_2 emissions.[1] Technological evolution has reduced the required energy per ton of steel from 47.4 GJ (45 million BTU) in 1950 to 17.9 GJ (17 million BTU) in 2000. Carbon dioxide emissions, stated in terms of carbon equivalent (CE) units (0.27 x tons CO_2), have only been tracked since 1990, but they exhibit a similar trend to the reduction in energy use. Integrated mills produce more CO_2 than mini-mills because of their reliance on coke making and blast furnace ironmaking. In the year 2000, integrated mills produced 33.46 million tons of CO_2 (CE units), of which 64% (21.47 million tons) came from the production and use of coke. Mini-mills produced 13.65 million tons of CO_2 (CE units), of which 80% (10.86 million tons) came from electrical production at the power plant. On average the U.S. steel industry produced 0.42 carbon equivalent tons of CO_2 per ton of steel shipped in 2000.

Carbon dioxide emission data from the steel industries of several other countries are available from the literature. Afonin provides data for the steelmaking sector in Russia.[2] Based on 1998 data, the total CO_2 emissions from integrated steelmaking stands at 48.6 million tons carbon equivalent, which is 8.5% of all Russian CO_2 emissions. On an intensity basis, this equals 1.4 tons CE per ton of steel produced. Data from Birat et al. show that in 1989 the French integrated-steel industry produced a total of 26.3 million metric tons of

CO_2 total at an intensity of 0.42 tons CE per ton steel.[3-6] This is comparable to the U.S. emission rates of 2000. By 1994, the CO_2 intensity had dropped in France to 0.40 tons CE per ton steel, which is approaching the theoretical limit. France reported an extremely low CO_2 emission rate of 0.03 tons CO_2 per ton of steel for EAF steelmaking with 100% scrap, due to their high reliance on nuclear power. Holappa reports data from Finnish ironmaking that can be used to estimate the carbon dioxide intensity for that region, which is approximately 0.53 tons CE per ton of steel for integrated steelmaking.[7] Data from Emi and Gielen show that the 2005 carbon intensity rate for Japanese integrated steelmaking is 0.46 tons CE per ton of steel.[8,9]

Anderson et al. reported the results of a study comparing the carbon dioxide emissions and energy requirements for 30 different steelmaking routes.[10] To the BF/BOF baseline of 89% hot metal/11% scrap, they have compared EAF steelmaking using standard and alternative iron sources/steelmaking routes at 80%, 50%, and 30% replacement of scrap. The carbon dioxide emission data from this publication in 2002 for a U.S. basis are shown in Figure 1. The highest CO_2 producer is the traditional BF-BOF route at 519 kg CE per ton of liquid steel. The lowest CO_2 producer is 100% scrap in an EAF at 119 kg CE per ton of liquid steel (CE/t LS). All other processes fall between these boundaries. As the amount of scrap blending is increased, the carbon dioxide production decreases. Comparison of data from Goodfellow et al. on 100% scrap in an EAF shows that the indirect sources produce almost 70% of the CO_2 generated, with the largest fraction from electricity generation.[11,12] These authors showed that U.S. EAF production with 100% scrap produces 140 kg CE/t LS (compared with 119 kg CE from Anderson[10]) due to the high fraction of electricity supplied from hydrocarbon combustion sources (69%). However, on the same basis, Canadian EAF's generate 89 kg CE due to the lower fraction of electrical supply from hydrocarbon fuel (32%), and French EAF's generate 46 kg CE due to an even lower reliance on hydrocarbon-based fuels (5%).

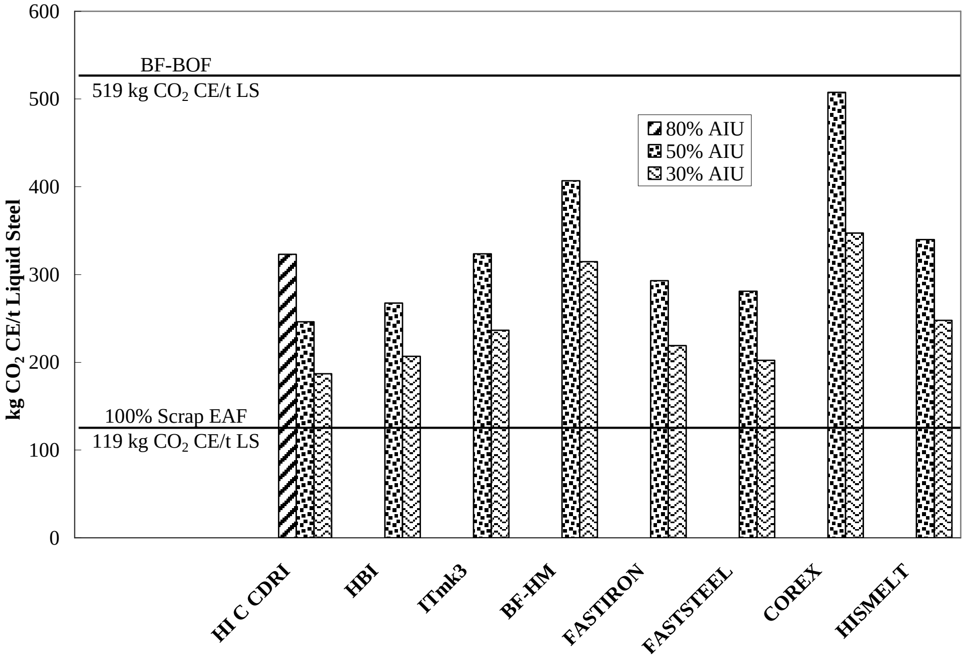

Figure 1 CO_2 emission amount (carbon equivalent tons per ton of liquid steel) for EAF steelmaking with 30%, 50%, and 80% addition of alternative iron units (AIU) to scrap, data from Anderson 2002[10]

The composition of steelmaking offgas changes during the stages of the steelmaking heat, such as charging, blowing, refining, and tapping. Knowledge of composition variation is necessary for feedback control and mitigation technologies. Evenson et al. reported on an expert system relying on feedback control from offgas analysis in EAF operations.[13] Sampling probes installed at the entrance to the fixed duct after the combustion gap and at the end of the water-cooled duct downstream of the combustion chamber provide real time composition analysis. For an average of 30 heats, the concentration averages upstream and downstream, respectively, were 22.7±2.4% and 10.3±1% for CO_2, 21±2.5% and 0±0% for CO, 0.6±0.5% and 11.3±0.7% for O_2, and 8.1±1.2% and N/A for H_2. This data is reported for an upstream flow rate of 15900 Nm^3/hr (9358 SCFM) and a downstream flow rate of 68400 Nm^3/hr (40259 SCFM), yielding a dilution flow ratio of 4.3. Grant reports EAF offgas data from a U.S.-based shop (location not specified) in his work with post-combustion optimization.[14] The offgas composition profile at the inlet of the fixed duct just after the combustion gap (same upstream location as Evenson et al.) for a period of 15 heats shows that the CO_2 average is a little lower (~15%), the CO average is similar (~18%), the O_2 value is higher (~4%), and the H_2 average is similar (~6%). The high downstream O_2 value shows less combustion of the CO.

The current project has worked to establish an understanding of the CO_2 concentration in offgas for the design and placement of a sequestration system. The concentrations of CO_2, CO, H_2, and O_2 were measured using a water-cooled probe placed in the offgas ducting just after the combustion gap (pre-combustion) of a northeastern U.S. EAF shop. The data was analyzed for 10 heats, and the concentration of CO_2 in the offgas during the stages of one heat is shown in Figure 2. The carbon dioxide content averaged near zero during charging, as the roof was moved to the side and offgas did not flow through the duct during that time. During the melt, CO_2 concentration averaged 20-25% from the combustion of natural gas in the oxy-fuel burners and other sources of carbon in the charge. The CO_2 concentration reached its highest peak of 30-35% during the oxygen blow from the combustion of dissolved carbon and carbon injected into the slag. The average CO_2 concentration across the entire heat is about 18%, which corresponds well with the values shown by Evenson[13] and Grant.[14] Remarkable consistency was shown for the 10 heats with peak CO_2 concentrations averaging 30-35% and an overall average at 18-20%.

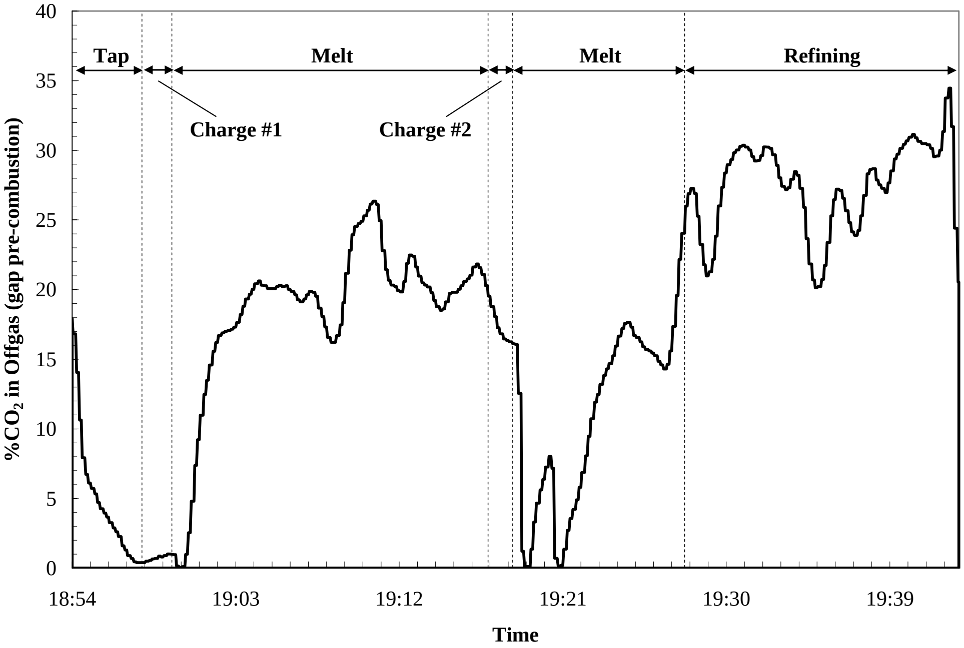

Figure 2 CO_2 concentration (volume %) measured in the offgas collection system at the 4th hole gap prior to combustion during stages of a heat (data from northeastern U.S. EAF shop)

Combining the concentration data in Figure 2 with the temperature profile and operation of the offgas system yields the estimated CO_2 concentration at the discharge point (stack). The fourth-hole combustion zone operates at 1760°C and after dilution the offgas is cooled to 450°C. Based on the heat capacity of air, and assuming full combustion of CO to CO_2, the peak carbon dioxide concentration drops to 14-15% with an average to 6-7%. Further dilution and quenching is required to drop the offgas temperature to 90°C for discharge through the baghouse. The carbon dioxide concentration in the stack discharge is 10-11% peak and 4-5% average. A CO_2 capture and sequestration system will most likely be installed after the baghouse to prevent dust contamination. Therefore, the final discharge values should be used in the design. These values are significantly higher when compared to the CO_2 concentration of 350-370 PPM in ambient air.

Analysis of the steelmaking process shows that energy conservation provides the most cost effective method for reduction of CO_2 emissions. Energy conservation minimizes the direct CO_2 sources (less combustion of carbon) and indirect sources (reduction in electricity). The U.S. has focused on energy reduction as a primary goal, which will, in turn, reduce CO_2 emissions. These reductions will mostly be realized from indirect sources as the U.S. relies heavily on hydrocarbon fuels for electrical generation (69%). In Stubbles' analysis of the history of energy reduction in the U.S. steel industry, he found the drive towards near net shape final products has provided the largest gains. Continuous casting and thin slab casting have reduced energy consumption from 36.9 GJ/t to 21.1 GJ/t (35 million BTU/t to 20 million BTU/t). The move towards strip casting and closure of inefficient facilities should drop the industry amount to 14.8 GJ/t (14 million BTU/t) by 2010.[1] In addition, the data from Anderson et al. clearly shows that steel production from scrap provides the lowest amount of CO_2 emissions and energy requirement.

Alternative iron and steel making technologies will also provide reductions in carbon dioxide emissions, primarily through energy reduction, but also through operational changes. Europe and Japan have undertaken proactive research initiatives for the purpose of reducing carbon dioxide emissions, and in some cases, to develop carbon-free steelmaking. Most of the research involves the use of new technologies to replace or augment the traditional blast furnace ironmaking. Emi lists injection of pulverized coal, plastic, and LNG, as well as increased blast temperatures and decreased moisture, as current technologies to reduce CO_2 emissions by up to 23%

in Japanese iron making.[8] Alternative iron technologies, such as ITmk3® and HIsmelt®, may provide further 20-25% reduction but are still in development. Birat lists several carbon-free technologies being proposed, but they are many years from large-scale commercial development.[7] These technologies include hydrogen reduction and direct electrolytic production of iron. Both technologies require a source of electricity that is not hydrocarbon-based, in order to provide a net reduction in CO_2 emissions. In all cases, recycling is being researched as the most powerful method of reducing CO_2 emissions for the material community as a whole. This includes use of the steel scrap in the EAF and use of the slag to offset the limestone used in cement production.

Sequestration technologies provide direct reduction in CO_2 emissions and will be effective at specific source point mitigation where further energy or technological changes cannot be made. At the present time, most sequestration technologies provide a negative cost impact to the steel producer. If CO_2 regulations develop to the point where emission credits are bought and sold, then the cost-benefit of installing a sequestration technology versus paying an emission penalty will be weighed. The current research project seeks to develop a cost-effective sequestration technology using slag, which is available in plentiful amounts at the steel plants, to permanently sequester carbon dioxide. A side benefit is that the formation of carbonates in slag will render the slag immune to in-situ swelling or leaching, thus stabilizing it for immediate commercial use.

SLAG CHARACTERIZATION

The potential of steelmaking slag to react with CO_2 to form permanent carbonate minerals (sequestration) is derived from slag's high concentration of alkaline earth metal oxides. Two alkaline earth metal oxides in sufficient quantity to possibly sequester CO_2 are CaO and MgO. These oxides report to the slag from the fluxing agents used during steelmaking, which are primarily standard and dolomitic lime or limestone. Table 1 shows the composition of nine slags surveyed in this project. A total of six sites are represented (A1, B1, C1, D1, E1, and E2), with multiple EAF slag samples taken at some sites. In addition, at site A1 an LMF sample was taken for comparison.

Table 1 Composition of nine steelmaking slags surveyed in this project

	A1α	**A1β**	**A1γ**	**B1α**	**C1α**	**D1α**	**D1β**	**E1α**	**E2α**	**Avg.***
Type	EAF	EAF	(LMF)	BOF	BOF	EAF	EAF	EAF	EAF	-
CaO	27.34	31.22	47.02	40.90	40.53	33.02	34.49	31.91	35.86	34.41
SiO_2	14.84	13.86	6.07	12.89	10.42	12.43	15.08	17.32	9.93	13.35
FeO	30.05	24.96	5.02	21.72	21.65	27.93	25.76	20.20	27.98	25.03
MgO	10.55	11.61	10.03	11.98	13.81	10.98	11.76	12.85	10.13	11.71
Al_2O_3	7.02	8.61	26.55	5.22	6.65	8.74	5.56	6.79	9.22	7.23
MnO	6.51	6.07	1.04	4.67	4.50	3.98	4.85	7.07	4.29	5.24
TiO_2	0.39	0.42	0.41	0.68	0.47	0.50	0.55	0.49	0.49	0.50
ZrO_2	<0.01	0.03	0.20	0.08	0.28	<0.01	<0.01	0.16	0.02	0.08
Cr_2O_3	2.48	1.98	0.25	0.31	0.42	0.87	0.78	1.62	0.95	1.18
K_2O	0.05	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
Na_2O	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.10
S	0.16	0.27	1.35	0.12	0.11	0.21	0.08	0.22	0.30	0.18
P	0.16	0.16	0.02	0.42	0.45	0.25	0.32	0.18	0.28	0.28
C	0.11	0.26	0.38	0.67	0.40	0.22	<0.1	0.32	<0.1	0.27
Sr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
F	0.33	0.54	1.66	0.33	0.33	0.87	0.75	0.86	0.55	0.57

* The average of all slags except A1γ, which is from the LMF at an EAF mill.

The sequestration potential of a slag can be determined from the formation reactions with carbon dioxide at ambient conditions (1 atm, 25°C). Both CaO and MgO exhibit a negative ΔG°_f in the reaction with CO_2, and thus they readily form carbonates. The other major phases (SiO_2, FeO/Fe_2O_3, Al_2O_3, and MnO) are inert to spontaneous reactions with carbon dioxide, and thus they are precluded from the sequestration potential. Both K_2O and Na_2O will readily form carbonates, but neither is present in sufficient quantities to be significant. Both CaO and MgO react with CO_2 in a 1:1 molar combination to form $CaCO_3$ and $MgCO_3$, respectively. On a weight basis, 1000 kg of CaO will capture 785 kg of CO_2, which can be expressed as 214 kg CE units. Using the same basis, 1000 kg of MgO will capture 1092 kg of CO_2, or 298 kg CE units. Using the average values for CaO and MgO of 34.41% and 11.71%, respectively, from Table 1, 1000 kg of steelmaking slag has the potential to sequester 398 kg of CO_2, or 109 kg CE units. The National Slag Association estimates that per metric ton of steel produced, BOF operations generate 75-150 kilograms of slag, while EAF operations generate less at 65-80 kilograms.[15] Combining this with the carbon emission values from Anderson et al. of 519 kg CE/t LS for BF-BOF steelmaking and 119 kg CE/t LS for 100% scrap EAF will yield the overall effective yield potential. At these values, the slag produced per ton of liquid steel can sequester 2.4% of BF-BOF and 3.3% of EAF carbon dioxide emissions. Segregating the slag types in Table 1 (EAF or BOF) and using the average values for their respective processes yields an average carbon equivalent sequestration potential of 2.7% for BF-BOF and 3.2% for EAF.

The above estimates are based on full conversion to carbonate at ambient temperature and pressure, assuming pure CaO and MgO in the slag reacting with an atmosphere carbon dioxide at unity partial pressure (P_{CO2}=1). These estimates represent the thermodynamic potential. A system designed for reacting slag with offgas CO_2 will deviate from most all of these assumptions. The offgas stack temperature for the data in Figure 2 is 90°C, but in some plants this may increase to 150°C. The total gas pressure will be at ambient conditions (1 atm.), but the partial pressure of CO_2 will be in the range of 4-11% (P_{CO2}=0.04-0.11 atm). Steelmaking slag contains only a few percent of free lime or magnesia, and thus these compounds cannot be considered in the pure state. Predominately the CaO and MgO will form silicate, aluminate, or ferrite phases. The results of XRF analysis showed that the slags listed in Table 2 contain dicalcium silicate and larnite (Ca_2SiO_4), akermanite ($Ca_2MgSi_2O_7$), C_5MS_3 ($Ca_5MgSi_3O_{12}$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), magnesio-wustite ($MgFeO_2$), hatrurite (Ca_3SiO_5), periclase (MgO), and lime (CaO). Small amounts of free alumina, wustite, and silica have been found, but these do not contribute to carbon dioxide sequestration.

The ability of specific phases in steelmaking slag to sequester carbon dioxide into stable carbonates under non-ideal conditions can be expressed in the phase stability diagram shown in Figure 3. Each line shown, generated from data in FactSage™ 5.4, represents the reaction of a slag phase to form a carbonate versus temperature and equilibrium partial pressure of carbon dioxide (P_{CO2}). For example, the bottom line labeled “CaO” represents the reaction $CaO+CO_2 \rightarrow CaCO_3$. The top line similarly represents the reaction $MgSiO_3+CO_2 \rightarrow MgCO_3+SiO_2$. Above each line the carbonate is stable (i.e., reaction proceeds to the right), and correspondingly below each line the oxide is stable (i.e., reaction proceeds to the left). As the temperature increases (right to left), the carbonate stability region for each phase shrinks. Therefore at high temperature the carbonates will decompose to form oxides. The concentration of CO_2 in the atmosphere surrounding the slag also affects the carbonate stability. As P_{CO2} increases, the carbonate becomes more stable, thus requiring a higher temperature to calcine the material. For example, magnesite ($MgCO_3$) decomposes to magnesia (MgO) at 210°C in ambient air (P_{CO2}=350 PPM), but if it is placed in a pure CO_2 atmosphere (P_{CO2}=1) , then it does not decompose until 389°C.

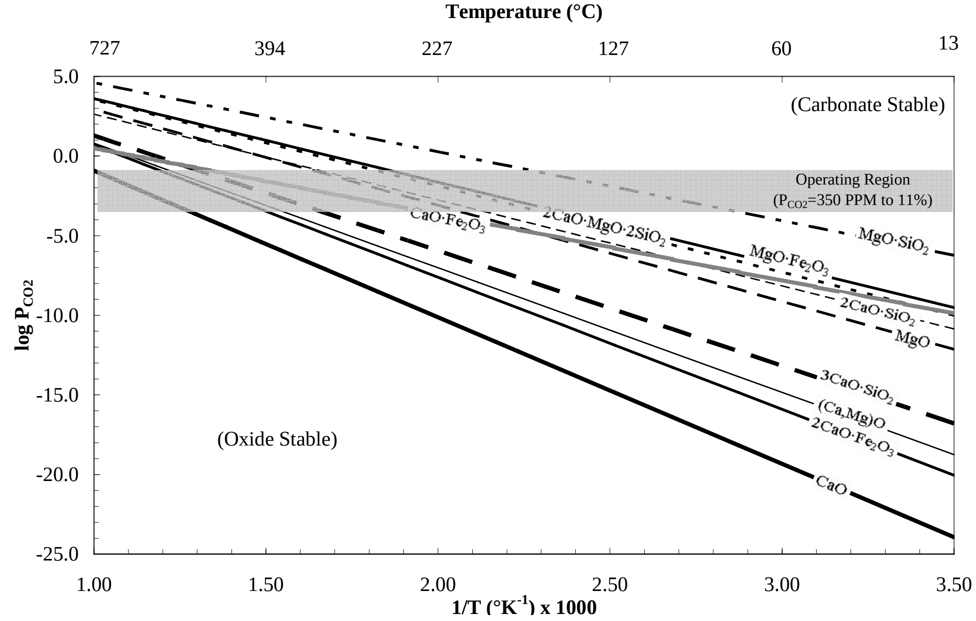

Figure 3 Carbonate stability diagram for alkaline earth metal oxide phases found in steelmaking slag (data generated from FactSage™ 5.4)

The sequestration of carbon dioxide by slag operates opposite to calcining. When calcining limestone, carbon dioxide is driven off in the clinker by the application of heat. To capture CO_2 in lime or in other slag phases, lower temperatures provide more favorable thermodynamic stability. At ambient conditions (25°C, P_{CO2}=350 PPM), all phases listed in Figure 3 are stable as carbonates, and thus the slag will spontaneously react to sequester CO_2. However, the major hurdle to the realization of slag sequestration is that the reaction kinetics are extremely slow. Some states require steelmaking slag to stabilize in stockpiles for three to six months prior to use.[16,17] The limiting rate step in slag carbonation is the diffusion of the CO_2 into the slag particles. The CO_2 diffusion rate can be improved by increasing the reaction temperature. However, an upper boundary is set by the phase stability of carbonate formation. The gray shaded region in Figure 3 shows the P_{CO2} operating region exhibited by the stack offgas, as calculated from Figure 2 data. The lower limit is 350 PPM, which is the approximate ambient CO_2 concentration. The upper limit is 11%, with an average of 4%. As P_{CO2} increases, the allowable reaction temperature for carbonate formation also increases. Thus, considering a slag containing clinoenstatite ($MgSiO_3$), under ambient CO_2 concentration, the carbonate formation reaction can proceed up to 74°C. However, exposing slag to offgas at 11% carbon dioxide increases the allowable reaction temperature to 168°C. An analysis of the slag phases is critical to the sequestration system design to determine the maximum allowable temperature to allow carbonate formation while enhancing reaction kinetics.

The objective of the current project is to develop and demonstrate a process for sequestering CO_2 from steelmaking offgas by forming carbonates with the alkaline earth oxide-containing phases in slag. To achieve this result, the process kinetics of the carbonate formation reaction must be improved to allow the design of a commercially feasible reactor. This reactor will contact stack exhaust gas with fresh or minimally processed slag allowing rapid sequestration of the CO_2 and stabilization of the slag.

CARBONATE FORMATION IN STEELMAKING SLAG

Two different reactor design bases ("wet" and "dry") are proposed for contacting slag and offgas. The first basis ("dry") is a solid-gas contactor with either a plug flow or rotary design. In this system, the stack offgas would be directed through an atmospheric pressure-rated vessel containing slag particles. Only the sensible heat of the offgas would be used to provide a temperature increase of the system. After sufficient reaction time, the carbonated slag is dumped, and fresh slag is input to repeat the process. To allow continuous operation, a plug flow design would use two parallel contacting vessels, and thus while one is dumping/loading the other is reacting. A rotary design would be similar to a cement clinker, with slag particles flowing countercurrent to the offgas. The other basis ("wet") of design allows for slurry contact, and thus the slag is mixed with water through which the offgas is bubbled. The slurry reactor would require continuous stirring, and thus it could be modeled after a mechanical flotation cell, which allows for intimate gas-solid contact in a water-dispersed system. While a slurry reactor is more complicated for operations, the water addition may be necessary to achieve sufficient reaction kinetics. Both design bases are being investigated in this project through bench-scale testing.

Investigation of the solid-gas contactor design basis is done with a large-scale thermogravimetric analyzer designed for this project. A drawing of the bench-scale TGA is shown in Figure 4. A traditional TGA apparatus is designed to handle samples of just a few grams, but due to the heterogeneous nature of slag, much bigger samples are required. The TGA for this project can handle a gross sample weight of 410g with a resolution of 0.001g. The central chamber is a vertically oriented tube furnace capable of operation to 1100°C. The furnace controller allows a programmable ramp rate (1-100°C/min) and hold time. Samples are suspended in the furnace from a digital balance, which records the sample weight. Samples for gas-solid contact are held in a 304SS mesh basket or by a platinum wire (single particle). Samples for decomposition analysis are placed in an alumina crucible held by a platinum wire. The digital balance is protected from the furnace heat output through a tortuous path barrier, cross flow fan, and reflective radiation shield. The bottom entrance of the tube furnace contains a gas distribution device through which reaction gases are introduced. Up to three gases can be metered individually or in combination. The gases used in this project are Ar, CO_2, N_2, and air. In addition, the introduced gas can be humidified by bubbling through a heated water column. Weight and temperature data are collected to a computer through a portable data acquisition system.

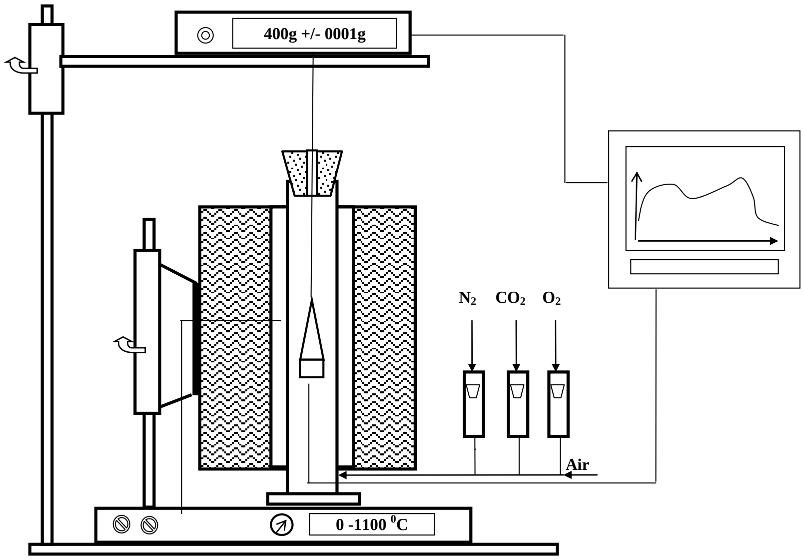

Figure 4 Bench-scale TGA used for slag-CO_2 reaction measurements of gas-solid carbonation kinetics

Baseline testing to determine the effect of temperature and humidity on the carbonation rate was conducted with “Hi-cal” lime obtained from a project sponsor. The “Hi-cal” lime has a composition of 95% CaO, 3% MgO, and 2% SiO_2. Single particles of lime, with an average 1.5 cm equivalent spherical diameter, were suspended into the TGA from a platinum wire holder. The first series of tests were conducted at 200°C, 300°C, 400°C, and 500°C with dry CO_2 (P=1 atm). A second series of tests was conducted at the same temperature points. However, the CO_2 gas was humidified through a bubbling column. In each test, the lime single-particle was suspended in the TGA furnace in an Ar atmosphere while the temperature was ramped to the testing point. Once the temperature reached the desired test point, the particle was held in the Ar atmosphere for one hour. After one hour, the Ar was turned off and the desired CO_2 stream (dry or humidified) was introduced into the furnace chamber. The lime sample was allowed to react with CO_2 for approximately 5.5 hours, after which the Ar stream was reintroduced while the sample cooled to room temperature. A plot of weight change versus time for each sample is shown in Figure 5.

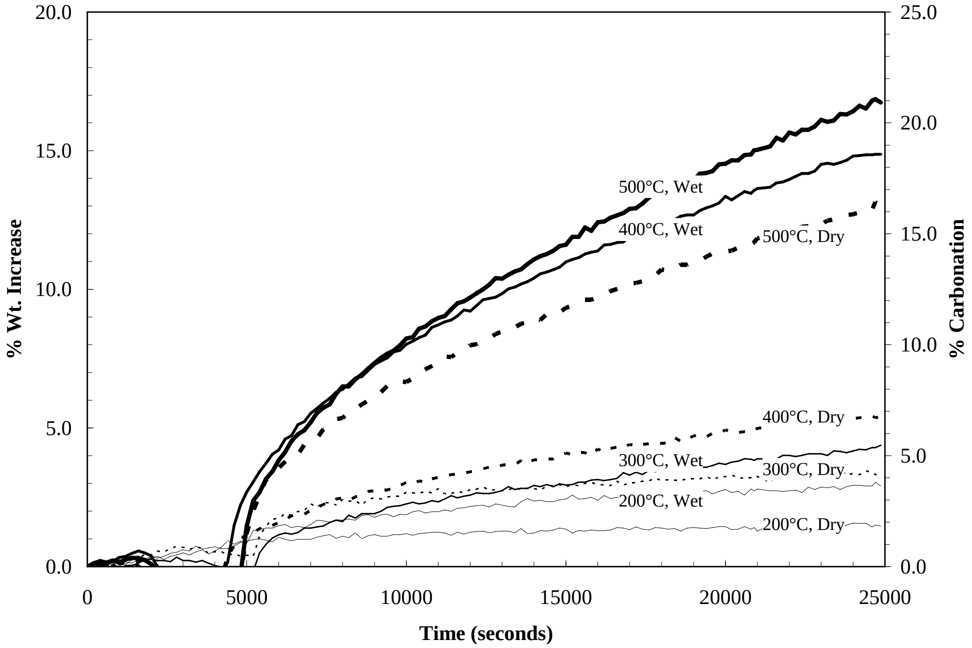

Figure 5 Carbonation rate of Hi-cal lime (95% CaO) in dry and humid CO_2 atmosphere (P_{CO2}=1) at 200°C, 300°C, 400°C, and 500°C

Each dry sample exhibited an increase in weight with time as it was allowed to react with CO_2 at the test temperature. The total weight increase at 200°C in dry CO_2 at 5.5 hours was marginal (~1.25%). This corresponds to 2% carbonation. The percent carbonation is defined as the fraction of lime converted to calcium carbonate (assuming only $CaCO_3$ formed). Increasing the temperature to 300°C and 400°C showed incremental increases up to approximately a five weight percent increase for the latter temperature. A test temperature of 500°C in dry CO_2 showed a significant jump to a 13 weight percent increase, which is equivalent to 16.5% carbonation. Increasing the temperature alone has a significant impact on the reaction kinetics by increasing the diffusion rate of CO_2 into the lime particle.

Humidifying the CO_2 provided as significant of an impact as increasing the reaction temperature. The total weight increase at 200°C in humid CO_2 at 5.5 hours was approximately double (2.5%) of that exhibited with dry CO_2. The weight gain at 300°C in humid CO_2 was higher than that with dry CO_2, but not twice as much. The largest difference occurred in humid CO_2 at 400°C, which showed a weight gain of 15%, which is three times that shown for the dry CO_2 at the same temperature. The highest weight gain of 17% occurred at 500°C in humid CO_2, which corresponds to 21% carbonation of the lime sample. Humidification of the reaction gas has a catalytic effect in dramatically increasing the reaction rate between CO_2 and lime.

The catalytic effect of a humid CO_2 stream in reacting with alkaline earth metal oxide-based solids has been noted by several researchers. Both Lackner et al. and Zevenoven et al. noted in their work with serpentine ($Mg_3Si_2O_5(OH)_4$) that humidity greatly increased the percent conversion to carbonate with all other factors equal.[18,19] Hills et al. also reported in their work the importance of humidifying the CO_2 stream with accelerated carbonation of slag and other cementitious wastes.[20,21] They propose that CO_2 from the air permeates through the solid, which is the diffusion controlled rate-limiting step. The presence of water forms a gel on the lime particle surface into which CO_2 solvates. CO_2 hydrates to H_2CO_3 in the surface gel, which is then ionized to H^+, HCO_3^-, and CO_3^{2-}. The pH in the water drops, thus assisting in the dissolution of the lime. The reaction rate in solution is much faster than between the gas and solid state. In the current project, temperature, humidification, and particle size will be evaluated for their effect on the reaction rate of the industrial slag.

Investigation of the “wet” process, based on a water-solid-gas reactor design, was done with a bench-scale flotation cell using a two-liter chamber with an internally rotated impeller. The rate of the carbonation reaction was studied under intensive mixing as shown in Figure 6. The rate of slag reaction was compared with the rate of “Hi-cal” lime reaction under the same test conditions. For each test, 50g of solid material was crushed and graded to <106μm then mixed with two liters of tap water. Bottled CO_2 was injected into the slurry at a rate of 1459 cm^3/min for a total of two hours (lime only). Periodic slurry samples of 3-5g in size were taken, decanted through vacuum filtration, and then dried in an oven. Oven drying took place at 220°C for one hour, followed by calcium hydrate decomposition at 480°C for two hours and calcium carbonate decomposition at 920°C for two hours. These temperatures were chosen on the basis of thermodynamic equilibrium of the CaO-CO_2-H_2O system as determined by FactSage 5.4. Parallel samples were taken and subjected to analysis in the TGA.

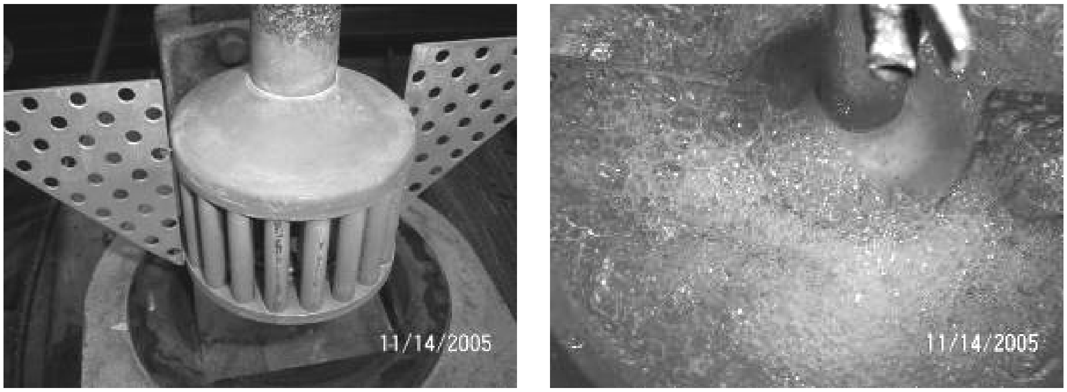

Figure 6 Bench-scale slurry mixer with internally rotated impeller (left) and mixing process with slag-CO_2-water (right)

Three types of materials were tested in the slurry reactor: “Hi-cal” lime, eight of the industrial slags in Table 1, and three synthetic slags produced from reagent grade material in an induction furnace. The compositions of the mixtures used to produce the three synthetic slags are shown in Table 2. The synthetic slag composition was selected to represent a low, medium, and high basicity in slag A, B, and C, respectively. Synthetic slags A and B exhibited a “falling” condition and self-disintegrated into a powder during cooling. This is a result of the β–γ polymorphic transformation of calcium disilicate. Slag C did not exhibit self-disintegration, and thus it was crushed after cooling to produce the same particle size as slags A and B. Each synthetic slag was screened to produce particles <106μm.

Table 2 Mixture composition of synthetic slags used in slurry testing (by weight)

Component	**Slag A**	**Slag B**	**Slag C**
CaO	40%	49%	56%
FeO	15%	15%	15%
SiO_2	26%	20%	15%
MgO	10%	7%	5%
Al_2O_3	5%	5%	5%
MnO	4%	4%	4%

The test results with “Hi-cal” lime are shown in Figure 7. Within the first two minutes, the pH rose from a background level of 5.8 in carbonated tap water to 12 after the addition of lime, indicating a relatively rapid dissolution of CaO and showing the gas-liquid-solid mixing process was very efficient. A sample taken at this time showed 47% carbonation of the lime and full utilization of the CO_2. At six minutes, the pH stayed at 12 and the percent carbonation jumped to 84%. As the lime consumed the CO_2, the pH and CO_2 efficiency began to rapidly drop. By 20 minutes, both the pH and percent carbonation had stabilized, thus very little further CO_2 was consumed causing the CO_2 efficiency to rapidly drop. Samples taken at 120 minutes showed little change in the percent carbonation and pH, indicating the process had essentially reached completion.

A similar procedure was used for the evaluation of the slag carbonation rate in the slurry reactor. However, based on the rapid reaction of lime in this process, testing with the slag materials was conducted for only 60 minutes. As an initial comparison of reactivity between the slags to lime, the change in pH with time is plotted in Figure 8. Slag A1γ (LMF slag) and lime proved to have similar reactivity dropping to just a few percent more than the background pH in five minutes, and reaching the background pH in 30 minutes. Slags D1α, A1α, and A(synthetic), respectively, exhibited decreasing initial pH values, however they all dropped to the same baseline level in 30 minutes. These latter slags are less reactive compared with lime and slag A1γ, showing the CaO/MgO species to be more tightly bound in the slag.

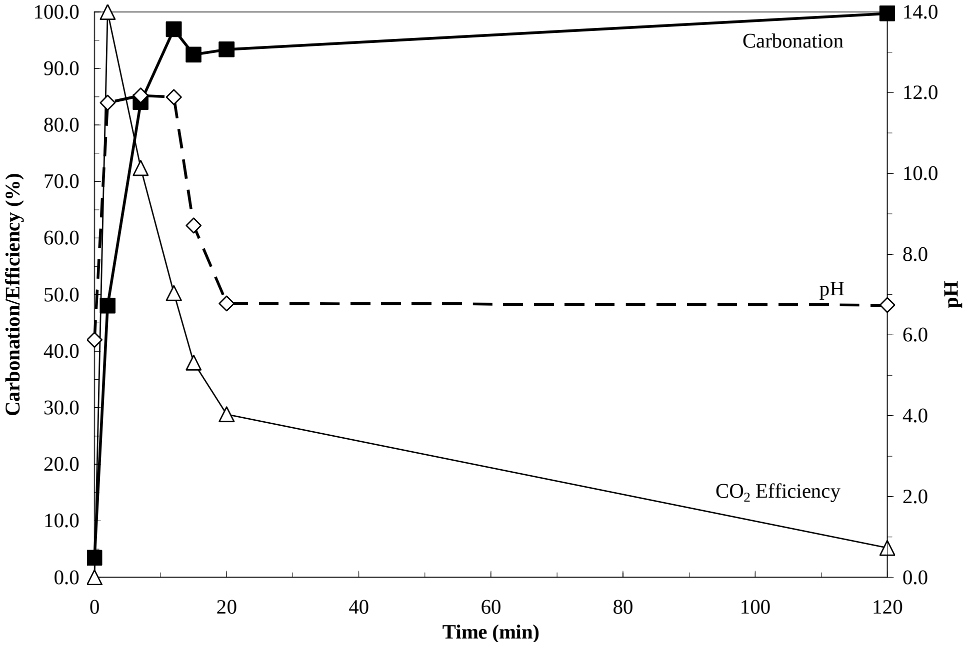

Figure 7 Reaction rate of CO_2 with lime (95% CaO) in gas-liquid-solid slurry reactor process

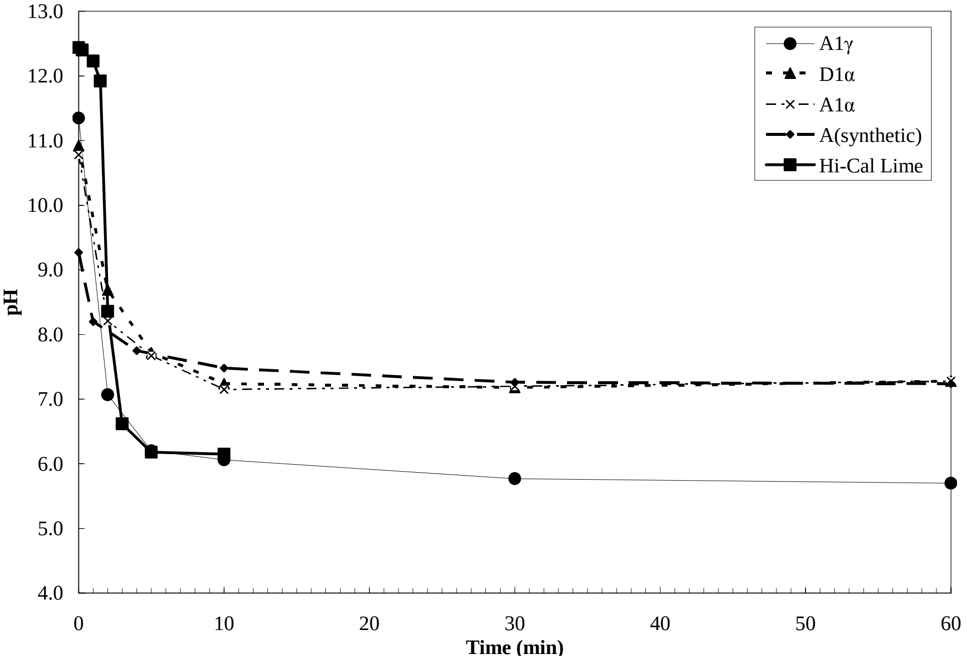

Figure 8 Change of slurry pH with time during reaction of slags and lime with carbon dioxide

The percent carbonation for eight of the steelmaking slags from Table 1 is shown in Figure 9. The results are presented as the percentage of weight loss from calcium carbonate decomposition and as the percent carbonization, calculated in reference to the calcium concentration in each slag sample. The percent carbonation at 60 minutes varied from zero for slag A1α to a high of 57.5% for slag A1γ. Each sample either reached or approached stead-state carbonation within 10 minutes of starting the reaction indicating good efficiency of mixing and contact in the slurry reactor vessel. The lack of further carbonation after five minutes indicates that the slags become passivated in respect to reacting with CO_2 after reaching a steady state. Future analysis will focus on the analysis of the raw and passivated slag samples to determine the change in surface composition and morphology and the corresponding effect on the diffusion of CO_2 into the slag particle.

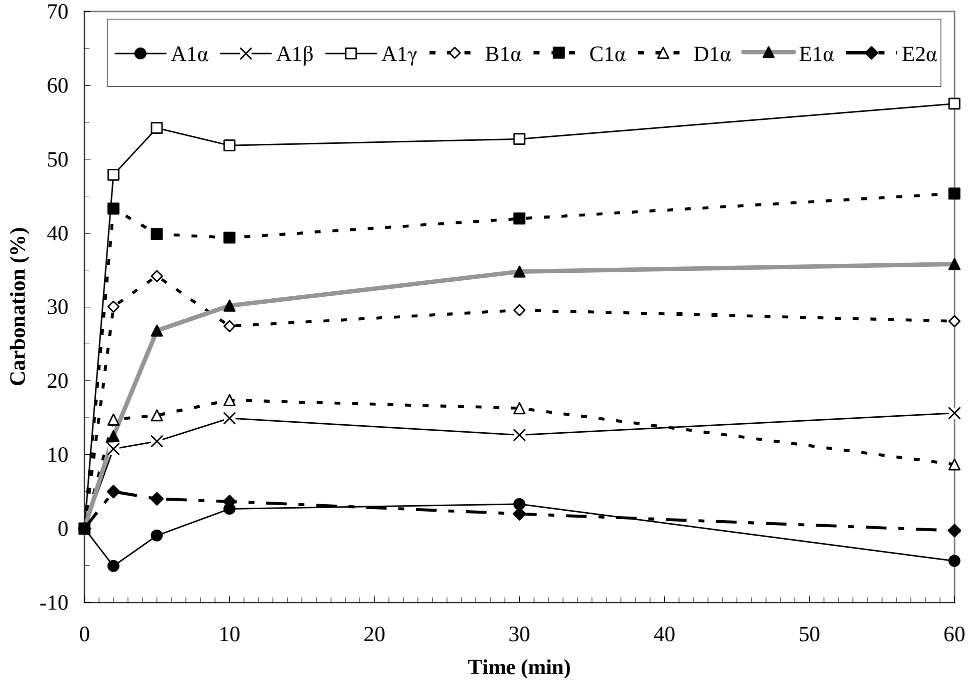

Figure 9 Percent carbonation versus time for eight industrial steelmaking slags in a slag-water-CO_2 slurry reactor

A correlation between the end point carbonation percent from Figure 9 and the amount of CaO in each slag is shown in Figure 10. As expected from the thermodynamic calculations, the amount of CaO is proportional to the slag reactivity to CO_2. Phase determination was not undertaken on the samples to determine the amount of free versus combined CaO (i.e., into silicates or ferrites). Two slag samples (A1α and E1α), however, showed no reactivity to CO_2 in the slurry reactor. Phase characterization of the slags will be undertaken in future work to determine the effect of bulk and surface phase composition on carbonation reactivity.

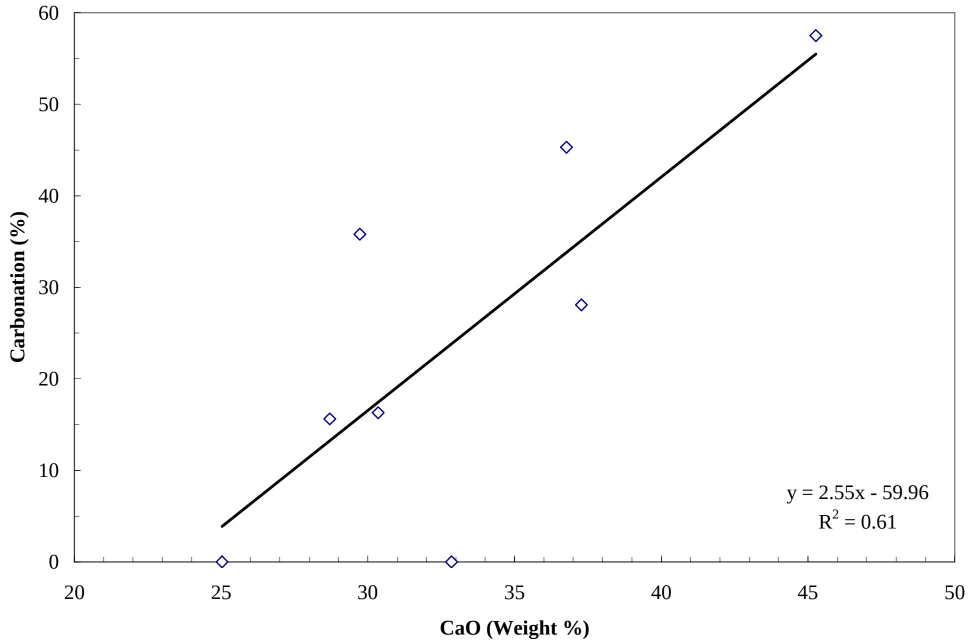

Figure 10 End point carbonation percent from slurry reaction with
CO_2 versus CaO content (weight %) in industrial steelmaking slags

SUMMARY

The results of bench-scale CO_2 sequestration tests by steelmaking slags are presented in this paper. In the “dry” process, the rate of reaction of solid lime or slag increases proportionally to the reactor temperature. However, an upper boundary condition exists, defined by a thermodynamic phase stability diagram, that must be identified for each phase in the slag. Tests results showed that the addition of water vapor (humidification) to the CO_2 gas significantly accelerated the carbonation reaction of pure lime. The mechanism of this catalytic effect is possibly defined by the formation of intermediate calcium hydrate gel on the solid particle surface. A “wet” process, which includes the interaction between three phases (water-solid slag-CO_2 gas), has a much higher carbonation reaction rate when compared with the “dry” process. The percent of carbonation statistically correlated to the CaO contents of industrial slags. This data will be used to determine the design parameters for a lab-scale reactor for CO_2 sequestration by steelmaking slags.

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EXPERIMENTAL STUDY OF CO_2 SEQUESTRATION BY STEELMAKING SLAG

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Key Words: Steelmaking Slag, Carbon Dioxide, Sequestration

Abstract

Steelmaking processes intensively use carbon-containing materials and generate a significant amount of carbon dioxide emissions. The U.S. steel industry produces ~1.75 tons CO_2 for every ton of steel shipped. At the same time, steelmaking processes use calcium and magnesium oxide containing minerals for slag formation, which are excellent CO_2 capture agents. The goal of this investigation was to experimentally study carbon dioxide sequestration by steelmaking slag with simultaneous acceleration of the slag stabilization processes in preparation for re-use as a construction material. Thermogravimetric methods and a slurry reactor were used to study reaction kinetics. The degree of slag carbonization was evaluated for industrial and synthetic slags in dry and wet and processes.

Carbon Dioxide Emission In Steelmaking

Carbon dioxide is generated directly through iron or steel metallurgical processes (blast furnace, BOF or EAF), or through indirect means (coke ovens or coal burning power plant providing electricity to processes). A comparison of CO_2 emissions according to geographic regions and steelmaking technologies was made from published data. Stubbles provides trends of U.S. domestic steel industry energy use and CO_2 emissions.[1] Technological evolution has reduced required energy per ton of steel from 47.4 GJ (45 million BTU) in 1950 to 17.9 GJ (17 million BTU) in 2000. Carbon dioxide emissions, stated in terms of carbon equivalent (CE) units (0.27 x tons CO_2), have been tracked since 1990, but exhibit a similar trend to reduction in energy use. Integrated mills produce more CO_2 than mini-mills because of their reliance on coke making and blast furnace ironmaking. In the year 2000, integrated mills produced 33.46 million tons of CO_2 (CE units) of which 64% (21.47 million tons) came from the production and use of coke. Mini-mills produced 13.65 million tons of CO_2 (CE units), of which 80% (10.86 million tons) came from electrical production at the power plant. The U.S. steel industry on an average produced ~0.42 carbon equivalent tons of CO_2 per ton of steel shipped in 2000.

Carbon dioxide emission data from the steel industries of several other countries is available from the literature. Afonin provides data for the steelmaking sector in Russia.[2] Based on 1998 data, the total CO_2 emissions from integrated steelmaking stand at 48.6 million tons carbon equivalent, which is 8.5% of all Russian CO_2 emissions. On an intensity basis, this equals 1.4 tons CE per ton of steel produced. Data from Birat et al. shows that in 1989 the French integrated steel industry produced a total of 26.3 million metric tons CO_2 total, at an intensity of 0.42 tons CE per ton steel.[3-6] This is comparable to U.S. emission rates of 2000. By 1994, the CO_2 intensity had dropped in France to 0.40 tons CE per ton steel, which is approaching the theoretical limit. France has an extremely low CO_2 emission rate of 0.03 tons CO_2 per ton steel considering EAF with 100% scrap, due to their high reliance on nuclear power. Holappa reports data from Finnish ironmaking that can be used to estimate the carbon dioxide intensity for that region, which is approximately 0.53 tons CE per ton steel for integrated steelmaking.[7] Data from Emi and Gielen show the 2005 carbon intensity rate for Japanese integrated steelmaking is 0.46 tons CE per ton of steel.[8,9]

Anderson et al. reported the results of a study comparing the carbon dioxide emissions and energy requirements for 30 different steelmaking routes.[10] To the BF/BOF baseline of 89% hot metal/11% scrap, they have compared standard and alternative iron sources/steelmaking routes at 80%, 50%, and 30%. The carbon dioxide emission data from this publication in 2002 for a U.S. basis is shown in Figure 1. The highest CO_2 producer is the traditional BF-BOF route at 519 kg CE per ton of liquid steel. The lowest CO_2 producer is 100% scrap in an EAF at 119 kg CE per ton liquid steel (CE/t LS). All other processes are for EAF production and fall in between these boundaries. As the amount of scrap blending is increased, the carbon dioxide production decreases. Comparison of data from Goodfellow et al. on 100% scrap in an EAF shows that the indirect sources produce almost 70% of the CO_2 generated, with the largest fraction from electricity generation.[11,12] These authors showed that U.S. EAF production with 100% scrap produces ~140 kg CE/t LS (compared to 119 kg CE from Anderson[10]) due to high fraction of electricity supplied from hydrocarbon combustion sources (69%). However on the same basis, Canadian EAF generates 89 kg CE due to lower fraction of electrical supply from hydrocarbon fuel (32%) and French EAF generates 46 kg CE due to an even lower reliance on hydrocarbon-based fuels (5%).

The composition of steelmaking offgas is changed during the stages of the steelmaking heat, such as charging, blowing, refining, and tapping. Knowledge of composition variation is necessary for feedback control and mitigation technologies. Evenson et al. reported on an expert system relying on feedback control from offgas analysis in EAF operations.[13] Sampling probes installed at the entrance to the fixed duct after the combustion gap and at the end of the water-cooled duct downstream of the combustion chamber provide real time composition analysis. For an average of 30 heats, the concentration averages upstream and downstream respectively were 22.7±2.4% and 10.3±1% for CO_2, 21±2.5% and 0±0% for CO, 0.6±0.5% and 11.3±0.7% for O_2, and 8.1±1.2% and N/A for H_2. This data is reported for an upstream flow rate of 15900 Nm^3/hr (9358 SCFM) and a downstream flow rate of 68400 Nm^3/hr (40259 SCFM), yielding a dilution flow ratio of 4.3. Grant reports EAF offgas data from a U.S. based shop (location not specified) in his work with post-combustion optimization.[14] The offgas composition profile at the inlet of the fixed duct just after the combustion gap (same as Evenson et al. upstream location) for a period of 15 heats shows the CO_2 average a little lower (~15%), CO average similar (~18%), O_2 value higher (~4%), and H_2 average similar (~6%). The high downstream O_2 value shows less combustion of the CO.

Analysis of the steelmaking process shows that energy conservation provides both the most significant and cost effective method for reduction of CO_2 emissions. Energy conservation minimizes the direct CO_2 sources (less combustion of carbon) and indirect sources (reduction in electricity). The drive towards near net shape final product has provided the largest gains. Continuous casting and thin slab casting have reduced energy consumption from 36.9 GJ/t to 21.1 GJ/t (35 million BTU/t to 20 million BTU/t). The move towards strip casting and closure of inefficient facilities should drop the industry amount to ~14.8 GJ/t (14 million BTU/t) by 2010.[1] In addition, steel production from scrap provides the lowest amount of CO_2 emissions and energy requirement. Alternative iron and steel making technologies will also provide reductions in carbon dioxide emissions, primarily through energy reduction, but also through operational changes. Emi lists pulverized coal, plastic, and LNG injection, increased blast temperature, and decreasing moisture as current technologies to reduce CO_2 emissions by up to 23% in Japanese iron making.[8] Most of the research involves the use of new technologies to replace or augment the traditional blast furnace ironmaking. Alternative iron technologies, such as ITmk3® and

HIsmelt® may provide further 20-25% reduction but are still in development. Birat lists several carbon free technologies being proposed, but they are many years from large-scale commercial development.[7] These technologies include hydrogen reduction and direct electrolytic production of iron. Both technologies require a source of electricity that is not hydrocarbon based, in order to provide a net reduction in CO_2 emissions. In all cases recycling is being researched as the most powerful method of reducing CO_2 emissions for the material community as a whole. This includes use of the steel scrap in the EAF and use of the slag to offset limestone used in cement production.

Progress in steelmaking processes will decrease the total value of direct and indirect carbon dioxide emission but full elimination of this emission will be possible only with introduction of effective carbon dioxide sequestration processes. Unfortunately, at the present time, most sequestration technologies provide a negative cost impact to the steel producer. Moreover, some sequestration processes, which used high pressure/temperature apparatuses, require additional energy and have the low value of "global" efficiency when the direct and indirect balance is taken into account. The current research project seeks to develop a cost effective sequestration technology using slag, which is available in plentiful amounts at the steel plants, to permanently sequester carbon dioxide. A side benefit is that the formation of carbonates in slag will render the slag immune to in-situ swelling or leaching, thus stabilizing it for immediate commercial use.

CO_2 Sequestration Possibility Of Steelmaking Slag

The potential of steelmaking slag to react with CO_2 to form permanent carbonate minerals (sequestration) is derived from the high concentration of alkaline earth metal oxides. The alkaline earth metal oxides present in significant quantity in steelmaking slag are CaO and MgO. These oxides enter the slag from the fluxing agents used during steelmaking, which are primarily standard and dolomitic lime or limestone. Table 1 shows the composition of nine slags surveyed in this project. A total of six sites are represented (A1, B1, C1, D1, E1, and E2), with multiple EAF slag samples taken at some sites. In addition at site A1 an LMF sample was taken for comparison.

The sequestration potential of a slag can be determined from the formation reactions with carbon dioxide at ambient conditions. Both CaO and MgO exhibit a negative ΔG°_{f} in the reaction with CO_2, thus readily forming carbonates. The other major phases (SiO_2, FeO/Fe_2O_3, Al_2O_3, and MnO) are inert to spontaneous reaction with carbon dioxide thus are precluded from the sequestration potential. Both K_2O and Na_2O will readily form carbonates, but are not present in sufficient quantities to be significant. Both CaO and MgO react with CO_2 in a 1:1 molar combination to form $CaCO_3$ and $MgCO_3$ respectively. On a weight basis 1000 kg of CaO will capture 785 kg CO_2, which can be expressed as 214 kg CE units. Using the same basis 1000 kg of MgO will capture 1092 kg CO_2, or 298 kg CE units. Using the average values for CaO and MgO of 34.41% and 11.71% respectively from Table 1, 1000 kg of steelmaking slag has the potential to sequester 398 kg CO_2, or 109 kg CE units. The National Slag Association estimates that per metric ton of steel produced, BOF operations generate 75-150 kilograms of slag, while EAF operations generate less at 65-80 kilograms.[15] Combining this with the carbon emission values from Anderson et al of 519 kg CE/t LS for BF-BOF steelmaking and 119 kg CE/t LS for 100% scrap EAF will yield the overall potential sequestration capacity. At these values, the slag produced per ton of liquid steel can sequester 2.4% BF-BOF and 3.3% of EAF of total, direct and indirect, carbon dioxide emissions. Segregating the slag types in Table 1 (EAF or BOF) and using the average values for their respective processes yields an average carbon equivalent sequestration potential of 2.7% for BF-EAF and 3.2% for EAF. Significantly higher percentage of CO_2, generated directly by EAF, could be captured by slag. Estimated volume of sequestrated by slag direct EAF CO_2 emission could exceed 15%.

Table 1 Composition of nine steelmaking slags surveyed in this project

	A1α	**A1β**	**A1γ**	**B1α**	**C1α**	**D1α**	**D1β**	**E1α**	**E2α**	**Avg.**
Type	EAF	EAF	(LMF)	BOF	BOF	EAF	EAF	EAF	EAF	-
CaO	27.34	31.22	47.02	40.90	40.53	33.02	34.49	31.91	35.86	34.41
SiO_2	14.84	13.86	6.07	12.89	10.42	12.43	15.08	17.32	9.93	13.35
FeO	30.05	24.96	5.02	21.72	21.65	27.93	25.76	20.20	27.98	25.03
MgO	10.55	11.61	10.03	11.98	13.81	10.98	11.76	12.85	10.13	11.71
Al_2O_3	7.02	8.61	26.55	5.22	6.65	8.74	5.56	6.79	9.22	7.23
MnO	6.51	6.07	1.04	4.67	4.50	3.98	4.85	7.07	4.29	5.24
TiO_2	0.39	0.42	0.41	0.68	0.47	0.50	0.55	0.49	0.49	0.50
ZrO_2	<0.01	0.03	0.20	0.08	0.28	<0.01	<0.01	0.16	0.02	0.08
Cr_2O_3	2.48	1.98	0.25	0.31	0.42	0.87	0.78	1.62	0.95	1.18
K_2O	0.05	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02
Na_2O	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.10
S	0.16	0.27	1.35	0.12	0.11	0.21	0.08	0.22	0.30	0.18
P	0.16	0.16	0.02	0.42	0.45	0.25	0.32	0.18	0.28	0.28
C	0.11	0.26	0.38	0.67	0.40	0.22	<0.1	0.32	<0.1	0.27
Sr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
F	0.33	0.54	1.66	0.33	0.33	0.87	0.75	0.86	0.55	0.57

The above estimates are based on full conversion to carbonate at ambient temperature and pressure, assuming pure CaO and MgO in the slag reacting with an atmosphere carbon dioxide at unity partial pressure ($P_{CO2}=1$), thus they represent the thermodynamic potential. A system designed for reacting slag with offgas CO_2 will deviate from most all these assumptions. The total gas pressure will be at ambient conditions (1 atm.), but the partial pressure of CO_2 will be in the range of 4-11% ($P_{CO2}=0.04\text{-}0.11$ atm). Steelmaking slag contains only a few percent of free lime or magnesia, thus these compounds cannot be considered in the pure state. Predominately the CaO and MgO will form silicate, aluminate, or ferrite phases. The results of XRD analysis showed that the slags listed in Table 1 contain dicalcium silicate and larnite (Ca_2SiO_4), akermanite ($Ca_2MgSi_2O_7$), C_5MS_3 ($Ca_5MgSi_3O_{12}$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), magnesio-wustite ($MgFeO_2$), hatrurite (Ca_3SiO_5), periclase (MgO), and lime (CaO). Small amounts of free alumina, wustite, and silica have been found, but these do not contribute to carbon dioxide sequestration.

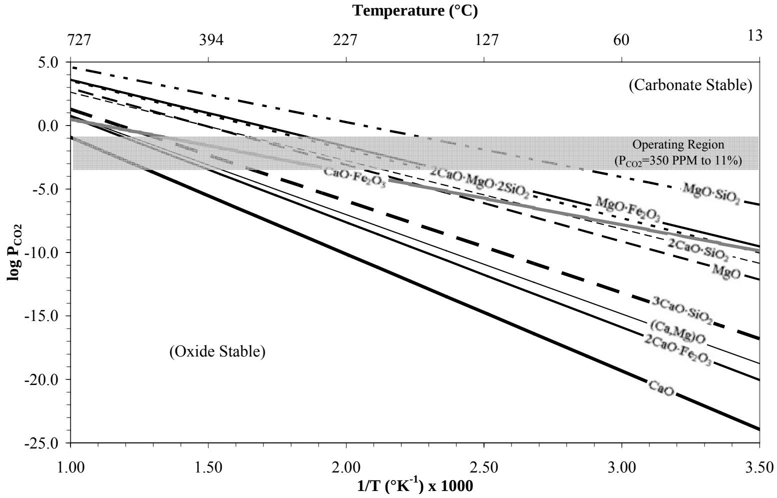


Figure 1 Carbonate stability diagram for alkaline earth metal oxide phases found in steelmaking slag (data generated from FactSage™ 5.4)

The ability of specific phases in steelmaking slag to sequester carbon dioxide into stable carbonates under non-ideal conditions can be expressed in the phase stability diagram shown in Fig. 1. Each line shown, generated from data in FactSage™ 5.4, represents the reaction of a slag phase to form carbonate versus temperature and equilibrium partial pressure of carbon dioxide (P_{CO2}). For example the bottom line labeled "*CaO*" represents the reaction $CaO+CO_2 \rightarrow CaCO_3$. The top line similarly represents the reaction $MgSiO_3+CO_2 \rightarrow MgCO_3+SiO_2$. Above each line the carbonate is stable (i.e. reaction proceeds to the right), and correspondingly below each line the oxide is stable (i.e. reaction proceeds to the left). As temperature increases (right to left) the carbonate stability region for each phase shrinks, hence at high temperatures the carbonates will decompose to form oxides (e.g. as in calcining operations). The concentration of CO_2 in the atmosphere surrounding the slag also affects the carbonate stability. As P_{CO2} increases the carbonate becomes more stable, thus requiring a higher temperature to calcine the material. For example magnesite ($MgCO_3$) decomposes to magnesia (MgO) at 210°C in ambient air (P_{CO2}=350 PPM), but if it is placed in a pure CO_2 atmosphere (P_{CO2}=1) it does not decompose until 389°C. The sequestration of carbon dioxide by slag operates opposite to calcining. When calcining limestone, carbon dioxide is driven off in the clinker by the application of heat. To capture CO_2 in lime, or other slag phases, lower temperatures provide more favorable thermodynamic stability. At ambient conditions (25°C, P_{CO2}=350 PPM), all phases listed on Fig. 1 are stable as carbonates thus the slag will spontaneously react to sequester CO_2.

However the major hurdle to realization of slag sequestration is that the ambient reaction rate is extremely slow and could be limited by CO_2 diffusion into solid slag particles. Some states require steelmaking slag to stabilize in stockpiles for three to six months prior to use.[16,17] The CO_2 diffusion rate can be improved by increasing the reaction temperature however an upper boundary is set by the phase stability of carbonate formation. The gray shaded region in Fig. 1 shows the P_{CO2} operating region exhibited by the stack offgas. The lower limit is 350 PPM, which is the approximate ambient CO_2 concentration. The upper limit is 11%, with an average of 4%. As P_{CO2} increases, the allowable reaction temperature for carbonate formation also increases. Thus considering a slag containing clinoenstatite ($MgSiO_3$), under ambient CO_2 concentration the carbonate formation reaction can proceed up to 74°C. However exposing slag to offgas at 11% carbon dioxide increases the allowable reaction temperature to 168°C. An analysis of the slag phases is critical to the sequestration system design to determine the maximum allowable temperature to allow carbonate formation while enhancing reaction kinetics. The reaction rate is the limiting factor for CO_2 sequestration when EAF offgas interacts directly with slag at atmospheric pressure.

An alternative processing route using water or steam assist greatly accelerates the reaction kinetics. The catalytic effect of a humid CO_2 stream in reacting with alkaline earth metal oxide based solids has been noted by several researchers. Both Lackner et al. and Zevenoven et al. noted in their work with serpentine ($Mg_3Si_2O_5(OH)_4$) that humidity greatly increased the percent conversion to carbonate with all other factors equal.[18,19] Hills et al. also reported the importance of humidifying the CO_2 stream in their work with accelerated carbonation of slag and other cementitious wastes.[20,21] They propose that CO_2 from the air permeates through the solid, which is the diffusion controlled rate-limiting step. The presence of water forms a gel on the lime particle surface into which CO_2 solvates. CO_2 hydrates to H_2CO_3 in the surface gel, which is then ionized to H^+, HCO_3^-, and CO_3^{2-}. The pH in the water drops assisting in the dissolution of the lime. The reaction rate in solution is much faster than between the gas and solid state. In the current project, temperature, humidification, and particle size will be evaluated for their effect on reaction rate of the industrial slag. In, so called, slurry process, the formation of intermediate phases on solid slag particle, could promote the reaction of calcium carbonate formation at room temperature and under normal atmospheric pressure.

The objective of the current project is to develop and demonstrate a process for sequestering CO_2 from steelmaking offgas by forming carbonates with the alkaline earth oxide containing phases in slag. To achieve this result, the process kinetics of the carbonate formation reaction must be improved to allow the design of a commercially feasible reactor. This reactor will contact stack exhaust gas with fresh or minimally processed slag allowing rapid sequestration of the CO_2 and stabilization of the slag.

Experimental Study Of Carbonate Formation In Steelmaking Slag

Two different types of reactor design concepts (packed bed and slurry process) were proposed for contacting steelmaking slag and offgas. The first concept (packed bed) is a solid-gas contactor with either plug flow or rotary design. In this system the stack offgas would be directed through an atmospheric pressure rated vessel containing slag particles. Only the sensible heat of the offgas would be used to provide a temperature increase of the system. After sufficient reaction time the carbonated slag is dumped, and fresh slag is input to repeat the process. To allow continuous operation a plug flow design would use two parallel contacting vessels, thus while one is dumping/loading the other is reacting. A rotary design would be similar to a cement clinker, with slag particles flowing countercurrent to offgas. The other basis (slurry) of design allows for slurry contact, thus the slag is mixed with water through which offgas is bubbled. The slurry reactor would require continuous stirring, thus could be modeled after a mechanical flotation cell, which allows for intimate gas-solid contact in a water-dispersed system. While a slurry reactor is more complicated for operations, the water addition may be necessary to achieve sufficient reaction kinetics. Both design bases are being investigated in this project through bench-scale testing.

Packed bed process. Investigation of the solid-gas contactor packed bed approach is done through a large-scale thermogravimetric analyzer purpose-built for this project. Samples are suspended in the furnace from a digital balance which records sample weight. Samples for gas-solid contact are held in a 304SS mesh basket or by a platinum wire (single particle). Samples for decomposition analysis are placed in an alumina crucible held by a platinum wire. Up to three gases can be metered individually or in combination. The gases used in this project are Ar, CO_2, N_2, and air. In addition the introduced gas can be humidified by bubbling through a heated water column. Weight and temperature data are collected to a computer through a portable data acquisition system.

Baseline testing to determine the effect of temperature and humidity on carbonation rate was conducted with “Hi-cal” lime obtained from a project sponsor. The “Hi-Cal” lime has a composition of 95% CaO, 3% MgO, and 2% SiO_2. Single particles of lime, with an average ~1.5 cm equivalent spherical diameter, were suspended into the TGA from a platinum wire holder. The first series of tests were conducted at 200°C, 300°C, 400°C, and 500°C with dry CO_2 (P=1 atm). A second series of tests was conducted at the same temperature points however the CO_2 was first humidified with the gas bubbling column. In each test, the lime single-particle was suspended in the TGA furnace in an Ar atmosphere while the temperature was ramped to the testing point. Once the temperature reached the desired test point, the particle was held in the Ar atmosphere for one hour. After one hour, the Ar was turned off and the desired CO_2 stream (dry or humidified) was introduced into the furnace chamber. The lime sample was allowed to react with CO_2 for approximately 5.5 hours, after which the Ar stream was reintroduced while the sample cooled to room temperature. A plot of weight change versus time for each sample is shown in Fig. 2.

Each dry sample exhibited an increase in weight with time as it was allowed to react with CO_2 at the test temperature. The total weight increase at 200°C in dry CO_2 at 5.5 hours was marginal

(~1.25%). This corresponds to 2% carbonation. The percent carbonation is defined as the fraction of lime converted to calcium carbonate (assuming only $CaCO_3$ formed). Increasing the temperature to 300°C and 400°C, showed incremental increases up to approximately five weight percent increase for the latter temperature. A test temperature of 500°C in dry CO_2 showed a significant jump to 13 weight percent increase, which is equivalent to 16.5% carbonation. Increasing temperature alone has a significant impact on the reaction kinetics by increasing the rate of the limiting kinetic step.

Humidifying the CO_2 provided as significant impact as increasing the reaction temperature. The total weight increase at 200°C in humid CO_2 at 5.5 hours was approximately double (2.5%) of that exhibited with dry CO_2. The weight gain at 300°C in humid CO_2 was higher than that with dry CO_2, but not twice as much. The largest difference occurred in humid CO_2 at 400°C, which showed a weight gain of 15%, which is three times that shown for the dry CO_2 at the same temperature. The highest weight gain of 17% occurred at 500°C in humid CO_2, which corresponds to 21% carbonation of the lime sample. Humidification of the reaction gas has a catalytic effect in dramatically increasing the reaction rate between CO_2 and lime.

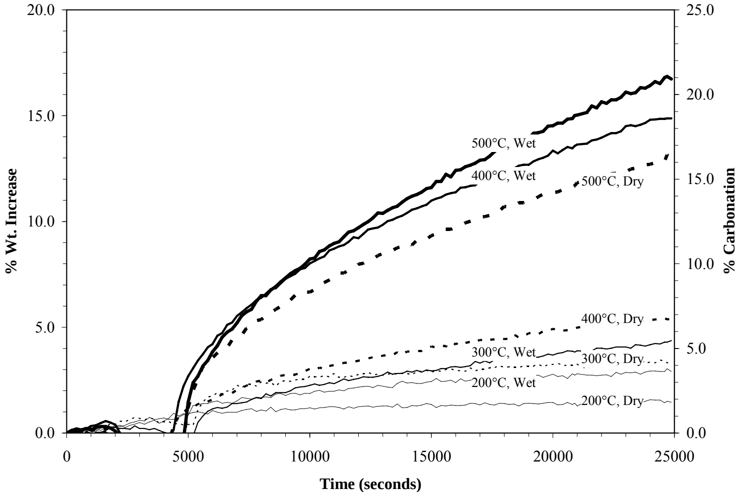
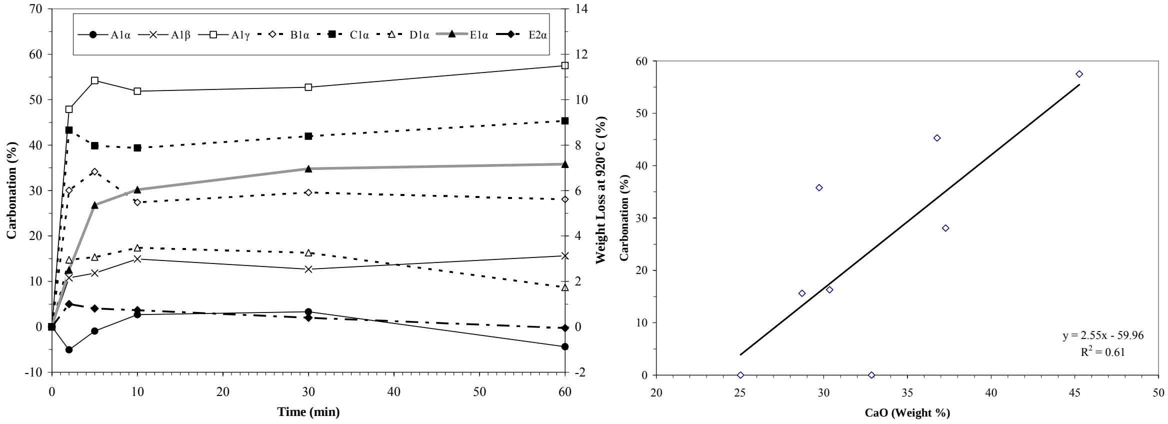


Figure 2 Carbonation rate of Hi-cal lime (95% CaO) in dry and humid CO_2 atmosphere ($P_{CO2}=1$) at 200°C, 300°C, 400°C, and 500°C

Slurry process. Investigation of the slurry process, using a water-solid-gas reactor basis, was done with a bench-scale flotation cell containing a two-liter chamber and internally rotated impeller. The rate of the carbonation reaction was studied under intensive mixing. The rate of slag reaction was compared to rate of "Hi-cal" lime reaction under the same test conditions. For each test, 50g of solid material was crushed and graded to <106 μm then mixed with two liters of tap water. Bottled CO_2 was injected into the slurry at a rate of 1459 cm^3/min for a total of two hours (lime only). Periodic slurry samples of 3-5g in size were taken, decanted through vacuum filtration, and then dried in an oven. Oven drying took place at 220°C for one hour, followed by calcium hydrate decomposition at 480°C for two hours and calcium carbonate decomposition at 920°C for two hours. These temperatures were chosen on the basis of thermodynamic equilibrium of the CaO-CO_2-H_2O system as determined by FactSage 5.4. Parallel samples were taken and subjected to analysis in the TGA. Three types of materials were tested in the slurry reactor; "Hi-cal" lime, the nine industrial slags in Table 1, and three synthetic slags produced from reagent grade material in an induction furnace. The synthetic slag compositions were selected to represent a low (40% CaO, 26% SiO_2), medium (49% CaO, 20% SiO_2), and high basicity (56% CaO, 15% SiO_2), in slag A, B, and C respectively. Synthetic slags A and B exhibited a "falling" condition and self-disintegrated into a powder during cooling.

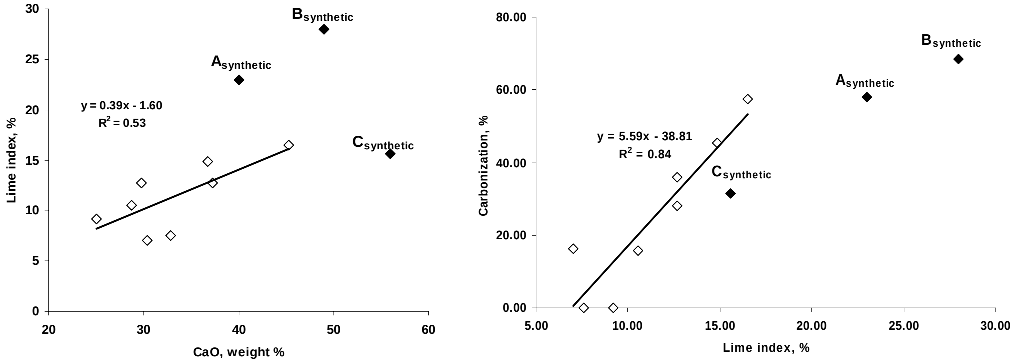
The percent carbonation for eight of the steelmaking slags from Table 1 is shown in Fig. 3a. The results are presented as the percentage of weight loss from calcium carbonate decomposition and as the percent carbonization, calculated in reference to the calcium concentration in each slag sample. The percent carbonation at 60 minutes varied from a low of -4.4% for EAF slag to a high of 57.5% for LMF slag. A correlation between the final carbonation percent and the amount of *CaO* in slag is shown in Fig. 3b. As expected from thermodynamic calculations, the amount of *CaO* is proportional to the slag reactivity to CO_2.



a) b)

Figure 3 Carbonation versus time (a) and final carbonization versus *CaO* in slags (b)

Phase determination was not undertaken on the samples to determine the amount of free versus combined *CaO* (i.e. into silicates or ferrites). For example, two EAF slag samples showed no reactivity to CO_2 in the slurry reactor in spite of calcium content in these slag. A faster procedure was used for rapid determination of reactive part of calcium oxide in steelmaking slag. A "free lime index" was determined using titration with diluted acids (8.8 weight % H_2SO_4). All slag were tested in powder condition (< 0.1 mm). Free lime index was calculated as a percentage ratio of the volume of acid used for full neutralization of solution. The procedure involved mixing 2g slag with 100g water for 60 minutes. The data was compared to the volume of acid required for neutralization of pure lime in the same conditions. For example, if 2 g pure lime is neutralized by 50 ml of acid solution and the same weight of slag is neutralized only by 15 ml, the free lime index of this slag is 100*15/50=30%. If the slag contains a total of 40% calcium, only 30% of calcium in slag to reacted with acid in this particular condition. Statistical analysis of correlation between *CaO* in steelmaking slag and free lime index is given in Fig. 4a and correlation between of degree of carbonization in slurry process with free lime index is illustrated in Fig. 4b.



a) b)

Figure 4. Correlations between free lime index and *CaO* contents in slag (a) and plot of slag carbonization in versus free lime index (b). Equations applied only for industrial slag.

Summary

The results of bench-scale CO_2 sequestration tests by steelmaking slag are presented in this paper. In the packed bed process, the rate of reaction of solid lime or slag increases proportional to the reactor temperature. However, an upper boundary condition exists, defined by a thermodynamic phase stability diagram that must be identified for each phase in the slag. Tests results showed that the addition of water vapor (humidification) to the CO_2 gas significantly accelerated the carbonation reaction of pure lime. The mechanism of this catalytic effect is possibly defined by the formation of intermediate calcium hydrate gel on the solid particle surface. A slurry process, which includes the interaction between three phases (water-solid slag-CO_2 gas), has a much higher carbonation reaction rate when compared to packed bed process. The percent of carbonation statistically correlated to the CaO contents of industrial slags. This data will be used to determine the design parameters for a pilot-scale reactor for CO_2 sequestration by steelmaking slags.

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The Use of Steelmaking Slag for Mineralogical Sequestration of Carbon Dioxide - Aqueous Processing

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INTRODUCTION

Carbon dioxide is generated directly from the furnaces used in iron and steel production, or indirectly from supply systems such as coal-burning power plants providing electric power to the plant. Steelmaking CO_2 emissions vary by geographic region and the production method. For example, integrated steel mills generate more CO_2 per ton of steel than mini-mills generate due to the use of coke and iron-making pre-processes. In 2000, U.S. integrated mills emitted 33.5 million tons of CO_2 in carbon equivalent (CE) units, of which 64% was generated through the production and use of coke.[1] During the same year, U.S. mini-mills generated 13.7 million tons of CO_2 CE, where 80% was generated from the supply power plants.[1] On average, in 2000 the U.S. steel industry produced 0.42 tons of CO_2 CE per ton of steel shipped. Table I compares the rates of CO_2 emissions in the U.S. with several European countries and Japan. Most countries are approaching the theoretical production limit of 0.40 tons of CO_2 CE per ton of steel shipped, indicating that emission reductions from technological changes in production methods will have less of an impact in the future.

Table I Comparison of CO_2 emission amounts from integrated steelmaking by geographic region

Region	Year Reported	Amount (tons CE per ton steel)	Reference
Russia	1998	1.4	Afonin[2]
France	1989	0.42	Birat et al.[3-6]
	1994	0.40	Birat et al.[3-6]
	1994	0.03 (EAF/100% scrap)	Birat et al.[3-6]
Finland	1994	0.53	Holappa[7]
Japan	2005	0.46	Emi and Gielen[8,9]
U.S.	2000	0.42	Stubbles[1]

Energy reduction provides the most direct method for reducing CO_2 emissions. However, most U.S. steel producers have optimized energy use to lower power costs, and further significant step changes are not expected. If reduction in CO_2 emissions becomes a governmental mandate, then source point mitigation to capture (sequester) the produced CO_2 will be required.

The aim of this project is to develop a functional sequestration technology using steelmaking slag to permanently capture carbon dioxide produced and currently emitted by steelmaking operations. A parallel benefit of slag-based CO_2 sequestration is chemical stabilization of slag minerals, thus rendering the slag immune to end-use swelling or leaching and eliminating the need for stockpile aging prior to commercial use. The potential of steelmaking slag to react with CO_2 to form permanent carbonate minerals is derived from slag's high concentration of alkaline earth metal oxides. The two most important oxides are CaO (lime) and MgO (magnesia), which range from 30-50% and 10-12% of the slag mass, respectively.[10] Both lime and magnesia readily form hydroxides or carbonate compounds under atmospheric conditions, with the carbonate compounds forming the most thermodynamically stable phase.

Previous work has shown that the slag produced during steelmaking has the potential of sequestering 5.0-10% of the BF-BOF CO_2 emissions and 28-34% of EAF carbon dioxide emissions. In addition, the estimated 15-20 kg of LMF slag produced per ton of steel has the potential of capturing an additional 1.0-1.3% of BOF and 7.8-10.4% of EAF CO_2 emissions. Thus, the total sequestration potential for steelmaking slag is 6-11% of the CO_2 emitted from integrated mills and 35-45% emitted from scrap-based steelmakers.[11] A furnace offgas CO_2 capture and sequestration system will most likely be installed after the baghouse to prevent contamination of the slag with baghouse dust. At this point offgas conditions at this point have been estimated to be 90-150°C, with a peak CO_2 concentration of 10-11 vol.% and an average of 4-5 vol.%.[10]

Two different designs are being tested for a slag-offgas reactor. The first design is a dry process using a plug flow or rotary reactor as detailed previously.[10] The second design is the focus of the current study and includes a wet process whereby slag is mixed with water to form a slurry through which offgas is bubbled. A two-stage system allows for aqueous dissolution of the alkaline oxides in the first stage, followed by a reaction of the resultant aqueous liquor with CO_2 in a separate vessel or location. Compared with a dry system, wet processing has a much higher CO_2 reaction rate, thus allowing for a smaller reactor vessel. In addition, catalytic agents such as carbonic anhydrase may be added to form an aqueous biomimetic process that has been shown to provide more tan two orders of magnitude increase in mineral carbonate formation in experiments for wet industrial CO_2 scrubbers.[12]

EXPERIMENTAL METHOD

To assess the feasibility of carbon dioxide sequestration with steelmaking slag, a series of experiments was undertaken to measure the kinetic reaction rate in an aqueous system. Three industrial slag samples were obtained from the project partners. Table III lists the slag compositions as determined by X-ray fluorescence (XRF) spectroscopy. Slag #1 is from an EAF mill and contains 32.1% CaO. Slags #2 and #3 are LMF slags from EAF mills and contain higher CaO content plus a Al_2O_3/SiO_2 in proportion to their respective steel deoxidation method. Steelmaking slag contains very little free lime (CaO) or free magnesia (MgO), thus these compounds cannot be considered in the pure state. Predominately CaO and MgO are present as silicate, aluminate, or ferrite phases. X-ray diffraction (XRD) phase analysis has shown that the slags listed in Table II contain primarily dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5) with lesser amounts of akermanite ($Ca_2MgSi_2O_7$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), and magnesio-wustite ($MgFeO_2$), and a few percent periclase (MgO) and lime. Small amounts of free alumina (Al_2O_3), wustite (FeO), and silica (SiO_2) have been found, but these do not contribute to carbon dioxide sequestration.

Table II Compositions of steelmaking slags used in the aqueous kinetics tests (in wt.%) as determined by XRF spectroscopy

Oxides	#1 (EAF)	#2 (LMF) Al-Killed	#3 (LMF) Si-Killed
CaO	32.1	49.9	51.3
SiO_2	19.4	4.5	28.3
Al_2O_3	8.6	32.3	4.9
TiO_2	0.4	0.3	0.3
MgO	9.4	4.3	4.3
MnO	6.8	0.8	1.3
Fe_2O_3	26.4	6.3	5.5
SO_3	0.6	1.0	1.6
V_{ratio}	1.7	1.4	1.5

All slag samples were obtained in 40-50 pound lots from steel plant stockpiles. The slags were obtained prior to on-site processing (<24 hours after production) in order to ensure minimal reaction with local ambient conditions. Slags #1 and #2 were crushed in a laboratory jaw crusher followed by a roll crusher to pass a 6-mesh sieve size (3.35 mm). Slag #3 is a falling slag, thus self-comminuted, and was used in the raw condition. Figure 1 shows the particle size analysis of slags #1 and #2 after crushing, along with Slag #3 in the raw state. Particle size analysis was obtained using a U.S. mesh series of 8” sieves on a vibratory shaker.

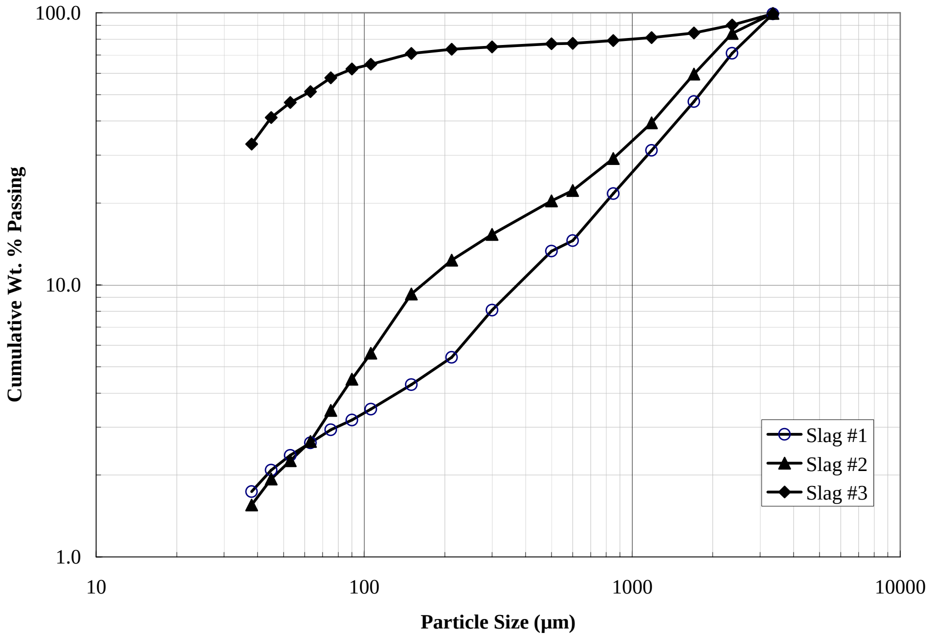

Figure 1 Particle size analysis of crushed (slags #1 & #2) and raw steelmaking slag (Slag #3) samples used in the aqueous kinetics tests

Laboratory flask tests were initially used to measure the reaction rate between the slag samples and carbon dioxide. Each slag type was graded into four size fractions: 45-75µm, 150-250µm, 425-589µm, and 1000-1500µm. Thirty grams of each size fraction was mixed with 250g of deionized water in an Erlenmeyer flask. Standard bottle grade CO_2 was introduced into the mixture through a 1mm glass capillary tube. Each sample was allowed to react for a designated period of time, after which the CO_2 flow was stopped. The slurry mixture was filtered through 11µm filter paper with a vacuum pump. The filtrand was dried at 180°C and analyzed for carbon content with a LECO$^{\copyright}$ carbon analyzer (combustion/IR) and/or a thermogravimetric analysis (TGA) device. An example of TGA analysis is given in Figure 2 (left), where weight loss at low temperatures (<600°C) indicates hydroxide decomposition and weight loss at high temperatures (>700°C) is associated with carbonate decomposition. Some samples were split to allow parallel testing, and the results showed that the two methods were in a good agreement. Weight loss from carbonate decomposition in the TGA device was correlated against the LECO$^{\copyright}$ method (Figure 2, right) which provides the weight percent of carbon. Error bars represent 95% confidence intervals comparing combustion and TGA measurements of parallel samples. The mass ratio of CO_2 to C is 3.6, which shows excellent agreement with the slope of 3.66 in Figure 2 (right), indicating that the results from each method can be used congruently with confidence.

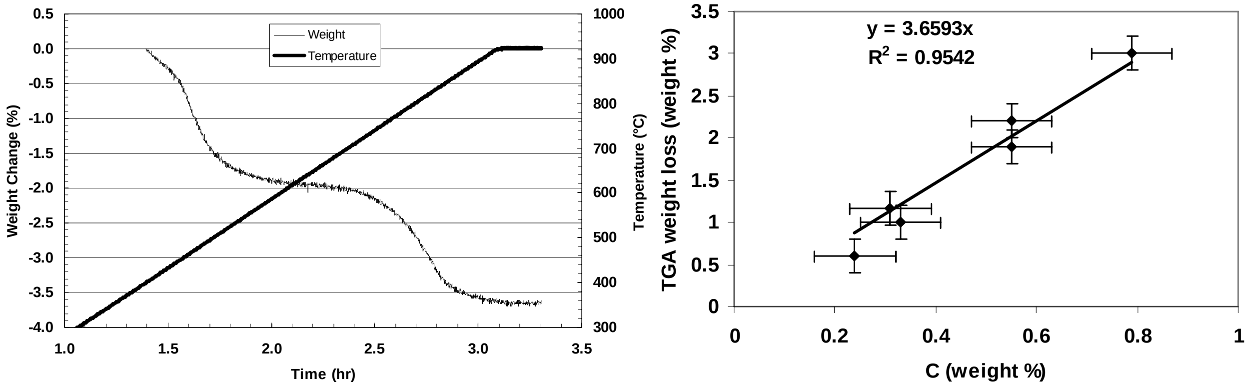

Figure 2 Example of TGA test results for the measurement of hydroxide and carbonate decomposition in slag after a flask test (left) and the correlation between TGA weight loss and changing carbon content of treated slags (right)

A bench scale slurry reactor apparatus was fabricated from two plastic tanks connected in a loop arrangement that allowed the exchange of aqueous solution via a positive displacement pump (Figure 3). Reactor 1 contained two kilograms of slag mixed with 20 liters of water. The aqueous liquor was exchanged at varying rates with Reactor 2, which has a two-liter volume. Standard bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles and to allow intimate mixing between the gas and alkaline solution. A multi-channel pH meter was used to measure the pH level in both reactors in-situ and allow for manual control of the process. At the completion of each test, a sample of the slurry mixture was filtered through 11µm filter paper with a vacuum pump. The filtrand was dried at 180°C and analyzed for carbon content with a LECO© carbon analyzer (combustion/IR) and thermogravimetric analysis (TGA) device.

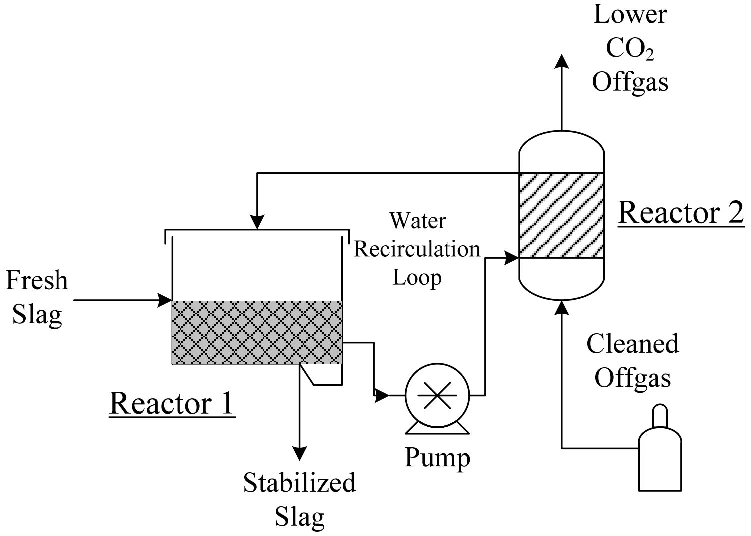

Figure 3 Flow schematic of two-stage slurry reactor contact of slag-water-CO_2

The apparatus was designed as a prototype for scale-up to industrial use. The two-stage reactor design allows for simpler retrofit into existing slag and offgas treatment facilities by allowing alkaline leaching (Reactor 1) and CO_2 absorption/reaction (Reactor 2) to take place in separate facilities. The rate of solution exchange and individual reactor volumes can be scaled to match the kinetic reaction rate and slag/offgas volumes.

RESULTS

Figure 4 presents the measured degree of carbonization from flask tests for Slag #1 and Slag # 2 at several size ranges. Note that the data are shown with a logarithmic time scale. The degree of carbonization is estimated on the basis of changing carbon content taking into account the calcium concentration initially present in the slag. For example, a 0.5% increase in carbon for Slag #2 equals 4.57% carbonization or 0.95 fractional conversion as shown in equations 1 and 2.

$$\frac{(\%C)(Ca_{MW})}{(C_{MW})(Wt.FractionCaO)(Ca_{MW}/CaO_{MW})} = \frac{(0.5)(40)}{(12)(0.513)(40/56)} = 4.57\% \tag{1}$$

$$(1 - Wt.FractionCarbonization) = (1 - 0.01 * 4.57) = 0.943 \tag{2}$$

The results indicate that particle size has a significant influence on the rate of carbonization. Comparing the 0.06 mm, 0.2 mm, 0.5 mm, and 1.25 mm particle sizes tested for Slag #1 (Figure 4, left) showed that the times to reach 6% carbonization were approximately 20 minutes, 800 minutes, 1500 minutes, and 4200 minutes, respectively. The data for Slag #2 shows a similar trend as shown in Figure 4 (right). The times for the four sizes to reach 1% carbonization are 1 minute, 10 minutes, 250 minutes, and 4000 minutes, respectively. All curves show an initial period of rapid carbonization followed by a leveling of the rate as indicated by a curving upward slope for the lines on each plot.

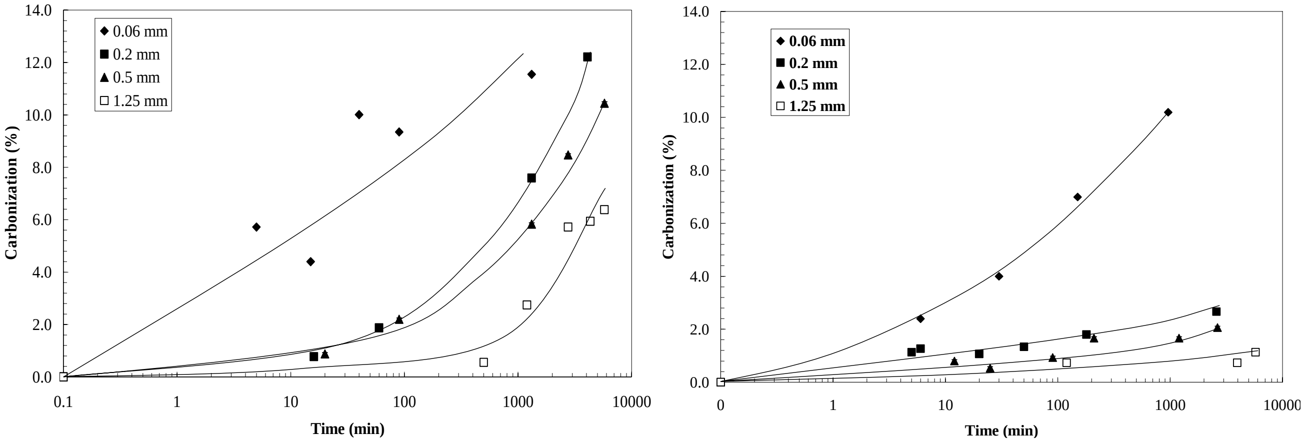

Figure 4 Degree of carbonization for slags #1 (left) and #2 (right) at four size fractions versus time (log scale)

Macroscopic observation (Figure 5) showed that slag samples initially had a small amount of surface carbonization (white spots) as a result of handling and air/moisture exposure during storage before the testing commenced. Slag samples taken after two hours in the flask study (pH 5.5-5.7) showed a significant increase in carbonization, as indicated in Figure 5 by the increase of white spots on the surface. Additional reaction time, from 48-96 hours, showed that the entire surface of the slag particle was carbonized as indicated by a white crust covering the entire particle surface.

Figure 5 Particles of Slag #2 (1000-1500 µm) before the reaction with CO_2/water (left),
after two hours of reaction (center), and after 96 hours of reaction (right)

Optical microscopy and scanning electron microscopy (SEM) was used for topological analysis of the resultant carbonate layers, as shown in Figure 6. As slag particles exhibit a very porous structure, interconnected channels allow surface reactions to take place deep inside the slag particle as shown in Figure 6 (upper left). A cross-sectional sample of slag allowed to react for two days showed a 10-20 µm thick carbonate layer on the surface, which extended into internal pores with sizes up to 100 µm. SEM analysis showed that the outside layer consisted of plate-like crystals in a high porosity structure with 1-3 µm pore size (Figure 6, upper right). Energy dispersive X-ray spectroscopy (EDS) analysis of the plates showed them to be composed primarily of Ca, O, and C, indicating a composition of calcium carbonate (Figure 6, bottom left). Internal surfaces that were connected to the surface through porosity channels were exposed through crushing. These surfaces showed a reaction layer with a significantly different structure of much smaller plates packed closer together (Figure 6, bottom right).

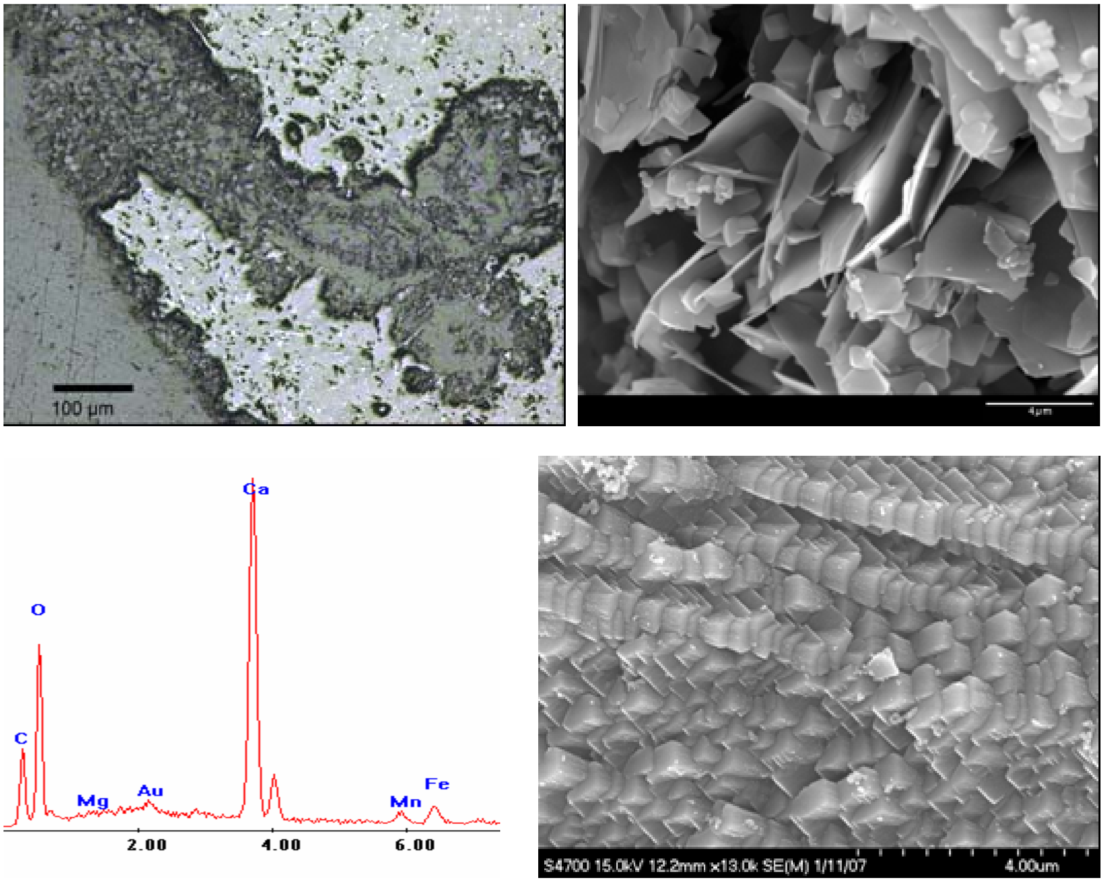

Figure 6 Optical image from Slag #2 (400-500 µm particle after 48 hours reaction time) showing the cross section of the internal pore structure (upper left), and SEM image showing the external surface carbonate layer (upper right) along with EDS analysis (bottom left), and the internal surface (pore) carbonate layer (bottom right)

A shrinking core model for heterogeneous reactions was used for analysis of experimental flask data and to determine the rate-limiting mechanism.[13] The three possible mechanisms include the reaction of the calcium at the slag surface with the aqueous carbonic acid ions (HCO_3^- and CO_3^{2-}), mass transport of the aqueous carbonic acid ions through the boundary layer, or diffusion through the porous product layer ($CaCO_3$) on the slag particle surface. Figure 7 shows the time required to achieve the same fractional conversion (8% carbonization) for different size fractions of Slag #1. The fractional conversion is heavily controlled by the particle size, and a linear approximation shows proportionality to the square root of time, indicating that product layer diffusion is the controlling rate step. The layer of calcium carbonate that forms on the surface retards the diffusion of both the alkaline ions to the slag particle surface and the carbonic acid ions into the slag particle. When the diffusion of the reactant through the product layer is limiting, Equations 3 shows the dependence on the molar transport of bulk fluid reactant A ($-dN_A/dt$, mol/sec) through the product layer of a particle with surface area $4\pi r^2$ (r is radius in cm) and effective diffusivity D_e (cm²/s).[13] The term C_A (mol/cm³) is the concentration of the reactant, which is a function of radius. At the radius of the unreacted core C_A is zero, while at the outer radius of the product layer (in contact with surrounding fluid), C_A is the concentration of the reactant ions in the bulk fluid. The gradient can be assumed fixed as the volume of the bulk fluid is much more than that of the particle, and with stirring of the fresh fluid is constantly being delivered to the particle surface.

$$\frac{-dN_A}{dt} = (4\pi r^2)(-D_e \frac{dC_A}{dr}) \qquad (3)$$

Given a constant gradient of bulk reactant A (carbonic acid ion) and constant effective diffusivity, the time to deliver a fixed number of moles of bulk reactant A (carbonic acid ion) through the product layer ($CaCO_3$) is proportional to the square of the radius.

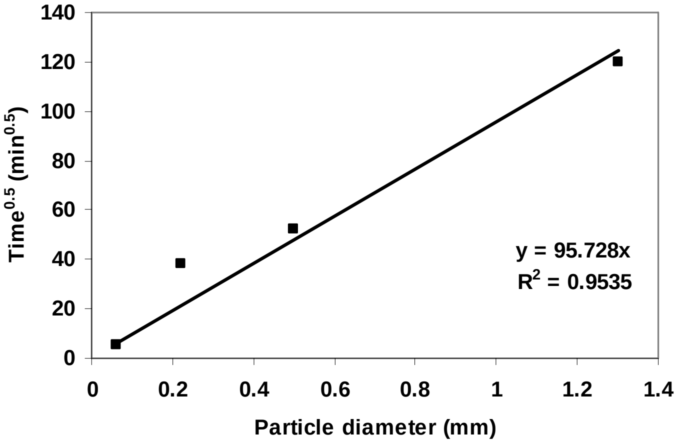

Figure 7 Analysis of the time required to achieve the same carbonization rate (8%) for different particle sizes of Slag #1 shows a reaction rate relationship proportional to (time)$^{0.5}$

With diffusion of carbonic acid ions through the product layer as the rate limiting step, the reaction time t (sec) can be expressed by the shrinking core model (Equation 4) as a function of the particle initial radius R (cm) and the unreacted core radius r (cm).[13]

$$t = \frac{\rho_B R^2}{6bDC}\left[1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3\right] \tag{4}$$

In this equation, ρ_B is the molar density of the product (mol/cm³), b is the stoichiometry coefficient, D is the diffusion coefficient (cm²/sec), and C is the molar concentration of the reactant in the aqueous solution (mol/cm³). Equation 4 was used to calculate the fraction converted to carbonate as a function of time, as well as the average thickness of the carbonized layer. The experimental data were fit to this equation to yield a diffusion coefficient of 5×10^{-9} cm^{2}sec^{-1} for Slag #1 (Figure 8, left) and Slag #2 (Figure 8, right). A decrease in the carbonate formation rate at extended reaction times is due to decreasing porosity of the carbonized layer (illustrated in Figure 6, bottom right), which will lower the diffusion rate.

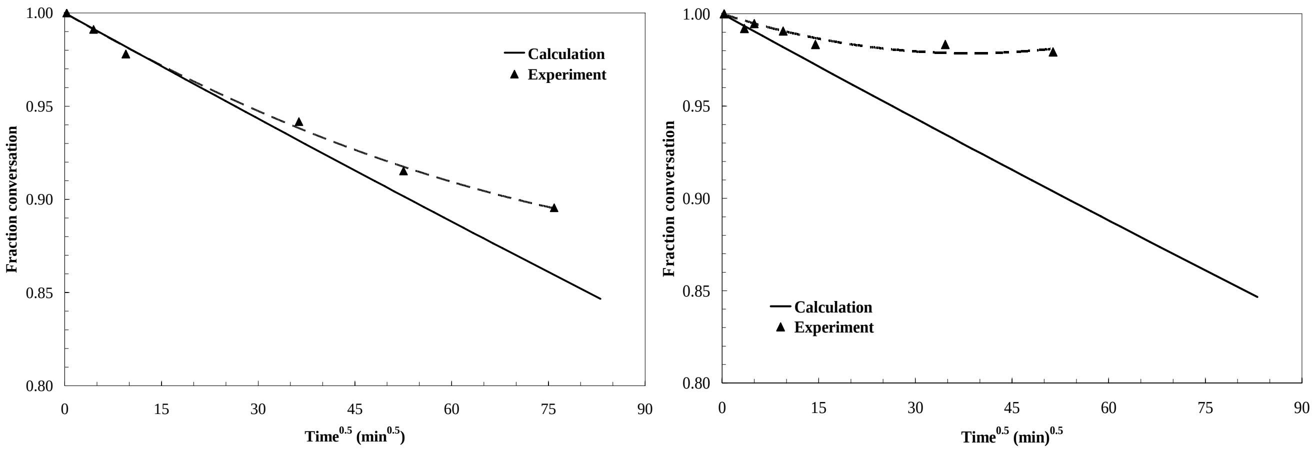

Figure 8 Comparison of calculated and experimental data for the carbonization of Slag #1 (left) and Slag #2 (right), each with an average particle diameter of 0.5 mm

In the two-stage reactor study experiments, all three slags listed in Table 1 were compared to pure lime. Figure 9 shows the results of a test with Slag #2 (200 g @ <3.2 mm) in tap water (20 liters). As water was added to the slag, calcium ions dissolved into solution, rapidly increasing the pH to nine. The resultant alkaline solution was pumped to Reactor 2 at 1.0 liter/min. Carbon dioxide was introduced into Reactor 2 at 1.5 g/min leading to a drop in pH by neutralization from the resultant carbonic acid. The pH of Reactor 1 dropped after a few minutes because that was the point of CO_2 introduction and this reactor has a small residence time (two minutes).

The pH of Reactor 2 dropped more slowly because the neutralized liquor had to recirculate back from Reactor 1, and Reactor 2 has a much larger residence time (~20 minutes). Figure 9 shows the comparison of times to reach the same pH (neutral).

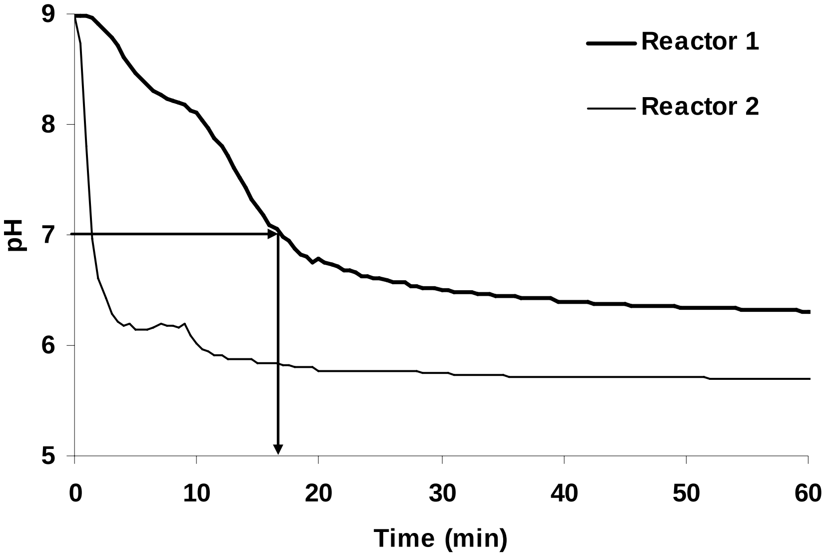

Figure 9 Changing pH of aqueous solutions in reactors during carbonization (200 g of crushed -3.2 mm Slag #2, -3.2 mm, 1.5 g/min flow rate CO_2)

Figure 10 contains a similar plot showing a comparison of all three slags with the same process parameters (200 g slag @ <3.2 mm in 20 liters tap water). Calcium content in the slag is directly proportional to the neutralization time. Slag #3 (51.3% CaO) took ~30 minutes to neutralize compared with Slag #2 (49.9% CaO) at ~17 minutes and Slag #1 (32.1% CaO) at ~11 minutes. The dramatic increase in neutralization time from Slag #2 to Slag #3, both of which have a similar CaO contents, is due to the influence of particle size distribution (PSD). Slag #3 has a much larger amount of fine material, with ~65% <100 µm compared with 5% passing the same size for Slag #2. The smaller PSD results in a much higher surface area for a reaction to take place, which proportionally increases the amount of calcium entering the solution during the same time period.

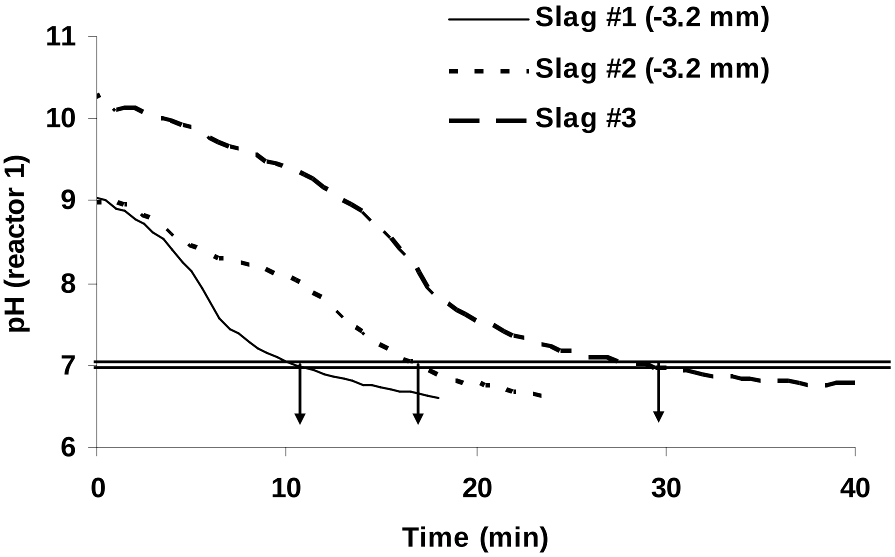

Figure 10 Comparison of neutralization time for the three slags tested in water (200 g slag, <3.2 mm) and reacted with carbon dioxide (1.5 g/min)

Figure 11 shows the degree of carbonization after 24 hours in the two-stage system for the three slags compared with lime. The test basis consisted of 200g of each respective material mixed in water at the size fraction stated. The degree of carbonization was directly proportional to the CaO content. In addition comparing two materials with the same CaO content, the degree of carbonization was inversely proportional to the particle size. The degree of carbonization at 24 hours for the slag samples varied from 5% to 20%.

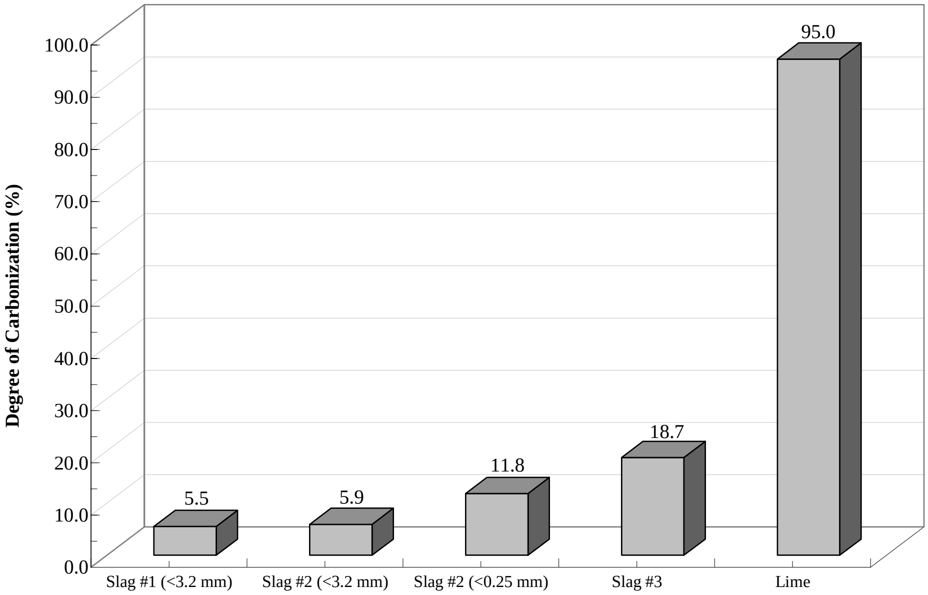

Figure 11 Comparison of slag and lime carbonization in a two-stage reactor system after 24 hours of treatment (200 g slag, 1.5 g/min CO_2)

To illustrate the reduction in slag reactivity due to formation of a carbonate product layer, a series of tests were conducted on fresh and aged slags as illustrated in Figure 12. For these tests, 2000g of freshly crushed Slag #1 (<3.2 mm) was soaked for 24 hours in Reactor 1, after which the liquor was reacted with CO_2 in Reactor 2. The resultant time to reach neutralization of the alkaline solution was 36 minutes. The slag was then subject to continuous treatment for five days in the two-stage system, after which the slag was soaked for 24 hours in Reactor 1. Using the same parameters, the liquor was reacted with CO_2 in Reactor 2. The neutralization time was decreased by 56% to 16 minutes, indicating the carbonate product layer was hindering the dissolution of alkaline ions into solution.

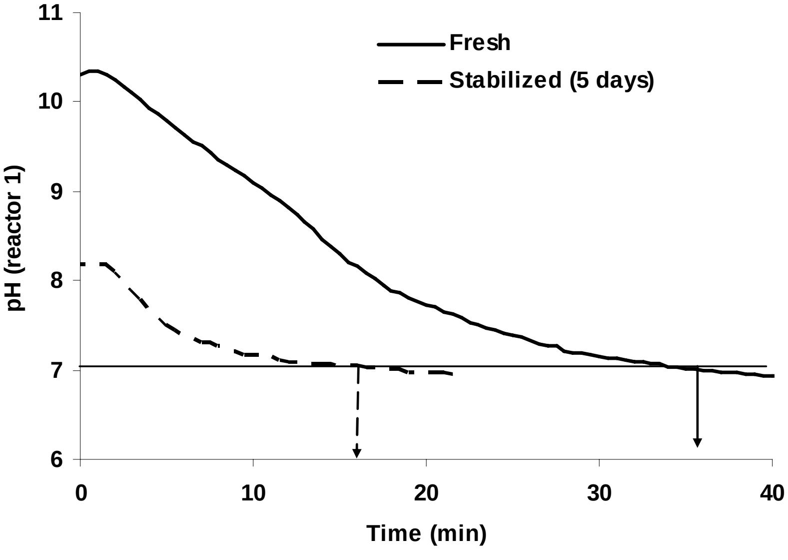

Figure 12 Comparison of neutralization time for Slag #1 in fresh crushed and aged conditions

CONCLUSIONS

Sequestration of carbon dioxide by steelmaking slag was studied for a three-phase system of industrial slag, water, and CO_2 gas. Slag-water slurries were reacted with CO_2 in laboratory flask tests showing that the degree of carbonization (formation of carbonate) is time- and particle size-dependent. The rate of carbonization fits well to the shrinking core model, showing that diffusion through the carbonate product layer is the rate limiting step with the reaction rate proportional to $(time)^{0.5}$. Testing in a two-stage wet reactor showed that degree of carbonization is proportional to slag alkaline content and particle surface area (i.e., reduction in particle size).

The testing of a bench-scale reactor prototype revealed the main process control parameters and will be used for industrial process scale-up.

ACKNOWLEDGEMENTS

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Mineralogical Sequestration of Carbon Dioxide through Aqueous Processing of Steelmaking Slag

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Keywords: Steelmaking Slag, CO_2, Sequestration, Kinetics, Shrinking Core Model

Abstract

Sequestration of carbon dioxide by steelmaking slag was studied for a three-phase system of industrial slag, water, and CO_2 gas. Slag-water slurries were reacted with CO_2 in laboratory batch tests showing that the degree of carbonization (formation of carbonate) is time and particle size-dependent. The rate of carbonization fits well to the shrinking core model, showing that diffusion through the carbonate product layer is the rate limiting step with the reaction rate proportional to the square root of time. Testing in a two-stage wet reactor showed that degree of carbonization is proportional to slag alkaline content and particle surface area (i.e., reduction in particle size).

Introduction

Carbon dioxide is generated directly from the furnaces used for iron and steel production, and indirectly from the electrical supply source, such as coal-burning power plants, which provide power to the mills. Steelmaking CO_2 emissions vary based on the production method. For example, integrated steel mills generate more CO_2 per ton of steel than mini-mills due to the use of coke and iron-making pre-processes. In 2000, U.S. integrated mills emitted 33.5 million tons of CO_2 in carbon equivalent (CE) units, of which 64% was generated through the production and use of coke[1]. During the same year, U.S. mini-mills generated 13.7 million tons of CO_2 CE, where 80% was generated from the supply power plants[1]. In 2000, the U.S. steel industry produced an average of 0.42 tons of CO_2 CE per ton of steel shipped approaching the theoretical CO_2 generation theoretical minimum of 0.40 tons CE per ton of steel. Energy reduction provides the most direct method for reducing CO_2 emissions. However, most U.S. steel producers have optimized energy use to lower power costs, and further significant step changes are not expected. If reduction in CO_2 emissions becomes a governmental mandate, then source point mitigation to capture (sequester) the produced CO_2 will be required.

The aim of this project is to develop a functional sequestration system using steelmaking slag to permanently capture carbon dioxide emitted in steelmaking offgas. A parallel benefit of slag-based CO_2 sequestration is chemical stabilization of the slag compounds subject to swelling. The stabilized slag is rendered immune to end-use swelling or leaching, thus eliminating the need for stockpile aging prior to commercial use.

The potential of steelmaking slag to react with CO_2 to form permanent carbonate compounds is derived from slag's high concentration of alkaline earth metal oxides. The two most important oxides are CaO (lime) and MgO (magnesia), which range from 30-50% and 10-12% of the slag mass, respectively[2]. Both lime and magnesia readily form hydroxides or carbonate compounds under atmospheric conditions, with the carbonate compounds forming the most thermodynamically stable phase. Previous work has shown that the slag produced during steelmaking has the potential of sequestering 5.0-10% of the BF-BOF CO_2 emissions and 28-34% of EAF carbon dioxide emissions. In addition, the estimated 15-20 kg of LMF slag produced per ton of steel has the potential of capturing an additional 1.0-1.3% of BOF and 7.8-10.4% of EAF CO_2 emissions. Thus, the total sequestration potential for steelmaking slag is 6-11% of the CO_2 emitted from integrated mills and 35-45% emitted from scrap-based steelmakers[3]. A furnace offgas CO_2 capture and sequestration system will most likely be installed after the baghouse to prevent contamination of the slag with baghouse dust, as shown in Figure 1. Offgas conditions exiting the baghouse have been estimated to be 90-150°C, with a peak CO_2 concentration of 10-11 vol.% and an average of 4-5 vol.%[2].

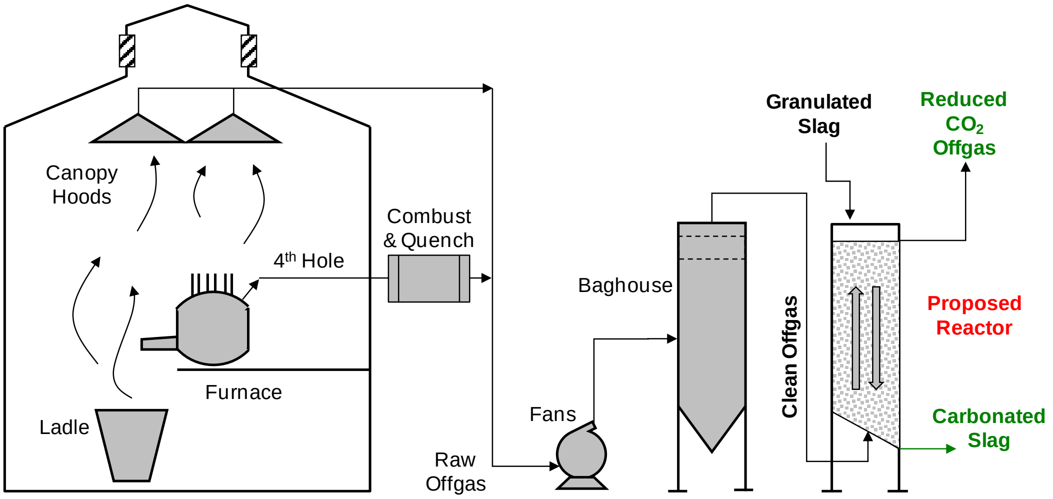

Figure 1 Schematic of CO_2 Capture System for EAF Offgas

Two different system concepts are being tested for the proposed slag-offgas reactor. The first concept is a dry process using a plug flow or rotary reactor as detailed previously[2]. The second concept, which is the focus of the current study, includes a wet process whereby slag is mixed with water to form a slurry through which offgas is bubbled. A two-stage system design allows for aqueous dissolution of the alkaline oxides in the first stage, followed by a reaction of the resultant aqueous liquor with CO_2 in a separate vessel or location. Compared with a dry system, wet processing has a much higher CO_2 reaction rate, thus allowing for a smaller reactor vessel. In addition, catalytic agents such as carbonic anhydrase may be added to form an aqueous biomimetic process that has been shown to provide more than two orders of magnitude rate increase in alkaline-earth carbonate formation in experiments for wet industrial CO_2 scrubbers[4].

Slag Analysis and Preparation

To assess the feasibility of carbon dioxide sequestration with steelmaking slag, a series of experiments was undertaken to measure the kinetic reaction rate in an aqueous system. Three industrial slag samples were obtained from the project partners. Table 1 lists the slag compositions as determined by X-ray fluorescence (XRF) spectroscopy. Slag #1 is from an EAF mill and contains 32.1 wt.% CaO. Slags #2 and #3 are LMF slags from EAF mills and contain higher CaO content plus Al_2O_3/SiO_2 in proportion to their respective steel deoxidation method. Steelmaking slag contains very little free lime (CaO) or free magnesia (MgO), thus these compounds cannot be considered in the pure state. Predominately CaO and MgO are present as silicate, aluminate, or ferrite phases. Small amounts of free alumina (Al_2O_3), wustite (FeO), and silica (SiO_2) have been found, but these do not contribute to carbon dioxide sequestration.

Table 1 Compositions of steelmaking slags (wt.%) used in the aqueous tests as determined by XRF

Oxides	***#1 (EAF)***	***#2 (LMF) Al-Killed***	***#3 (LMF) Si-Killed***
CaO	32.1	49.9	51.3
SiO_2	19.4	4.5	28.3
Al_2O_3	8.6	32.3	4.9
TiO_2	0.4	0.3	0.3
MgO	9.4	4.3	4.3
MnO	6.8	0.8	1.3
Fe_2O_3	26.4	6.3	5.5
SO_3	0.6	1.0	1.6
$\mathbf{V_{ratio}}$	1.7	1.4	1.5

All slag samples were obtained in 18-22 kg lots from steel plant stockpiles. The slags were obtained prior to on-site processing (<24 hours after production) in order to ensure minimal reaction with local ambient conditions. All slag samples were crushed to provide fresh surfaces for testing the reaction rate, as well as to provide a range of slag particle sizes from which to test the surface area effects. Slags #1 and #2 were crushed in a laboratory jaw crusher followed by a roll crusher to pass a 6-mesh sieve size (3.35 mm). Slag #3 is a falling slag, thus self-comminuted, and was used in the raw condition. Figure 2 shows the particle size analysis of slags #1 and #2 after crushing, along with Slag #3 in the raw state. Particle size analysis was obtained using a U.S. mesh series of 20 cm (8") sieves on a vibratory shaker.

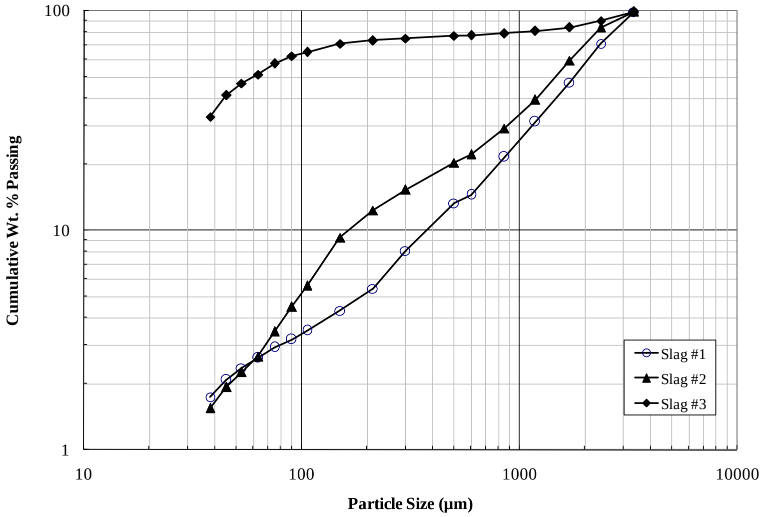

Figure 2 Particle size analysis of crushed (slags #1 & #2) and raw steelmaking slag (Slag #3) used in aqueous tests

Batch Tests

Laboratory batch tests were initially used to measure the effect of surface area and alkaline content on reaction rate between the slag samples and carbon dioxide. After crushing, each slag type was graded into four size fractions (45-75 µm, 150-250 µm, 425-589 µm, and 1000-1500 µm) which provided a wide range of surface area for testing. Thirty grams of each size fraction was mixed with 250 g of deionized water in an Erlenmeyer flask. Standard bottle grade CO_2 was introduced into the mixture through a 1 mm glass capillary tube. Each sample was allowed to react for a designated period of time, after which the CO_2 flow was stopped. The slurry mixture was filtered through 11 µm filter paper with a vacuum pump. The filtrand was dried at 180 °C and analyzed for carbon content with a LECO$^{©}$ carbon analyzer (combustion/IR) and/or a thermogravimetric analysis (TGA) device. An example of TGA analysis is given in Figure 3, where weight loss at low temperatures (<600 °C) indicates hydroxide decomposition and weight loss at high temperatures (>600 °C) is associated with carbonate decomposition.

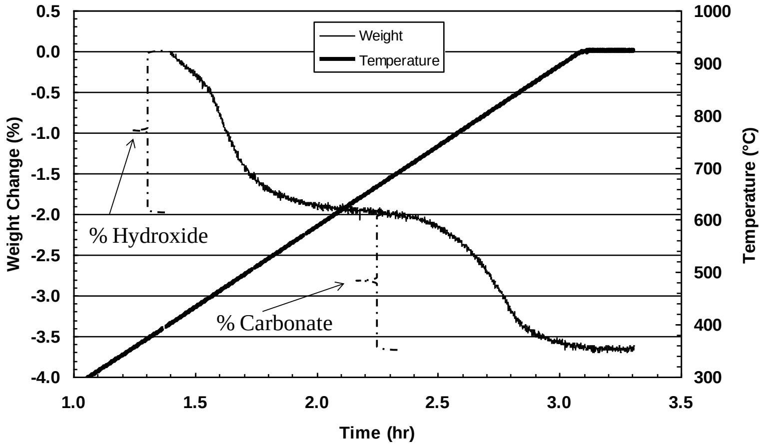

Figure 3 Example of TGA test results for the measurement of slag carbonation from a batch test

Figure 4 presents the measured degree of carbonization from flask tests for Slag #1 and Slag # 2 at several size ranges. Note that the data are shown with a logarithmic time scale. The degree of carbonization is the amount of CaO initially present in the slag converted to $CaCO_3$. For example, a 0.5% increase in carbon for Slag #2 equals 4.6% carbonization or 0.95 fractional conversion. The results indicate that particle size (surface area) has a significant influence on the rate of carbonization. Comparing the 0.06 mm, 0.2 mm, 0.5 mm, and 1.25 mm particle sizes tested for Slag #1 (Figure 4, top) showed that the times to reach 6% carbonization were approximately 20 minutes, 800 minutes, 1500 minutes, and 4200 minutes, respectively. The data for Slag #2 shows a similar trend as shown in Figure 4 (bottom). The times for the four sizes to reach 1% carbonization are 1 minute, 10 minutes, 250 minutes, and 4000 minutes, respectively. All curves show an initial period of rapid carbonization followed by a leveling of the rate as indicated by a curving upward slope for the lines on each plot.

Macroscopic observation (Figure 5) shows that slag samples initially had a small amount of surface product layer (white spots) as a result of handling and air/moisture exposure during storage before the testing commenced. Slag samples taken after two hours in the flask study (pH 5.5-5.7) showed a significant increase in product layer, as indicated in Figure 5 by the increase of white spots on the surface. Additional reaction time, from 48-96 hours, showed that the entire surface of the slag particle was covered by the product layer.

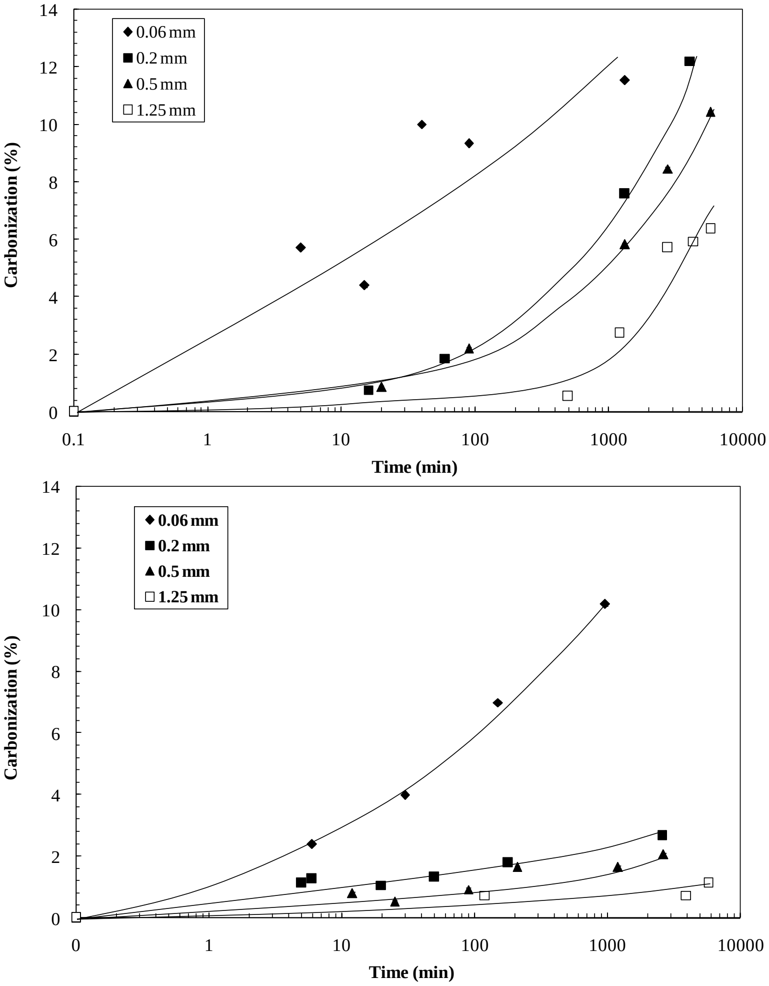

Figure 4 Degree of carbonization for Slag #1 (top) and Slag #2 (bottom) at four size fractions versus time

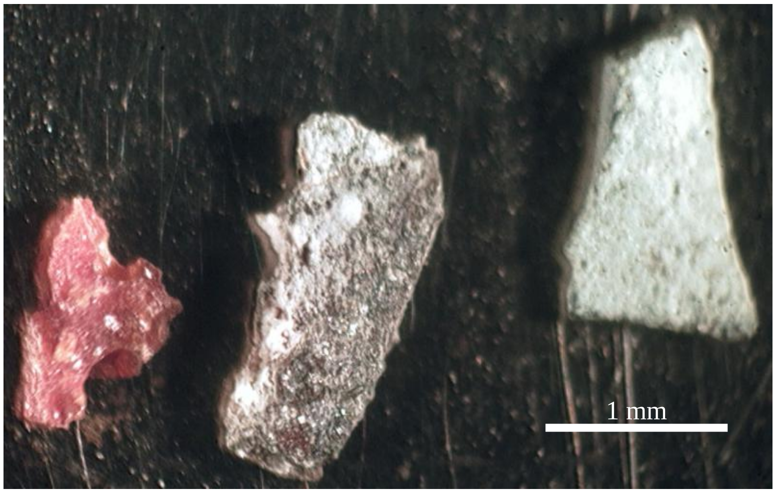

Figure 5 Particles of Slag #2 (1000-1500 μm) as received (left), after two hours of reaction (center), and after 96 hours of reaction (right)

Optical microscopy and scanning electron microscopy (SEM) was used for topological analysis of the resultant product layers, as shown in Figure 6. As slag particles exhibit a very porous structure, interconnected channels allow surface reactions to take place deep inside the slag particle as shown in Figure 6 (upper left). A cross-sectional sample of slag allowed to react for two days showed a 10-20 µm thick product layer on the outer surface, which extended into internal pores with sizes up to 100 µm. SEM analysis showed that the outside layer consisted of overlapping plate-like crystals in a high porosity structure with 1-3 µm pore size (Figure 6, upper right). Energy dispersive X-ray spectroscopy (EDS) analysis of the plates showed them to be composed primarily of Ca, O, and C, indicating a composition of calcium carbonate (Figure 6, bottom left). Internal surfaces that were connected to the surface through porosity channels were exposed through crushing. These surfaces showed a reaction layer with a significantly different structure of much smaller plates packed closer together (Figure 6, bottom right).

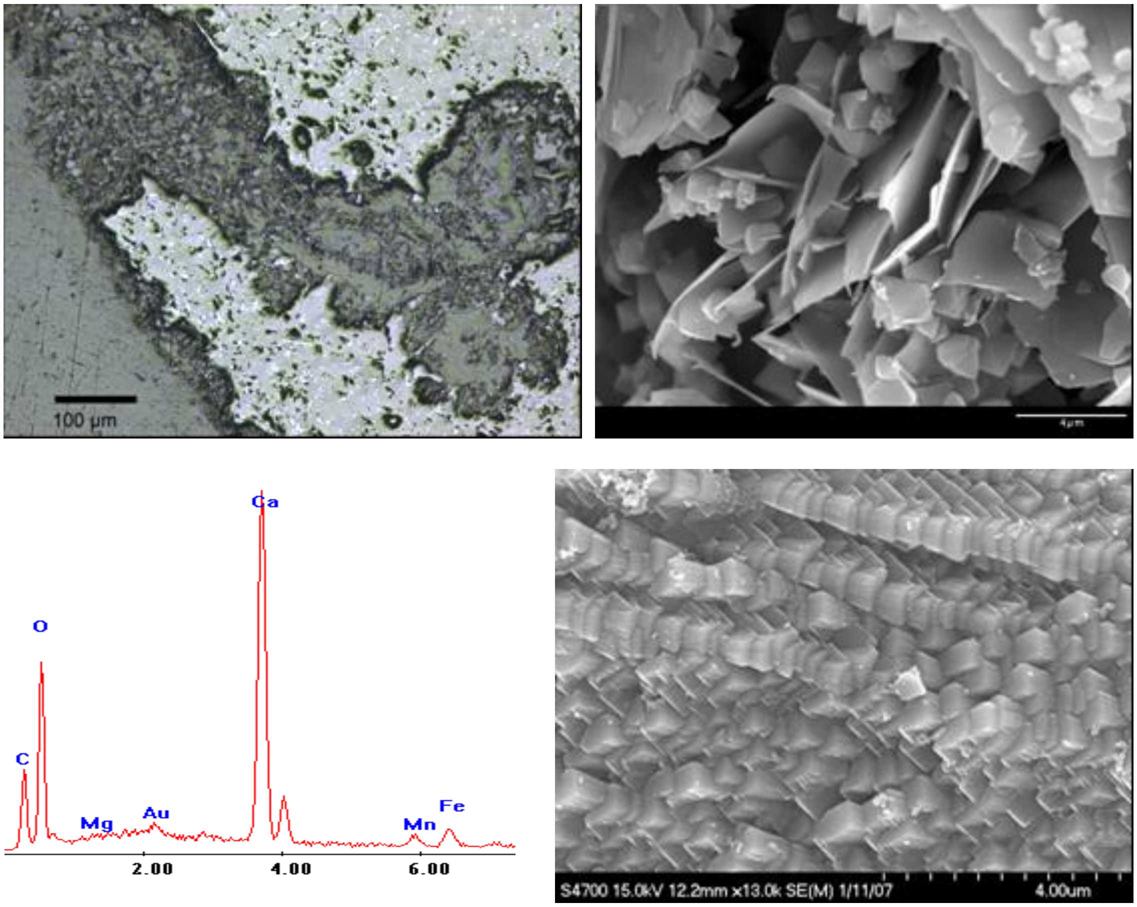

Figure 6 Optical image from Slag #2 (400-500 µm particle after 48 hours reaction time) showing the cross section of the internal pore structure (upper left), and SEM image showing the external surface carbonate layer (upper right)along with EDS analysis (bottom left), and the internal surface (pore) carbonate layer (bottom right)

The shrinking core model for heterogeneous reactions was used to analyze the batch test data and to determine the rate-limiting mechanism[5]. Three possible rate-limiting mechanisms include; (a) reaction of Ca^{2+} ions with the aqueous carbonic acid ions (HCO_3^- and CO_3^{2-}), (b) mass transport of the aqueous carbonic acid ions through the boundary layer, or (c) diffusion of Ca^{2+} through the product layer ($CaCO_3$) on the slag particle surface. Figure 7 shows the time required to achieve the same fractional conversion (8% carbonization) for the different size fractions tested of Slag #1.

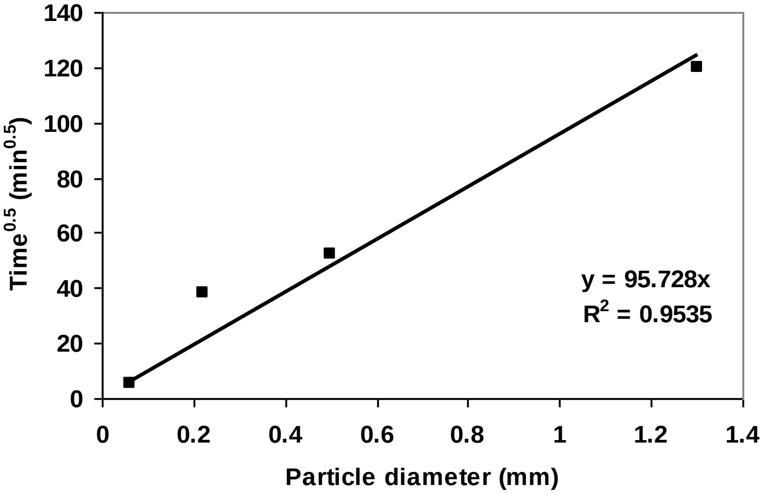

Figure 7 Analysis of the time required to achieve the same carbonization rate (8%) for different particle sizes of Slag #1 shows a reaction rate relationship proportional to (time)$^{0.5}$

The fractional conversion is heavily controlled by the particle size (surface area), and a comparison to the square root of time shows a linear proportionality, indicating that product layer diffusion is the controlling rate step. The layer of calcium carbonate that forms on the surface retards the diffusion of both the alkaline ions outward from the slag to the aqueous bulk, and carbonic acid ions inward to the slag particle surface. When the diffusion of reactants through the product layer is limiting, Equation 1 shows the dependence on the molar transport of bulk fluid reactant A ($-dN_A/dt$, mol/sec) through the product layer of a particle with surface area $4\pi r^2$ (r is radius in cm) and effective diffusivity D_e (cm²/s)[5]. The term C_A (mol/cm³) is the concentration of the reactant, which is a function of radius. At the radius of the unreacted core C_A is zero, while at the outer radius of the product layer (in contact with surrounding fluid), C_A is the concentration of the reactant ions in the bulk fluid. The gradient can be assumed fixed as the volume of the bulk fluid is much more than that of the particle, and with stirring of the fresh fluid is constantly being delivered to the particle surface.

$$\frac{-dN_A}{dt} = (4\pi r^2)(-D_e \frac{dC_A}{dr}) \tag{1}$$

Given a constant gradient of bulk reactant A (carbonic acid ion) and constant effective diffusivity, the time to deliver a fixed number of moles of bulk reactant A (carbonic acid ion) through the product layer ($CaCO_3$) is proportional to the square of the radius. Integration and rearrangement of Equation 1 provides a direct relationship between the reaction time t (sec) as a function of the particle initial radius R (cm) and the unreacted core radius r (cm), as given in Equation 2 [5].

$$t = \frac{\rho_B R^2}{6bDC}\left[1 - 3\left(\frac{r}{R}\right)^2 + 2\left(\frac{r}{R}\right)^3\right] \tag{2}$$

In Equation 2, ρ_B is the molar density of the product (mol/cm^3), b is the stoichiometry coefficient, D is the diffusion coefficient (cm^2/sec), and C is the molar concentration of the reactant in the aqueous solution (mol/cm^3). Equation 2 was used to calculate the fraction converted to carbonate as a function of time, as well as the average thickness of the carbonized layer. The experimental data were fit to this equation to yield a diffusion coefficient of $5x10^{-9}$ cm^2sec^{-1} for Slag #1 (Figure 8, top) and Slag #2 (Figure 8, bottom) during the initial period of time. A decrease in the carbonate formation rate was observed after ~30 minutes for Slag #1 and ~15 minutes for Slag #2. The reduced carbonate formation rate is due to decreasing porosity of the product layer as the slag pores fill with carbonate (illustrated in Figure 6, bottom right). The diffusion coefficient lowers to $(2\text{-}10)x10^{-9}$ cm^2sec^{-1}.

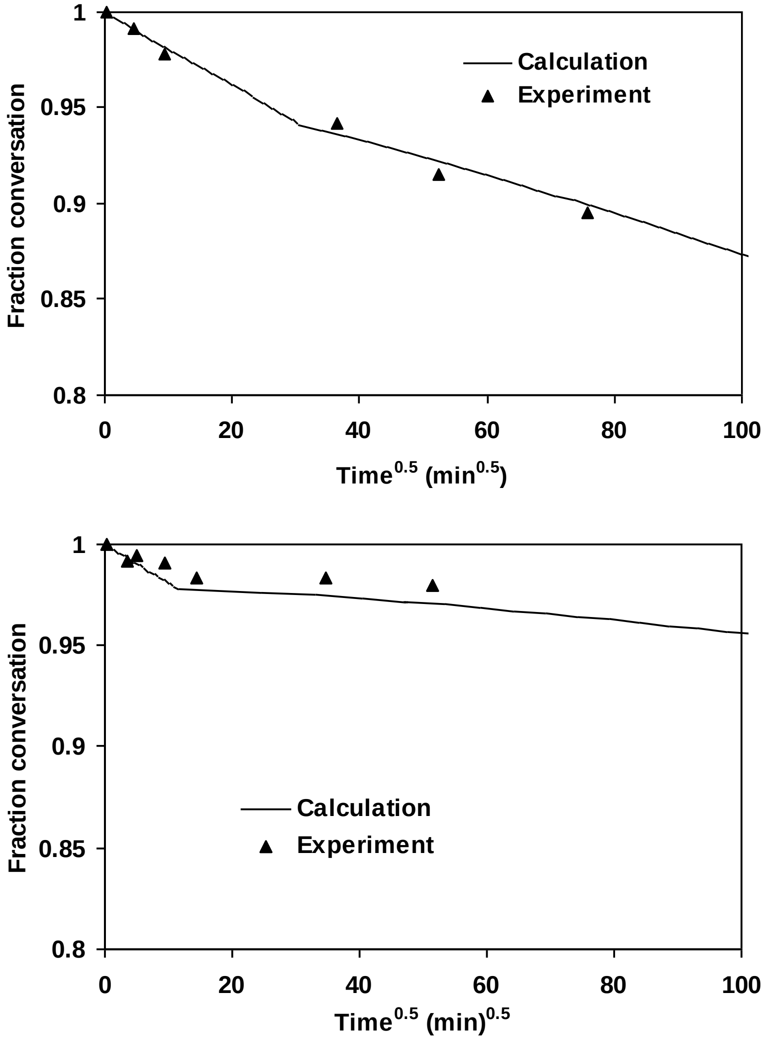

Figure 8 Comparison of calculated and experimental data for the carbonization of Slag #1 (top) and Slag #2 (bottom), each with an average particle diameter of 0.5 mm

Because slag reactivity is dependent upon true surface area, the specific surface area (m^2/g) was measured for the slag particle sizes using BET gas sorption. A comparison of measured specific surface area with calculated (hypothetical smooth uniform spheres) in Figure 9 showed that the LMF slag particles (Slag #2 and #3) had 10-50 times the surface area, while the EAF slag particles (Slag #1) have over 100 times the surface area. The higher surface area of

Slag #1compared with Slag #2 led to the longer transition time for decrease in the diffusion coefficient (~30 minutes vs. ~15 minutes) as more surface pores had to be filled in.

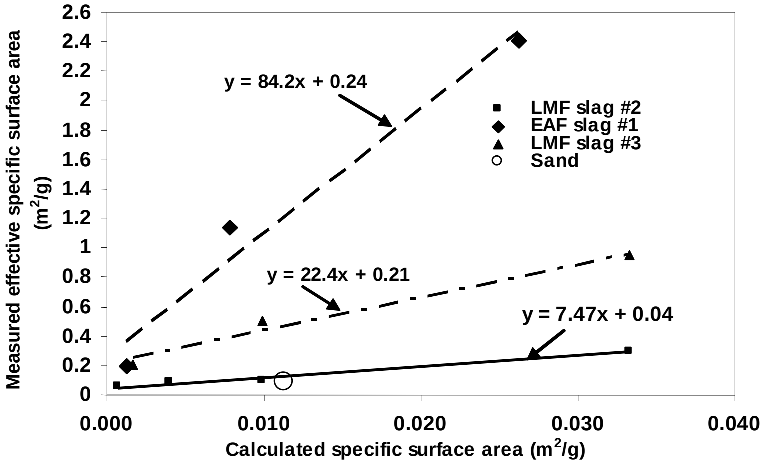

Figure 9 Comparison of calculated (uniform sphere model) with measured specific surface of different slags

Two-Stage Reactor Tests

A bench scale slurry reactor apparatus was fabricated from two plastic tanks connected in a loop arrangement that allowed the continuous exchange of aqueous solution via a positive displacement pump (Figure 10). Reactor 1 contained two kilograms of slag mixed with 20 liters of water. The aqueous liquor was exchanged at varying rates with Reactor 2, which has a two-liter volume. Standard bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles and to allow intimate mixing between the gas and alkaline solution. A multi-channel pH meter was used to measure the pH level in both reactors in-situ and allow for manual control of the process. At the completion of each test, a sample of the slurry mixture was filtered through 11 µm filter paper with a vacuum pump. The filtrand was dried at 180 °C and analyzed for carbon content with a LECO© carbon analyzer (combustion/IR) and/or thermogravimetric analysis (TGA) device.

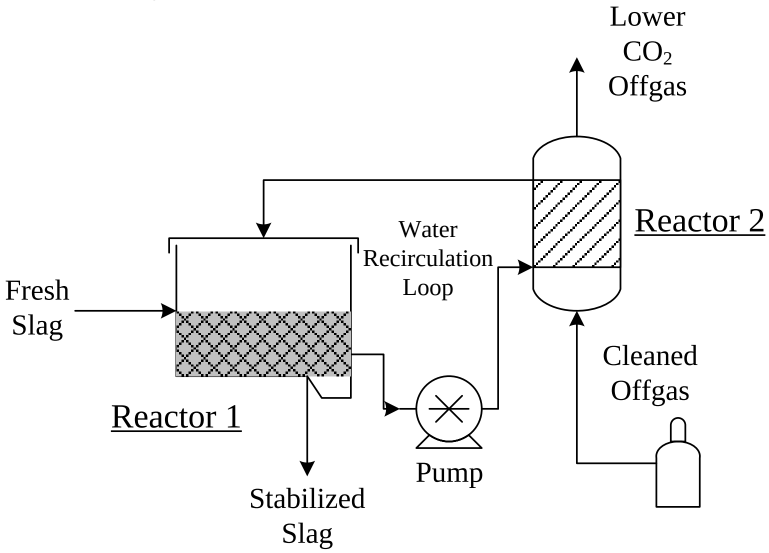

Figure 10 Flow schematic of two-stage slurry reactor contact of slag-water-CO_2

The apparatus was designed as a prototype for scale-up to industrial use. The two-stage reactor design allows for simpler retrofit into existing slag and offgas treatment facilities by allowing alkaline leaching (Reactor 1) and CO_2 absorption/reaction (Reactor 2) to take place in separate facilities. The rate of solution exchange and individual reactor volumes can be scaled to match the kinetic reaction rate and slag/offgas volumes.

In the two-stage reactor study experiments, all three slags listed in Table 1 were compared to pure lime. Figure 11 shows the results of a test with Slag #2 (200 g @ <3.2 mm) in tap water (20 liters). As water was added to the slag, calcium ions dissolved into solution, rapidly increasing the pH to nine. The resultant alkaline solution was pumped to Reactor 2 at 1.0 liter/min. Carbon dioxide was introduced into Reactor 2 at 1.5 g/min leading to a rapid drop in pH by neutralization from the resultant carbonic acid. The pH of Reactor 2 dropped after a few minutes because that was the point of CO_2 introduction and this reactor has a small residence time (two minutes). The pH of Reactor 1 dropped more slowly because the neutralized liquor had to recirculate back from Reactor 2, and Reactor 1 has a much larger residence time (~20 minutes). Figure 11 shows the comparison of times to reach the same pH (neutral).

Figure 12 contains a similar plot showing a comparison of all three slags with the same process parameters (200 g slag @ <3.2 mm in 20 liters tap water). Calcium content in the slag strongly influences the neutralization time with slag #3 (51.3% CaO) taking ~30 minutes to neutralize compared with Slag #2 (49.9 wt.% CaO) at ~17 minutes and Slag #1 (32.1 wt.% CaO) at ~11 minutes. The dramatic increase in neutralization time from Slag #2 to Slag #3, both of which have a similar CaO contents, is due to the influence of particle size distribution (PSD). Slag #3 has a much larger amount of fine material, with 65 wt.% <100 µm compared to 5 wt.% <100 µm for Slag #2. The smaller PSD results in a much higher surface area for the reaction to take place, which correspondingly increases the amount of calcium entering the solution during the same time period.

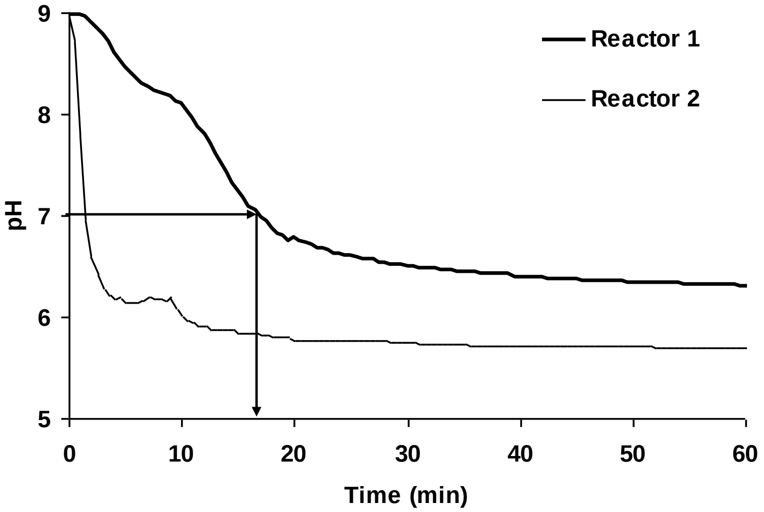

Figure 11 Changing pH of aqueous solutions in reactors during carbonization (200 g of crushed -3.2 mm Slag #2, -3.2 mm, 1.5 g/min flow rate CO_2)

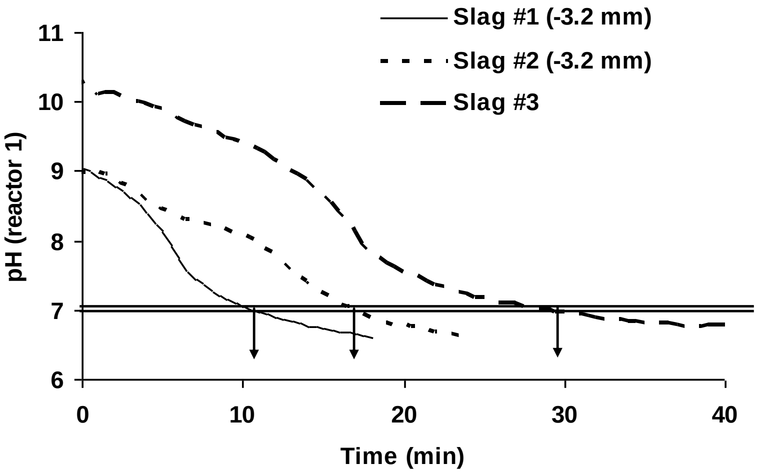

Figure 12 Comparison of neutralization time for the three slags tested in water (200 g slag, <3.2 mm) and reacted with carbon dioxide (1.5 g/min)

Figure 13 shows the degree of carbonization after 24 hours in the two-stage system for the three slags compared with lime. The test basis consisted of 200 g of each respective material mixed in water at the size fraction stated. The degree of carbonization generally increased with the CaO content. In addition, comparing two materials with the same CaO content, the degree of carbonization was inversely related to the particle size. The degree of carbonization at 24 hours for the slag samples varied from 5% to 20%.

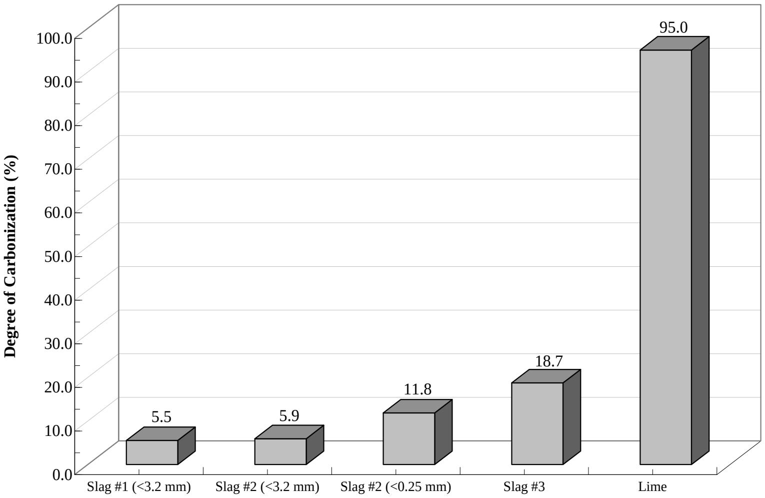

Figure 13 Comparison of slag and lime carbonization in a two-stage reactor system after 24 hours of treatment (200 g slag, 1.5 g/min CO_2)

To illustrate the reduction in slag reactivity due to formation of a carbonate product layer, a series of tests were conducted on fresh and aged slags as illustrated in Figure 14. For these tests, 2000 g of freshly crushed Slag #1 (<3.2 mm) was soaked for 24 hours in Reactor 1, after which the liquor was reacted with CO_2 in Reactor 2. The resultant time to reach neutralization of the alkaline solution was 36 minutes. The slag was then subject to continuous treatment for five days in the two-stage system, after which the slag was soaked for 24 hours in Reactor 1. Using the same parameters, the liquor was reacted with CO_2 in Reactor 2. The neutralization time was decreased by 56% to 16 minutes, indicating the carbonate product layer was hindering the dissolution of alkaline ions into solution.

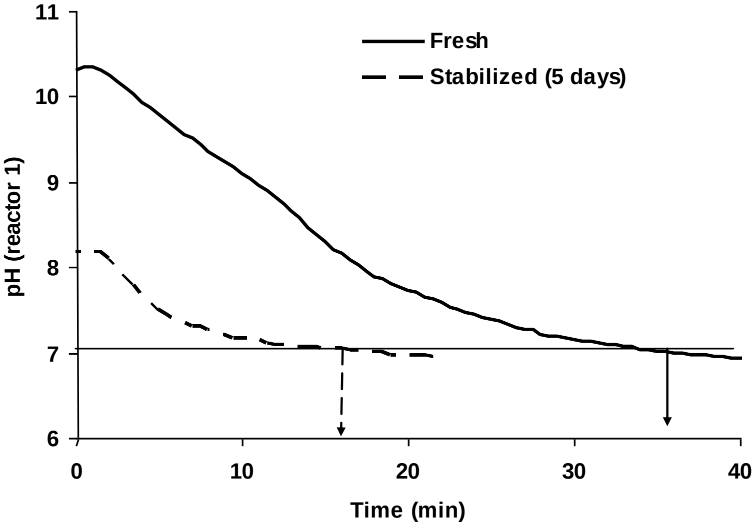

Figure 14 Comparison of neutralization time for Slag #1 in fresh crushed and aged conditions

Conclusions

Sequestration of carbon dioxide by steelmaking slag was studied for a three-phase system of industrial slag, water, and CO_2 gas. Slag-water slurries were reacted with CO_2 in laboratory batch tests showing that the degree of carbonization (formation of carbonate) is time- and particle size-dependent. The rate of carbonization fits well to the shrinking core model, showing that diffusion through the carbonate product layer ($CaCO_3$) is the rate limiting step with the reaction rate proportional to the square root of time. The calcium carbonate product layer consists of overlapping plates that increase in density with time. Testing in a two-stage wet reactor showed that degree of carbonization is dependent upon the slag alkaline content and particle surface area (i.e., reduction in particle size). The testing of a bench-scale reactor prototype allows the study of leaching and carbonation independently for scale-up to an industrial process model.

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Kinetics of Aqueous Leaching and Carbonization of Steelmaking Slag

S.N. LEKAKH, C.H. RAWLINS, D.G.C. ROBERTSON, V.L. RICHARDS,
and K.D. PEASLEE

Sequestration of carbon dioxide by steelmaking slag was studied in an atmospheric three-phase system containing industrial slag particles, water, and CO_2 gas. Batch-type reactors were used to measure the rate of aqueous alkaline leaching and slag particle carbonization independently. Four sizes of slag particles were tested for the Ca leaching rate in deionized water at a constant 7.5 pH in an argon atmosphere and for carbonate conversion with CO_2 bubbled through an aqueous suspension. Conversion data (fraction of Ca leached or converted to carbonate) were evaluated to determine the rate-limiting step based on the shrinking core model. For Ca leaching, the chemical reaction is the controlling mechanism during the initial period of time, which then switches to diffusion through the developed porous layer as the rate-limiting step. Carbonate conversion proceeded much slower than leaching conversion and was found to be limited by diffusion through the product calcium carbonate layer. The calculated value of diffusivity was found to be 5×10^{-9} cm^2/s, which decreased by an order of magnitude with increasing carbonization conversion as a result of changing density of the product layer. The experimental data fit the shrinking core model well after correction for the particle specific surface area.

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I. INTRODUCTION

THE United States produces 9 to 14 Mt of steelmaking slag annually, which represents approximately 10 to 15 wt pct of crude steel output.[1,2] Primary uses for steelmaking slag include high-quality mineral aggregate, Portland cement, soil conditioning, and pH neutralization of abandoned mine drainage.[3,4] The key factor prescribing slag use is the alkaline-earth metal (*e.g.*, Ca and Mg) oxide contents, which contribute to overall basicity and cementitious strength. However, as-produced steelmaking slag is chemically unstable as these oxides readily form hydroxides and carbonates through reaction with atmospheric gases. Both hydroxide and carbonate formation produce substantial mechanical swelling, leading to heave failure in confined construction applications; thus, many states dictate stockpile aging for 3 to 6 months prior to commercial use.[5,6]

Forced carbonation of steelmaking slag is a method to circumvent lengthy stockpile stabilization and provide the benefit of carbon dioxide sequestration. The conversion of CaO/MgO to carbonates serves both to stabilize the slag and to permanently capture and store the CO_2. Several research groups have started projects to determine the mechanisms involved in forced (accelerated) carbonation of steelmaking slag with the goal of using this material as a CO_2 sequestering agent. This work is an offshoot of a much larger-scale effort aimed at permanent geological sequestration of carbon dioxide with naturally occurring silicate or carbonate minerals.[7]

Huijgen and Comans measured the carbonation of steel slag in an autoclave reactor.[8,9] Particle size was found to have a strong effect on the extent of carbonation, while reactor temperature, reaction time, and CO_2 partial pressure had milder effects on Ca conversion. Carbonation was unaffected by stirring rate in the reactor, and Huijgen and Comans concluded that Ca diffusion through the product layer was the rate-limiting step. Huijgen and Comans concluded that their process can yield an 80 pct carbonation at relatively mild conditions (<38 μm, 200 °C, 1.0 MPa pCO_2, 15 minutes). In comparison with naturally occurring wollastonite ($CaSiO_3$), steel slag was able to sequester 11 times more CO_2 at ambient temperature. Eloneva *et al.* investigated acetic acid leaching of slag for extraction of Ca^{2+} to be used in producing precipitated calcium carbonate by reaction with CO_2 in a slurry crystallizer.[10] Leaching of slag resulted in extraction of 97 pct of the calcium ions compared to 38 pct extraction from wollastonite under the same conditions. Stolaroff *et al.* investigated the formation of dilute aqueous alkali-metal solution from steel slag that can be used to extract CO_2 from ambient air.[11,12] The rate and extent of calcium dissolution was found to be inversely related to

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particle size and pH, and near terminal concentration of Ca^{2+} may be reached in a few hours. Carbonation kinetics were not studied in this work; however, Huijgen and Comans suggest that Ca leaching and slag carbonation would occur simultaneously.

Extraction of CO_2 from steel manufacturing offgas using steelmaking slag is being studied to quantifying the extent and rate of carbonate formation under near-atmospheric aqueous conditions.[13] The value of CO_2 sequestration using steelmaking slag arises from its total carbonation potential and its ready availability as a co-product in steel production. A survey of industrial slags has found the CaO and MgO contents of BOF and EAF slags to average 30 to 50 wt pct and 10 to 12 wt pct, respectively.[13] Additionally, LMF slag contains 50 to 60 wt pct CaO and 10 to 12 wt pct MgO. The amount of slag produced per ton of steel is estimated at 75 to 150 kg for BOF, 65 to 80 kg for EAF, and 15 to 20 kg for LMF.[14] Production of a ton of steel generates 519 kg CO_2 carbon equivalent (CE) for BOF and 119 kg CO_2 CE for EAF. Assuming full stoichiometric conversion of CaO and MgO to carbonate, steelmaking slag has the potential to sequester 6 to 11 pct of the CO_2 generated from BOF production and 35 to 45 pct of the CO_2 generated from EAF production.[14]

While slag may contain a considerable fraction of CaO and MgO, these compounds are rarely present in pure form. The alkaline-earth metal oxides are primarily locked into silicate, aluminate, or ferrite phases. While the carbonation of these phases is highly exothermic (*e.g.*, $\Delta H^\circ_r = -116.2$ kJ/mole for $CO_2 + \frac{1}{2}Ca_2SiO_4 \rightarrow CaCO_3 + \frac{1}{2}SiO_2$), the reaction rates are very slow. Areas investigated to increase the reaction rate include fine grinding to increase surface area, increasing CO_2 partial pressure, increasing reactor temperature, and catalysis. The current study aims to quantify the reaction rate of steelmaking slag with CO_2 in aqueous systems operating at ambient pressure and temperature. Both the reaction rate of Ca leaching from slag into water and the direct carbonation of slag particles were investigated separately to understand the limiting mechanisms for the overall sequestration reaction.

II. EXPERIMENTAL

Batch-reactor experiments were conducted to measure the reaction rate of industrial EAF and LMF slags with carbon dioxide in an aqueous system. The effect of slag particle surface area and alkaline earth metal oxide content on the extent of carbonization (wt pct CaO converted to $CaCO_3$) were investigated. These two parameters were selected in order to determine the hydrometallurgical model that best fits aqueous-assisted carbonation of steelmaking slag.

Three industrial slag samples (18 to 22 kg each) were studied: slag 1 was from an electric arc furnace (EAF), slag 2 from an Al-killed ladle metallurgy furnace (LMF), and slag 3 from a Si-killed LMF. The as-received slags 1 and 2 were gravel sized with most particles 2.5 to 7.5 cm in diameter, while slag 3 was a "falling slag" present as a fine powder. The slags were obtained within 24 hours of production and prior to on-site crushing and magnetic separation in order to ensure minimal reaction with the local atmosphere. Each slag sample was stored in separate double sealed plastic bins containing a bulk desiccant.

A. *Slag Characterization and Sample Preparation*

Prior to beginning the reactor experiments, the chemical and physical characteristics of the slags were determined. X-ray fluorescence (XRF) spectroscopy was used to measure the elemental composition of each slag and assumes all components are present as oxides. X-ray diffraction (XRD) phase analysis (Scintag, Inc. PadX with Cu source) was used to indicate the phase components of the slag samples.

To obtain fresh particle surfaces and sufficient amounts of slag particles across a range of size fractions, slags 1 and 2 were crushed in a laboratory jaw crusher followed by a roll crusher to pass a 6-mesh sieve size (3.35 mm). Slag 3 contained a high fraction of dicalcium silicate thus self-comminuted upon cooling and was used in the raw condition. Particle size distribution (PSD) was obtained using a United States mesh series of 8-in.-diameter sieves on a vibratory shaker with ~700-g samples produced by riffle splitting. After crushing and particle size analysis, four size fractions—45 to 75 μm, 150 to 250 μm, 420 to 590 μm, and 2300 to 3300 μm—were chosen for subsequent testing. As the slag-CO_2 reaction may be governed by particle surface area, the specific surface area (m^2/g) was determined for several fractions of the crushed slag samples using the BET gas sorption method (Quantachrome Corp., NOVA 1000). Reflected light (RL) microscopy and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) were used to study the surface topology, structure, and composition throughout different stages of the testing.

B. *Reaction Kinetics*

Two sets of aqueous experiments were performed with the batch-type reactors. The first set of tests involved a simple stirred batch reactor to measure the leaching rate of calcium from the different size fractions of the slags. The leaching procedure was adopted from the work of Stolaroff.[12] Each leaching test was done in a 500 mL glass flask filled with 300 mL double de-ionized water and pH buffer TES (2-[(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)amino]ethanesulfonic acid). The buffer was used to maintain the pH between 7.0 and 7.5. The buffered water was degassed by Ar bubbling and sealed under Ar positive pressure during the experiments. A quantity of slag (400 mg) was added such that the aqueous solution would be not saturated by Ca^{2+} in the case of complete leaching. After a predetermined period of time, a 10 mL sample of the solution was taken from the reactor for each test and immediately filtered through 0.45-μm syringe filters to remove any suspended solids, leaving only the dissolved fraction of Ca^{2+}. The ICP-OES spectrometry (PerkinElmer OPTIMA* 2000 DV) was used to measure the Ca^{2+} concentration in the samples.

The second set of experiments involved measurement of the carbonization of slag particles in aqueous conditions. Thirty grams of each of the four size fractions from the slag samples were mixed with 250 mL of deionized water in a 500 mL flask. Standard grade CO_2 was introduced into the mixture through a 1.0-mm glass capillary tube. Each sample was allowed to react for a designated period of time, after which the CO_2 flow was stopped. The slurry mixture was filtered through 11-μm filter paper with a vacuum pump. The filtrand was dried at 180 °C and analyzed for carbon content using the combustion/IR method (LECO** CS600) or thermogravimetric analysis (TGA) in Ar atmosphere. Total weight loss up to ~600 °C gave the amount of hydroxide ($Ca(OH)_2$) formed and weight loss above this temperature was associated with the amount of carbonate ($CaCO_3$) formed.

III. RESULTS

A. *Slag Characterization*

Table I lists the slag chemical compositions obtained by XRF, assuming all components to be oxides. The EAF slag 1 contained 32.1 pct CaO, while LMF slags 2 and 3 contained a higher, but nearly equal, percentage of CaO plus an Al_2O_3/SiO_2 amount that reflected their respective steel deoxidation practices. The XRD showed that the three slags listed in Table I contained primarily dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5) with lesser amounts of akermanite ($Ca_2MgSi_2O_7$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), and magnesio-wustite ($MgFeO_2$). Only a minor amount of free periclase (MgO) and lime (CaO) was present, showing the alkaline earth metal oxides are primarily tied up as silicates, aluminates, and ferrites. Minor amounts of free alumina (Al_2O_3), wustite (FeO), and silica (SiO_2 quartz) were also found; however, these do not contribute to carbon dioxide sequestration.

Table I. Steelmaking Slag Composition (Weight Percent)

Sample Type	1 EAF	2 LMF Al killed	3 LMF Si killed
CaO	32.1	49.9	51.3
SiO_2	19.4	4.5	28.3
Al_2O_3	8.6	32.3	4.9
TiO_2	0.4	0.3	0.3
MgO	9.4	4.3	4.3
MnO	6.8	0.8	1.3
Fe_xO_y	26.4	6.3	5.5
SO_3	0.6	1.0	1.6

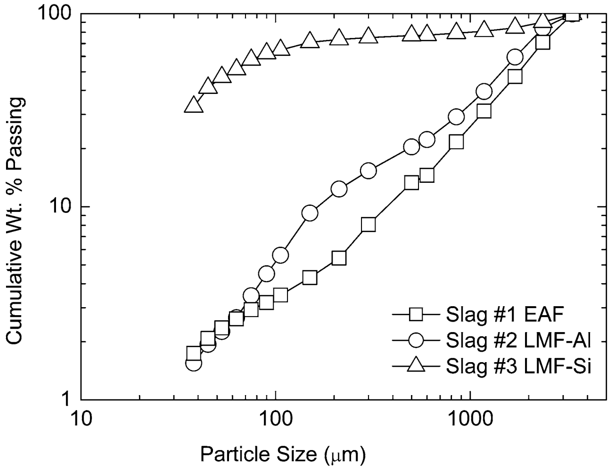

Fig. 1—Particle size analysis of slags 1 and 2 after crushing and slag 3 as received.

Figure 1 shows the particle size analysis of slags 1 and 2 after crushing, along with slag 3 in the raw state. Slags 1 and 2 have very similar PSD after crushing; however, slag 3 is much finer. The measured specific surface area (m^2/g) was compared with the calculated surface area for hypothetical smooth uniform spherical particles. The measured surface area of LMF slag particles was an order of magnitude larger than that calculated for uniform spheres, while the EAF slag particles had two orders of magnitude greater surface area because slag particles had internal and external porosity.

B. *Reaction Kinetics*

1. *Ca Leaching*

Figure 2 shows the effect of particle size, solution temperature, and slag composition on the aqueous extraction rate of Ca^{2+} from slag samples. The aqueous solution was maintained at a constant pH of 7.5 throughout each test. Figure 2(a) shows the amount of Ca^{2+} dissolved up to 24 hours for four size fractions of slag 2 (LMF slag with 49.9 pct CaO). The percentage of calcium dissolved was calculated from the concentration of Ca^{2+} in the solution and the total amount of Ca (as CaO) added to the batch reactor. The particle size (*i.e.*, surface area) had a dominant influence on the amount of calcium leached. During the first hour, approximately 33 pct of the calcium was leached from the 45- to 75-μm fraction, while less than 5 pct of the calcium was leached from the 2300- to 3300-μm fraction after 24 hours. The effect of temperature on Ca leaching, as shown in Figure 2(b), was more pronounced during the first few hours, but after 3 hours, the leaching rate (pct Ca dissolved/time) became similar for the two temperatures tested. Figure 2(c) shows the absolute value of Ca^{2+} (ppm) in solution *vs* time to provide a comparison of leaching different types of slags with the same size particles (150 to 200 μm). EAF slag 1 has less

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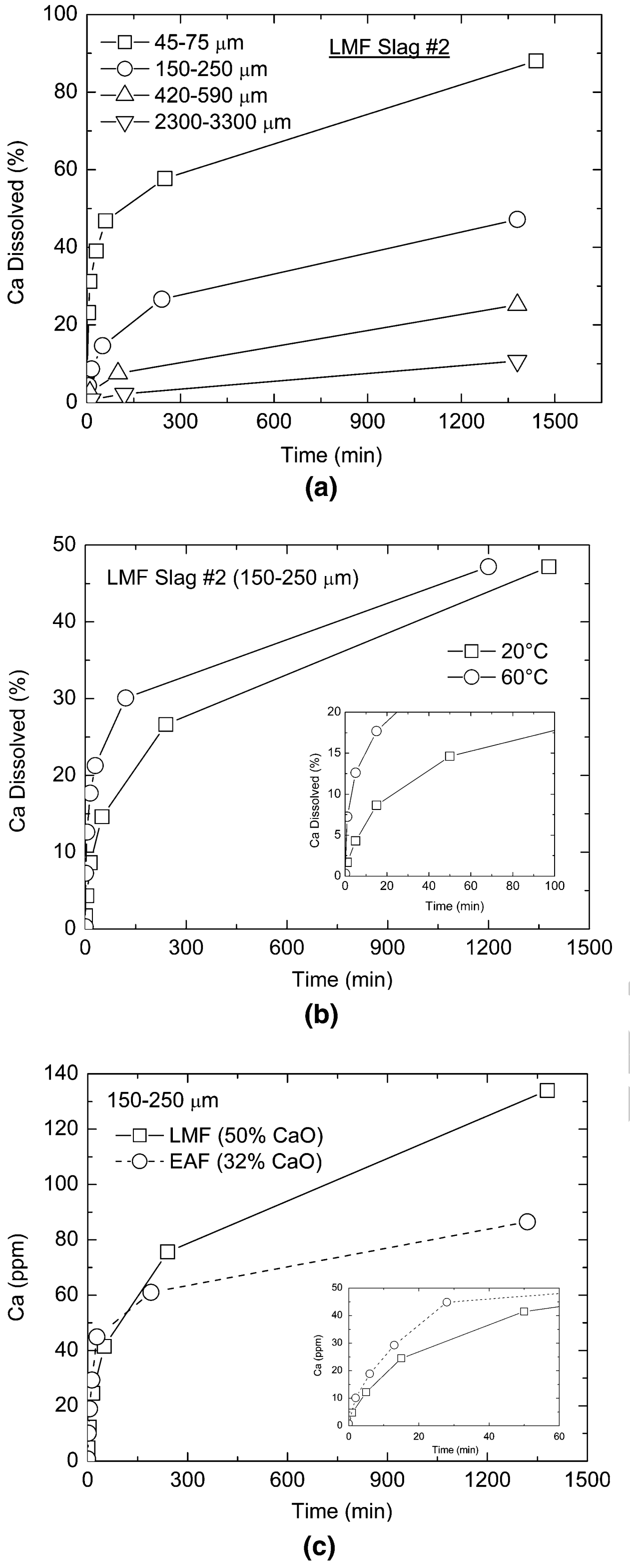


(a)

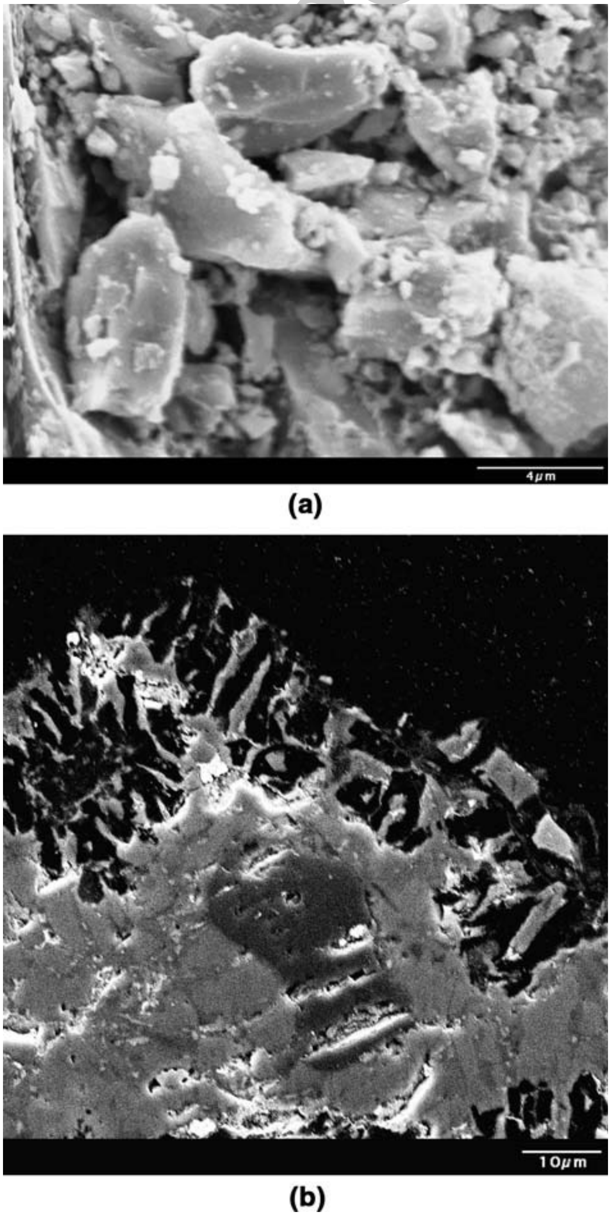
(b)

(c)

Fig. 2—Effect of (*a*) particle size, (*b*) temperature, and (*c*) CaO concentration in slag on the aqueous leaching rate of calcium.

CaO than LMF slag 2 (32.1 pct *vs* 49.9 pct), but a higher surface area. The leaching rate during the first 100 minutes was higher for slag 1 due to the increased surface area; however, the overall amount of calcium dissolved after 24 hours is significantly higher for slag 2 due to the higher starting CaO concentration.

The changes in particle morphology and composition during leaching were examined using SEM/EDS and XRD analysis. The leaching of Ca from a slag particle started at the slag surface including internal pores connected to the particle's external surface. Figure 3 shows the porous layer remaining on the external surface (Figure 3(a)) and internal surface (Figure 3(b)) after leaching of slag 1. The EDS analysis of the unreacted core and the surface after leaching showed that selective dissolution takes place. The concentration of Ca in the unreacted core is very high (44.5 wt pct), while the Ca at the surface after leaching is depleted (0.33 wt pct). Selective leaching of the Ca from the surface leaves behind an undissolved layer of mixed



(a)

(b)

Fig. 3—(*a*) External surface and (*b*) cross-sectional images of slag 1 after leaching.

(Al, Fe, Mn, Mg) oxides in different phases than the original slag. The XRD analysis showed that after 24 hours leaching, the alumino-calcium-silicate phase was eliminated.

2. *Slag Carbonization*

The degree of carbonization *vs* log (time) for four size fractions of slags 1 and 2 is presented in Figure 4. For both slags, the particle size is the dominant influence on the amount of carbonization. Comparing the 0.06-, 0.2-, 0.5-, and 1.25-mm average particle sizes tested for slag 1 (Figure 4(a)) showed that the time to reach 6 pct carbonization was approximately 20, 800, 1500, and 4200 minutes, respectively. The data for slag 2 (Figure 4(b)) showed the same relationship between particle size and degree of carbonization; however, the overall carbonization amount is less than that of slag 1 for all particle sizes. Measurement of the degree of carbonization is less precise than that of the Ca leaching tests due to the small amount of initial carbon present in the slag and the nature of carbon measurement with TGA compared to aqueous Ca ion measurement with ICP.

Morphological analysis of the resultant carbonate layers is shown in Figure 5. Because slag particles exhibit a highly porous structure, interconnected channels allow surface reactions to take place deep inside the

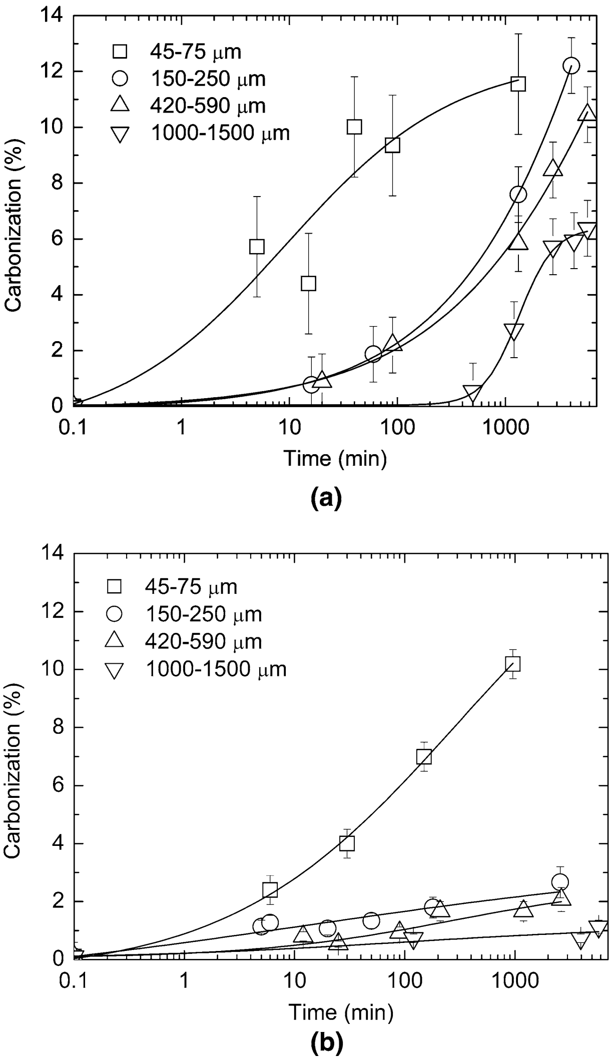


Fig. 4—Degree of carbonization *vs* time for four size fractions of (*a*) slag 1 and (*b*) slag 2.

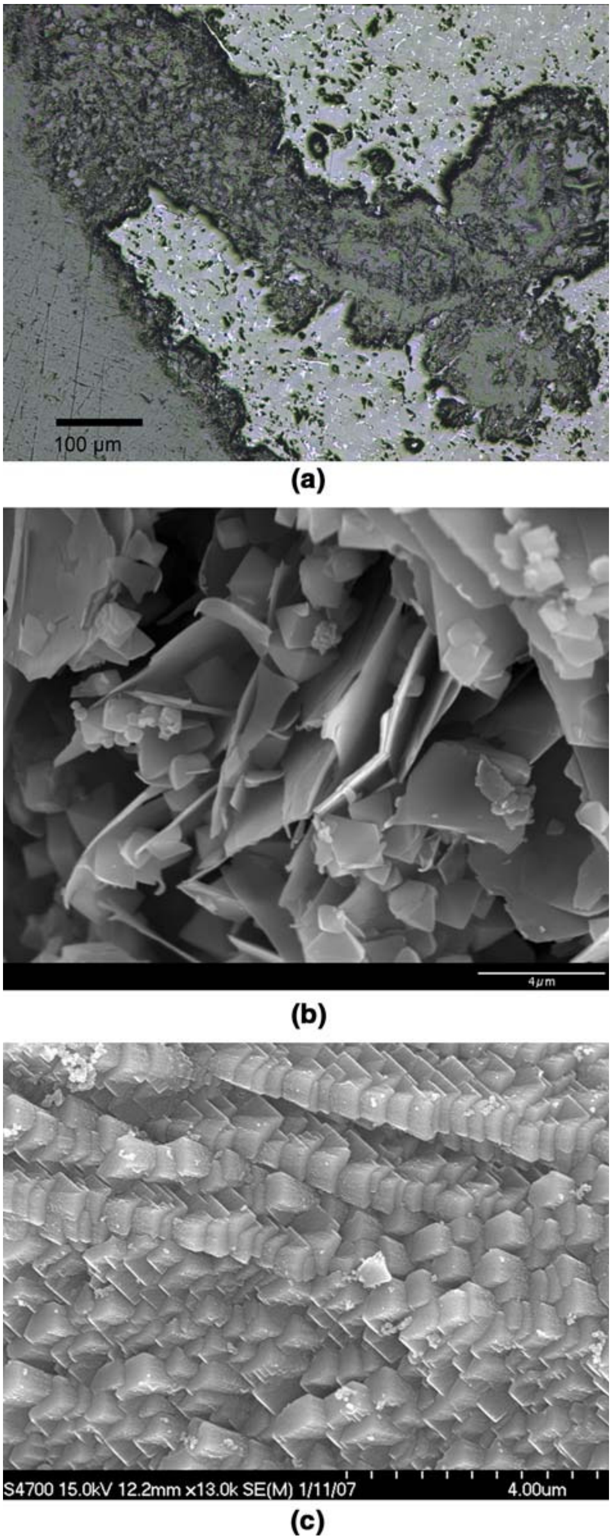


Fig. 5—(*a*) Optical image of slag 2 particle showing the cross section of a pore. SEM image of (*b*) the external surface carbonate layer and (*c*) the pore surface carbonate layer.

Table II. Specific Surface Area (m^2/g) of Slag after Aqueous Treatment

	Condition		
Slag (0.15 to 0.25 mm)	Initial	CO_2 Treated	Leached
EAF 1	1.13	12.6	5.42
LMF 2	0.092	4.4	NA

slag particle. A cross-sectional sample of a 0.5-mm particle from slag 2 (Figure 5(a)) after 48 hours carbonization treatment showed a 10- to 20-μm-thick carbonate layer on the external surface (dark region) extending into the pores, which are up to 100-μm diameter. The SEM analysis showed that the carbonate layer on the external surface of slag 2 consisted of platelike crystals in a random high-porosity structure with 1- to 3-μm openings (Figure 5(b)). The EDS analysis of the plates showed them to be composed primarily of Ca, O, and C, indicating a calcium carbonate composition. Pores connected to the slag surface through channels were exposed by crushing the particles prior to SEM analysis. The pore surfaces showed a reaction layer made of overlapping plates of calcium carbonate packed very close together, thus having a higher bulk density (Figure 5(c)).

Two different types of reactions between steelmaking slag and water were experimentally tested. The first reaction involved simple leaching of Ca^{2+} ions from slag into nearly pure water with constant pH and surrounded by an inert atmosphere. No hydrous CO_2 or other impurities were present to react with the calcium ions. In contrast, the second type of reaction allowed for the formation of calcium carbonate due to saturation of aqueous solution with CO_2. The progress of both types of reactions changed the specific surface area of the solid slag particles, as shown in Table II. Leaching increased the specific surface area by increasing the surface porosity as a result of selective dissolution of the Ca bearing phases (Figure 3), while the carbonization reaction increased the specific surface area by the production of a highly irregular product layer (Figure 5).

IV. DISCUSSION

The shrinking core model is typically used for analysis of heterogeneous solid-fluid reactions involving particles and for the determination of the rate-limiting mechanism. A description of this model can be found elsewhere.[15] Application of this model to slag carbonization reveals that the reaction steps must include (1) mass transport of the aqueous carbonic acid ions through the liquid boundary layer surrounding the particle, (2) diffusion of the reacting ions through the pores in the product layer ($CaCO_3$) accreted on the slag particle surface, and (3) the reaction of calcium ions at the solid surface with aqueous carbonic acid ions $\left(HCO_3^- \text{ and } CO_3^{2-}\right)$. For the Ca ion leaching-only process, the reaction steps are (1) the surface reaction of Ca bearing phases with water, (2) mass transport of the Ca^{2+} through the porous surface structure developed from selective leaching, and (3) mass transport of the calcium ion through the liquid boundary layer. According to the shrinking core model, originally developed for dense spherically shaped uniform sized particles, each reaction step possesses a specific time dependence, which has a characteristic proportionality to the particle surface area and solution temperature. The measured effective diffusivity was approximately 10^{-9} to 10^{-10} cm^2/s, while the diffusivity in the bulk liquid is on the order of 10^{-5} cm^2/s; thus, mass transport through the liquid boundary layer was neglected as the rate-limiting step. The slurry was intensively mixed with magnetic stirring to maintain a uniform concentration in the bulk solution. Therefore, the chemical reaction between the solid and liquid-ionic species or diffusion through the pores in the product layer can be assumed to control the rate of the processes studied.

When the diffusion of the reactants through the product layer is rate limiting, Eq. [1] gives the dependence of the molar transport of bulk fluid reactant A ($-dN_A/dt$, mol/s) through the product layer at a radius r (cm) and effective diffusivity D_e (cm^2/s).[15] The term C_A (mol/cm^3) is the concentration of the bulk reactant, which is a function of radius. At the radius of the unreacted core, C_A is zero, while at the outer radius of the product layer (in contact with surrounding fluid), C_{Ab} is the concentration of the reactant ions in the bulk fluid.

$$\frac{-dN_A}{dt} = (4\pi r^2)\left(-D_e\frac{dC_A}{dr}\right) \qquad [1]$$

Solving for the reaction time t (seconds), as shown in Eq. [2], shows dependence on the particle initial radius R (cm), the unreacted core radius r_c (cm), the molar density of the solid ρ_B (mol/cm^3), and the stoichiometric coefficient b.[15] In regard to particle size, the reaction time to a fixed level of completion is a function of the square of the particle radius.

$$t = \frac{\rho_B R^2}{6bD_eC_{Ab}}\left[1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right] \qquad [2]$$

When the chemical reaction between the solid and liquid-ion species is rate limiting, Eq. [3] gives the relationship between surface area, molar transport of bulk fluid reactant A, rate constant k_r (cm/s), and concentration of bulk reactant.

$$-\frac{1}{4\pi r^2}\frac{dN_A}{dt} = k_rC_A \qquad [3]$$

Rearrangement and integration of Eq. [3] provides the reaction time as a function of the parameters shown in Eq. [4]. In regard to particle size, the reaction time is a function of the particle radius to the first power.

$$t = \frac{\rho_B}{bk_rC_{Ab}}(R-r_c) \qquad [4]$$

For determination of the rate controlling step (*i.e.*, that governing the leaching rate of Ca or the degree of carbonization *vs* time), the influence of particle size and solution temperature was analyzed. Particle size effect on the time to reach the same level of Ca^{2+} in the solute (Figure 2) or the time to reach the same level of carbonization (Figure 4) was analyzed for the respective experiments. If the time has a squared dependence particle size, then the reaction is likely governed by product layer diffusion (Eq. [2]); however, if the time has a linear dependence on particle size, then the reaction is governed by the chemical reaction (Eq. [4]). The time dependence for both leaching and carbonization is analyzed based on calcium conversion, X_{Ca}, as a fraction of reacted calcium initially present in the slag.

A. *Ca Leaching*

Analysis of experimental data for slag 2 (Figure 2(a)) showed that both mechanisms were involved sequentially during Ca leaching from steelmaking slag. During the initial stage (*i.e.*, to 0.07 conversion), the reaction time showed linear proportionality to particle size (Figure 6(a)). This supports a chemical reaction controlled model whereby solid CaO dissolves into Ca^{2+} ions in the water. As the dissolution reaction progressed to 0.18 conversion, a porous surface structure developed, as shown in Figure 3, resulting in a tortuous path for the ions to travel. Subsequent diffusion through this structure became the rate-limiting step, as shown by the square root proportionality of the reaction time to particle size (Figure 6(b)).

Comparison of the experimental data for slag 2 (Figure 2(a)) with Eqs. [2] and [4] allows for direct correlation. Figure 7 shows a plot of the experimental data (45- to 75-μm particles) compared to the diffusion and reaction equations. A combination of the two equations shows that the experimental data fit well to a chemical reaction controlled mechanism up to ~0.3 conversion (60 minutes), and then switches to a combination of chemical reaction and porous diffusion layer control to the terminal conversion of 0.63.

Each reaction mechanism has a different sensitivity to the solution temperature. In the case studied, increasing the temperature of the aqueous solution enhanced Ca leaching at the initial reaction time period (Figure 2(b)). While the rate of dissolution increased significantly with temperature during the initial period, the rate of leaching at the end of the test did not differ greatly between 20 °C and 60 °C. This is because the solution temperature affects the rate of the chemical reaction more than it does the rate of diffusion.

In Figure 2(c), EAF slag 1 showed a higher Ca dissolution rate during the initial period even with a lower Ca concentration in slag when compared to LMF slag 2. This is inconsistent with a simple shrinking core model based on uniform smooth solid spheres. Correction of this model can be made by substituting an effective particle size, which is based on the measurement of specific surface area. Slag 1 had ~10 times the surface area of slag 2 for the same particle size. The much higher surface area led to an increased Ca dissolution rate during the initial period. However, as the Ca rapidly dissolved, the amount of Ca left in the slag decreased, providing less gradient to maintain the

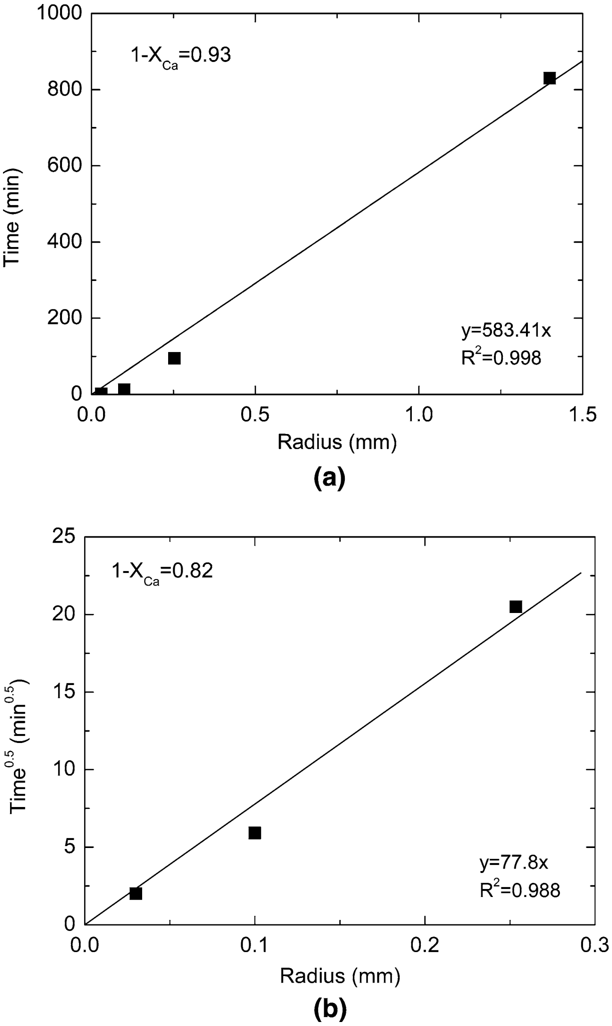


Fig. 6—Time dependence with particle size for Ca leaching from slag 2 for the (*a*) initial stage and (*b*) progressive stage.

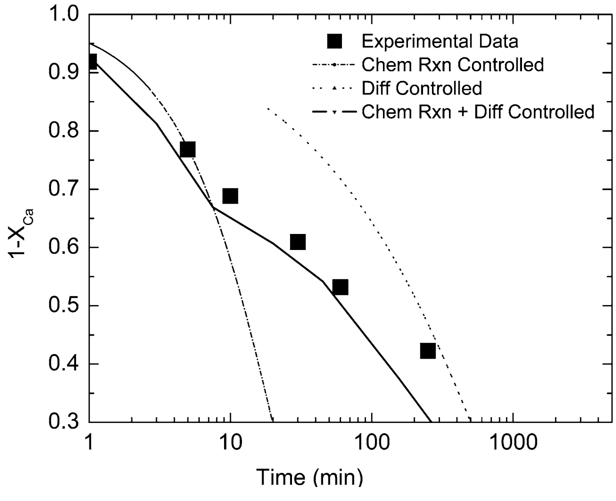


Fig. 7—Comparison of experimental data for Ca leaching from slag 2 (45- to 75-μm particle size) with chemical and diffusion reaction control mechanisms.

high dissolution rate. Slag 2 had 55 pct more Ca to start with; thus, it was able to maintain a higher gradient compared to the bulk solution, resulting in an overall higher amount of Ca leached.

B. *Slag Carbonization*

The slag carbonization data were analyzed in a similar manner to determine the controlling reaction mechanism. Figure 8(a) shows the time required to achieve 0.02 conversion (carbonate reaction) for four particle sizes of slags 1 and 2. Conversion was heavily dependent on particle size and showed proportionality to the square root of time, indicating that product layer diffusion was the rate controlling step. The layer of calcium carbonate formed on the surface (Figure 5) retarded the diffusion of carbonic acid ions into the slag particle. The different slopes exhibited by the two slags reflected the effect of true surface area. The effective diameters, calculated from specific surface measurements on the assumption of uniform spherical particles, were used to recalculate the curves shown in Figure 8(b), bringing both curves into congruence.

According to the shrinking core model, if product layer diffusion is the limiting mechanism (Eq. [2]), conversion should exhibit a dependence on the square root of reaction time. Figure 9(a) shows the experimental data for conversion of slag 1 *vs* [time$^{0.5}$]. During the initial reaction period (*i.e.*, to 0.03 conversion), the experimental results closely match the theoretical model. As the product layer increases in thickness, the reaction tends to decelerate. The changing density of the carbonized layer (Figure 5(a)) was not considered in this model and is a possible explanation for the decrease in reaction rate. Equation [2] was solved numerically by changing the effective diffusivity (*i.e.*, for increased product layer thickness) for the three conversion periods shown in Figure 9(a) (<0.03, 0.03 to 0.10, and >0.10) to allow the fraction converted to match the square root relationship. The experimental data were fit to the resulting equations to yield a diffusion coefficient that changed from 5×10^{-9} cm^2 s^{-1} at an initial period of

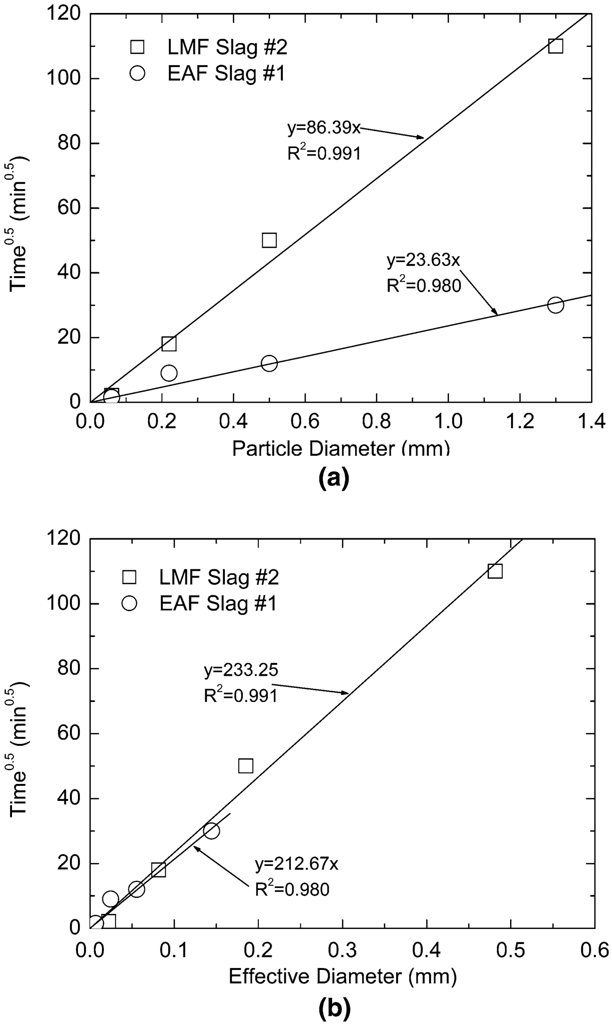


Fig. 8—Diffusion limiting model for the slag carbonization reaction at 0.02 Ca conversion using the (*a*) real particle diameter and (*b*) effective particle diameter.

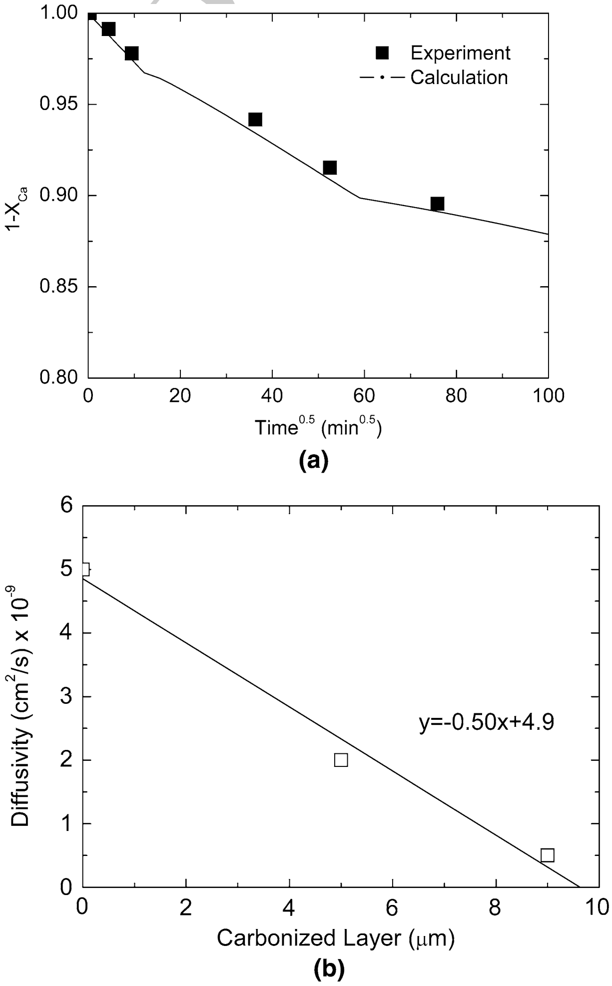


Fig. 9—(*a*) Comparison of calculated and experimental data for the carbonization of slag 1 with 0.5-mm average particle diameter and (*b*) dependence of diffusivity on the thickness of the carbonized layer.

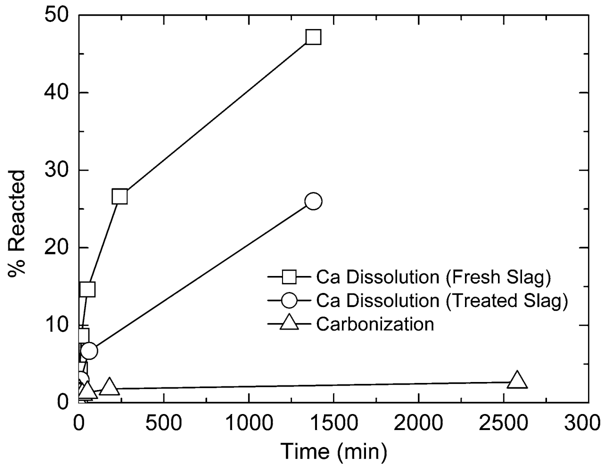


Fig. 10—Comparison of carbonized and leached Ca from fresh and stabilized LMF slag 2 in aqueous solutions.

time to 5×10^{-10} cm^2 s^{-1} when carbonate layer was formed, as shown in Figure 9(b).

Finally, data for the rate of Ca leaching were compared to data for the rate of Ca carbonization for the same slag. In both cases, some amount of calcium from the slag reacted with the aqueous solution; however, the rate of these reactions significantly differed due to the mechanisms and limiting steps involved. In the slag leaching test, Ca ions dissolved from the slag into the unsaturated aqueous solution. The limiting step was the diffusion of calcium ions through the developed porous layer. An additional Ca leaching test was performed on slag 2 (<200 μm), which had been preliminary partially carbonized. Figure 10 shows the percentage of reacted Ca from slag (leached or carbonized) *vs* reaction time. The comparison illustrates that slag carbonization proceeds slower than Ca leaching. In addition, the calcium carbonate product layer inhibits the Ca leaching process. The experimental data and kinetic parameters obtained will be used for modeling an industrial prototype reactor that can be used for sequestration of carbon dioxide with steelmaking slag.

V. CONCLUSIONS

Carbon dioxide sequestration with steelmaking slag was studied in a three-phase batch-system containing industrial slag, water, and CO_2 gas at ambient temperature and pressure. The reaction rates of aqueous Ca leaching and direct carbonization were quantified independently to yield the reaction parameters and rate-limiting mechanisms, as listed subsequently.

1. The specific surface area of slag particles is increased by leaching or carbonization. Selective dissolution of the Ca-bearing phase results in increased surface porosity, while carbonization produces overlapping plates of $CaCO_3$ product layer that create a highly irregular surface.
2. Both Ca leaching and carbonization were analyzed using the shrinking core model. The experimental data for both processes fit this model well, after correction for effective particle size, which is based on the measured specific surface area.
3. Analysis of Ca-leaching shows a linear proportionality to particle size during the initial stage (to 0.30 conversion), supporting a chemical reaction controlled model (CaO dissolution). The later stage of leaching is controlled by diffusion of the Ca^{2+} ions through the resulting porous surface layer, as shown by square-root proportionality of reaction time to particle size.
4. Increasing the leachate temperature from 20 °C to 60 °C (at atmospheric pressure) enhanced the Ca-leaching rate during the initial period time; however, the terminal amount of Ca leached after 24 hours did not differ greatly (47 pct *vs* 50 pct).
5. Carbonate conversion is heavily dependent on particle size, and the reaction is limited by product layer diffusion. The calculated value of diffusivity decreased by an order of magnitude from the initial value of 5×10^{-9} cm^2/s, as a result of the changing density of the product layer.
6. Carbonate conversion proceeded slower than did leaching conversion; however, both processes were inhibited by the calcium carbonate product layer.

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Sequestration of Carbon Dioxide by Steelmaking Slag: Process Phenomena and Reactor Study

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Keywords: Steelmaking Slag, CO_2, Sequestration, Kinetics, Reactor

Abstract

Steel-making processes generate carbon dioxide air emissions and a slag co-product. The aim of this project was to develop a functional sequestration system using steelmaking slag to permanently capture carbon dioxide emitted in steelmaking offgas. A possible parallel benefit of this process would be rapid chemical stabilization of the slag minerals with reducing swelling or leaching.

This paper summarizes the original results of the project, including mineralogical and structural features of carbon sequestration with steel making slag, mathematical modeling of reaction phenomena using a modified shrinking core model, METSIM modeling of several possible industrial applications, a thermo-gravimetrical study of the reaction between slags and different gases, and design and testing for a lab scale apparatus consisted of two reactors.

1. Introduction

The U.S. produces 9-14 Mt of steelmaking slag annually, which represents approximately 10-15 wt. % of crude steel output.[1,2] Primary uses for steelmaking slag include high quality mineral aggregate, Portland cement, unconfined fill, soil conditioning, and pH neutralization of abandoned mine drainage.[3,4] The key factor prescribing slag use is the alkaline-earth metal (e.g. Ca and Mg) oxides content, which contribute to overall basicity and cementitious strength. However, as-produced steelmaking slag is chemically unstable. Calcium and magnesium oxides readily form hydroxides and carbonates through reaction with atmospheric gases. Both hydroxide and carbonate formation produce substantial mechanical swelling leading to heave failure in confined construction applications, thus many states dictate stockpile aging for 3-6 months prior to commercial use.[5,6] Sequestration of carbon dioxide is a natural corollary to forced carbonation. The conversion of CaO/MgO to carbonates serves both to stabilize the slag, and permanently capture and store the CO_2.

Extraction of CO_2 from steel manufacturing offgas with steelmaking slag for geological sequestration is being studied by quantifying the extent and rate of carbonate formation under near-atmospheric aqueous conditions.[7] A survey of industrial slags has found the CaO and MgO contents of BOF and EAF slags to average 30-50 wt.% and 10-12 wt.%, respectively. Additionally, LMF slag contains 50-60 wt.% CaO and 10-12 wt.% MgO. The amount of slag produced per ton of steel is estimated at 75-150 kg for BOF, 65-80 kg for EAF, and 15-20 kg for LMF. Production of a ton of steel generates 519 kg CO_2 carbon equivalent (CE) for BOF and 119 kg CO_2 CE for EAF, respectively. Assuming full stoichiometric conversion of CaO and MgO to carbonate, steelmaking slag has the potential to sequester 6-11% of the CO_2 generated from BOF production and 35-45% of the CO_2 generated from EAF production[8].
This paper summarizes the original results[7-9] of the project, including mineralogical and structural features of carbon sequestration with steel making slag, experimental study and modeling of reaction phenomena and prototype of industrial reactor.

2. Slag characterization

Table I lists the slag chemical compositions obtained by XRF. EAF Slag #1 contained 32.1% CaO while LMF Slags #2 and #3 contained higher, but nearly equal, percentage of CaO plus an Al_2O_3/SiO_2 amount that reflected their respective steel deoxidation practice.

Table 1. Steelmaking Slag Compositions (Wt Pct)

Sample	#1	#2	#3
Type	EAF	LMF Al-Killed	LMF Si-Killed
CaO	32.1	49.9	51.3
SiO_2	19.4	4.5	28.3
Al_2O_3	8.6	32.3	4.9
TiO_2	0.4	0.3	0.3
MgO	9.4	4.3	4.3
MnO	6.8	0.8	1.3
Fe_xO_y	26.4	6.3	5.5
SO_3	0.6	1.0	1.6

XRD showed that the three slags listed in Table I contained primarily dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5) with lesser amounts of akermanite ($Ca_2MgSi_2O_7$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), and magnesio-wustite ($MgFeO_2$). Only a minor amount of free periclase (MgO) and lime (CaO) were present showing the alkaline earth metal oxides are primarily tied up as silicates, aluminates, and ferrites.

Slags #1 and #2 were crushed in a laboratory jaw crusher followed by a roll crusher to pass a 6-mesh sieve size (3.35 mm). Slag #3 contained a high fraction of dicalcium silicate thus self-comminuted upon cooling and was used in the raw condition. After crushing and particle size analysis, four size fractions—2.3-3.3 mm, 0.42-0.59 mm, 0.15-0.25 mm, and 0.045-0.075 mm—were chosen for subsequent testing. As the slag-CO_2 reaction may be governed by particle surface area, the specific surface area (m^2/g) was determined for several fractions of the crushed slag samples using BET gas sorption method. A comparison of measured specific surface area (m^2/g) with calculated surface area for hypothetical smooth uniform spherical particles approach is given in Fig. 1. The measured surface area of slag particles was an order of magnitude larger than calculated for uniform spheres.

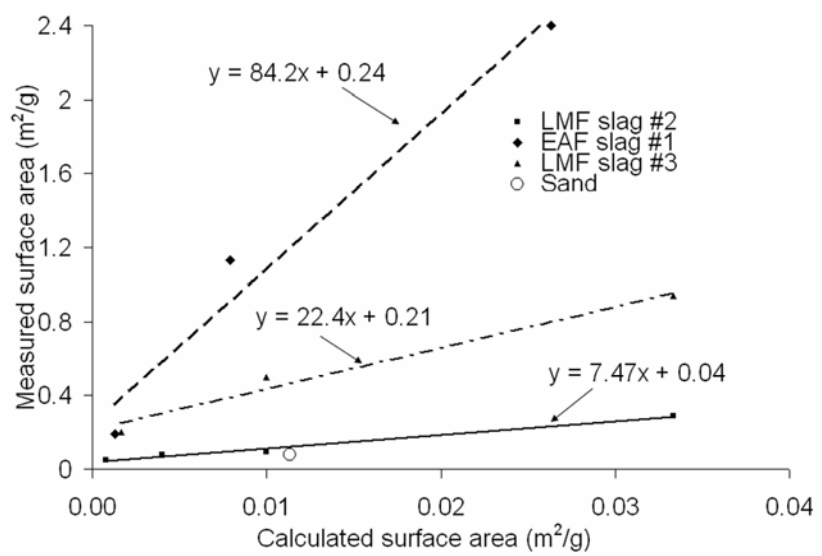


Fig. 1. Comparison of calculated (uniform sphere) with measured specific surface area for slag samples.

3. Process Phenomena

The ability of specific phases in steelmaking slag to sequester carbon dioxide into stable carbonates under non-ideal conditions can be expressed in the phase stability diagram shown in Fig. 2. Above each line the carbonate is stable. As temperature increases the carbonate stability region for each phase shrinks and the concentration of CO_2 in the atmosphere surrounding the slag also affects the carbonate stability. The gray shaded region in Fig. 2 shows the P_{CO2} operating region exhibited by the stack offgas. At ambient conditions, all phases listed on Fig.2 are stable as carbonates thus the slag will spontaneously react to sequester CO_2.

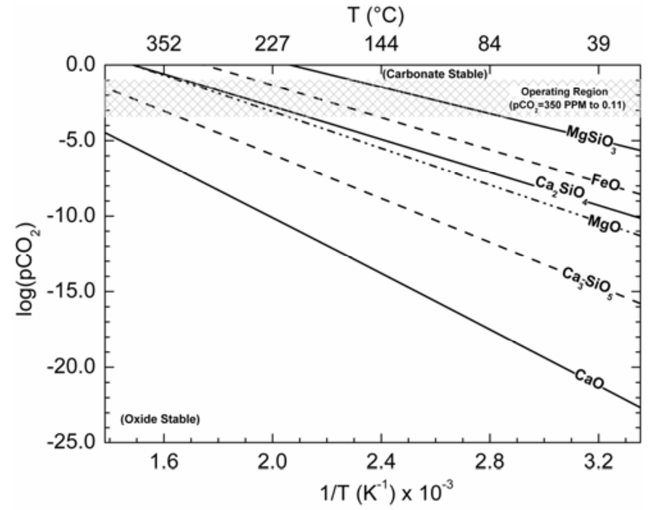


Fig. 2 Carbonate stability diagram for alkaline earth metal oxide phases found in steelmaking slag (data generated from FactSage™ 5.4).

However the major hurdle to realization of slag sequestration is that the rate of solid-gas reaction is extremely slow at the ambient pressure. An alternative processing route using water or steam assist greatly accelerates the reaction kinetics. Carbon sequestration through the aqueous-based reaction of CO_2 -containing offgas with lime-bearing steelmaking slag allows for several possible reactions to take place. A list of the key competing reactions is given in Table 2. For simplification the calcium containing phases are all designated as CaO.

Table 2. Reactions Occurring During Aqueous Slag-CO_2 Sequestration[10,11]

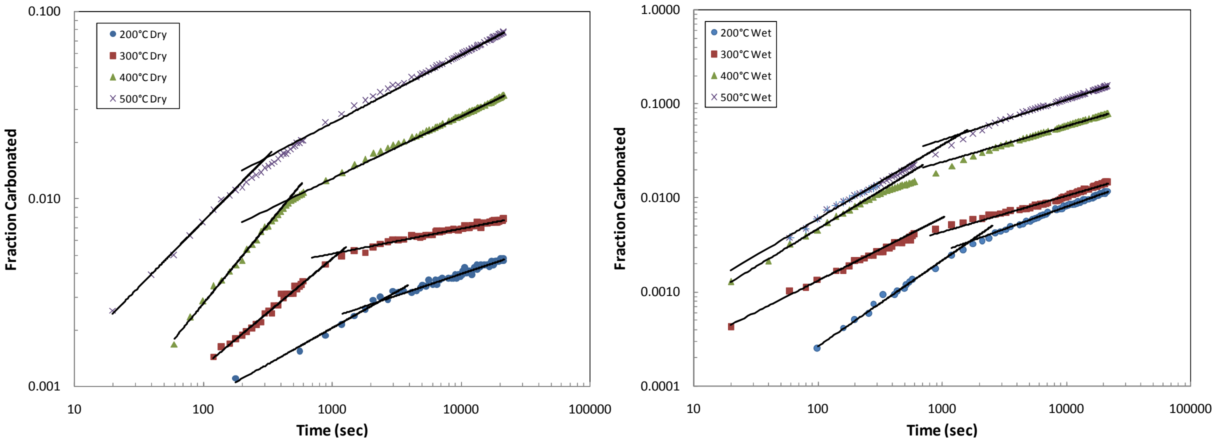
Description	Reaction
Ca leaching	$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2(OH^-)$
CO_2 dissolution	$CO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + CO^{2-}_{3(aq)}$
Carbonate precipitation	$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(s)}$
Ca direct carbonization	$CaO_{(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} = CaCO_{3(s)} + 2OH^-$
Water dissociation	$2(OH^-) + 2H^+ \rightarrow 2H_2O_{(l)}$

In the current project, the reaction phenomena of carbon dioxide sequestration by steel making slag was studied for solid-gas reaction and in, so called, slurry (aqueous) process under normal atmospheric pressure.

3.1. CaO-CO_2 Reaction Kinetics

Investigation of the gas-solid contactor packed bed design was performed with a large-scale (up to 400 g) thermo gravimetric analyzer (TGA) built for this project. To obtain a baseline for comparison with industrial slags, the reaction rate of CaO in dry and humidified CO_2 was measured. Humidification of the CO_2 was accomplished by bubbling the gas through a heated water column. All tests were conducted using reagent grade CaO pressed into a 3.8cm x 0.75cm disc in an atmospheric pressure furnace with $pCO_2>0.99$. Figure 3 shows the results from testing

CaO at 200-500°C in both dry and wet (humidified) CO_2. All test samples exhibited an increase in weight with time (conversion of CaO to $CaCO_3$), and increasing the test temperature provided a higher overall weight gain (e.g. fraction carbonation). Under dry conditions the fraction carbonation at six hours varied from 0.5% at 200°C to 7.7% at 500°C. Humidification doubled the fraction carbonation within the same time period with 1.2% and 15.3% achieved at 200°C and 500°C, respectively. Water vapor from the gaseous atmosphere collects on the lime sample surface to form a gel into which CO_2 and CaO solvates. The solvated CO_2 forms carbonic acid ions (HCO_3^-/ CO_3^{2-}), which react with the dissolved CaO (Ca^{2+}). The reaction rate in the gel (i.e. aqueous solution) is much faster than between the gas and solid resulting in the formation of more $CaCO_3$ for a fixed period of time.



a) b)

Fig. 3 Carbonation of CaO in dry (a) and humidified (b) CO_2 from 200-500°C.

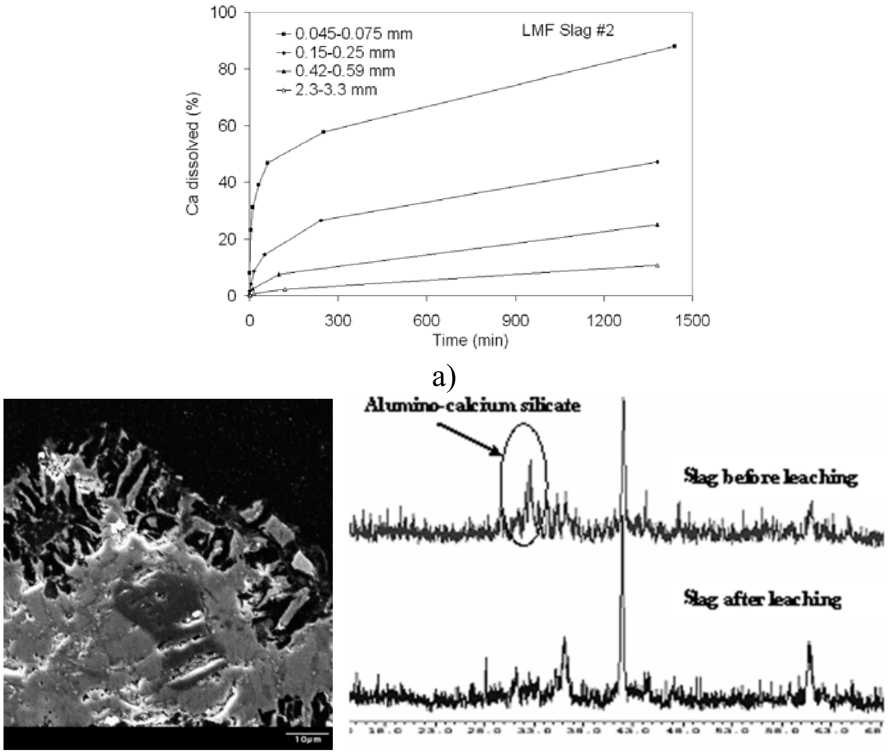
In each plot of Fig. 3 two distinct regions can be identified for each curve. The first region occurs from start of test to ~1000 seconds (region decreases with temperature increase). This region is characterized by a high slope indicating rapid carbonization of the CaO. The second region occurs after ~1000 seconds to test completion (6 hours), whereupon the slope decreases indicating slower carbonization rate. This change of carbonization mechanisms is evident in both dry and wet testing. The timeframe for completion of the initial mechanism occurs in a narrow time-band with only a slight variation due to humidification or reaction temperature. The initial mechanism is hypothesized to be rapid consumption of the lime (especially small particles) at the sample free surface. Once the initial layer of CaO is reacted a calcium carbonate product layer forms, which due to the increase in molar volume, partially blocks the sample pores and forms a barrier for CO_2 migration/diffusion into the sample. Exhaustion of lime at the free surface forces a change in the carbonation mechanism, whereby further carbonation can only occur after CO_2 diffuses deeper into the sample, through the $CaCO_3$ product layer. The activation energies for the two mechanisms in dry CO_2 are 46.1 kJ/mol and 121.5 kJ/mol, respectively. Humidification of the CO_2 lowers the activation energy for both mechanisms to 38.1 kJ/mol and 63.9 kJ/mol, respectively.

3.2. Ca leaching from slag in aqueous solution

Ca leaching from slag was performed with the batch type reactors in purified water with pH buffer to maintain the pH between 7.0-7.5[12]. ICP-OES spectrometry was used to measure the

Ca^{2+} concentration in the samples. Fig. 4a shows the effect of particle size on the aqueous extraction rate of Ca^{2+} from LMF Slag #2. The particle size (i.e. surface area) had a dominant influence on the amount of calcium leached. During the first hour approximately 33% of the calcium was leached from the 45-75 µm fraction while less than 5% of the calcium was leached from the 2300-3300 µm fraction after 24 hours.

The changes in slag particle morphology and composition during leaching were examined using SEM/EDS and XRD analysis. The leaching of Ca from a slag particle started at the slag surface including internal pores connected to the particle's external surface. Fig. 4b shows the developed porous layer after leaching. Micro- EDS and macro- XRD analysis showed that selective dissolution takes place. The concentration of Ca in the unreacted core was very high (44.5 wt.%), while the Ca at the surface after leaching was depleted (0.33 wt.%). The alumino-calcium-silicate phase has been eliminated after 24 hours leaching (Fig.4c).



a)

b) c)

Fig. 4 Ca leaching in aqueous solution from different fractions of LMF (a), selective phase dissolution (b), and XRD spectra before and after aqueous leaching (c).

The shrinking core model[13] was used for analysis of heterogeneous solid-fluid reactions involving particles and for the determination of the rate-limiting mechanism. Analysis of experimental data showed that the different limiting mechanisms were involved during Ca leaching from steelmaking slag. During the initial stage the reaction time showed linearly proportionality to particle size. This supports a chemical reaction controlled model whereby solid CaO dissolves into Ca^{2+} ions in the water. As the dissolution reaction progressed a porous surface structure developed, as shown in Fig. 4b, resulting in a tortuous path for the ions to travel. Subsequent diffusion through this structure became the rate-limiting step as shown by the square root proportionality of the reaction time to particle size. Fig. 5 shows a plot of the experimental data (45-75 μm particles) compared to the diffusion and reaction equations. A combination of the two equations shows that the experimental data fits well to a chemical reaction controlled mechanism up to ~0.3 conversion (60 minutes) then switches to a combination of chemical reaction and porous diffusion layer control to the terminal conversion of 0.63.

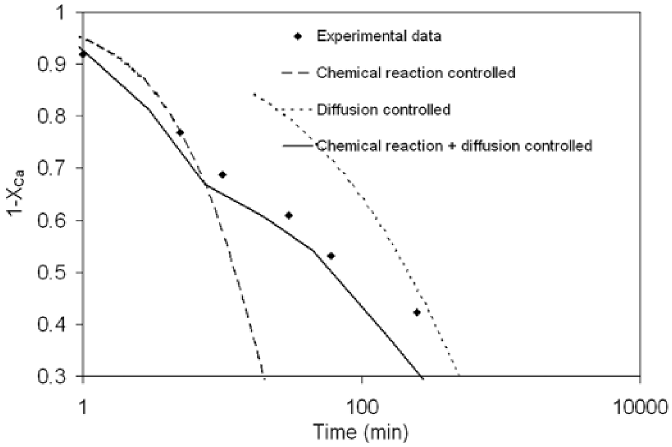


Fig. 5 Comparison of experimental data for Ca leaching from Slag #2 (45-75 μm particle size) with chemical and diffusion reaction control mechanisms.

3.3 Direct Carbonization of slag in aqueous solution saturated by CO_2

The degree of carbonization versus log (time) for four size fractions of LMF Slag #2 is presented in Fig. 6. The particle size had the dominant influence on the amount of carbonization. Morphological and chemical analysis of the resultant carbonate layers is shown in Fig. 7. Because slag particles exhibit a highly porous structure, interconnected channels allow surface reactions to take place deep inside the slag particle. A cross-sectional sample of a 0.5mm particle from Slag #2 (Fig.7a) after 48 hours carbonization treatment showed a 10-20 μm thick carbonate layer on the surface extending into the pores which are up to 100 μm diameter. SEM analysis showed that the carbonate layer on the external surface consisted of plate-like crystals in a random high-porosity structure with 1-3 μm openings (Fig. 7b). EDS analysis of the plates showed them to be composed primarily of Ca, O, and C, indicating a calcium carbonate composition. Pores connected to the slag surface through channels were exposed by crushing the particles prior to SEM analysis. The pore surfaces showed a reaction layer made of overlapping plates of calcium carbonate packed very close together, thus having a higher bulk density (Fig. 7c).

The slag carbonization data was analyzed in a similar manner to determine the controlling reaction mechanism. Conversion was heavily dependent on particle size, and showed proportionality to the square root of time, indicating that product layer diffusion was the rate-controlling step. The layer of calcium carbonate formed on the surface (Fig 7) retarded the diffusion of carbonic acid ions into the slag particle. The changing density of carbonized layer was not considered in the standard shrinking core model, and calculated data has significant departure from the experimental data when reaction continued (Fig. 8). The reaction rate expression increases in complexity because the porosity of the product layer decreases simultaneously along with shrinking of the core of unreacted slag (with radius r_c) in each particle (with initial radius *R*). The problem was solved by introduction the function (Eq. 4) of diffusivity (D) from thickness of product layer ($R\text{-}r_c$) in standard shrinking core model:

$$-\frac{dN_A}{dt} = -4\pi r^2 J_A \tag{1}$$

$$J_A = -D\frac{dC_A}{dr} \tag{2}$$

$$dN_A = 4\pi\rho_m r_c^2 dr_c \tag{3}$$

$$D = D_0 - k(R - r_c) \tag{4}$$

In this system, Eq. 1 is the reaction rate as a function of surface area and flux, Eq. 2 is the diffusion flux as a function of diffusivity and concentration gradient, and Eq. 3 is the mass balance of component A.[13] The parameter *k* was evaluated by fitting experimental data to the model with variations in diffusivity in three time steps to fit the experimental data. Comparison of the experimental results and those calculated from the modified shrinking core model using constant and decreasing diffusivity is shown in Fig. 8. The terms Ca_C and Ca_S are the fractions of calcium carbonized and calcium initial present in the slag, respectively

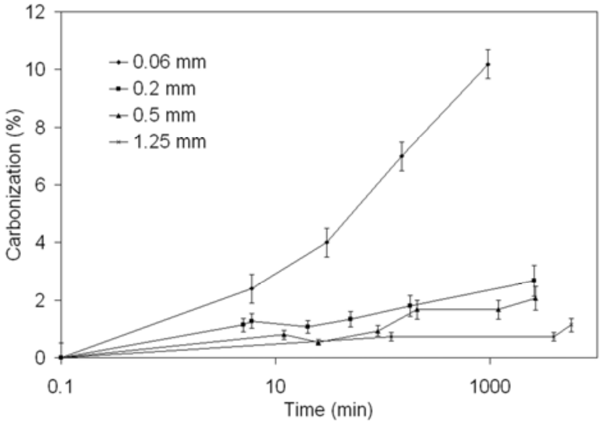
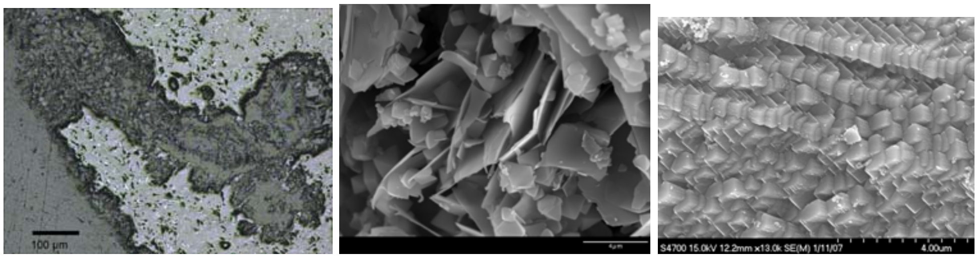


Fig. 6 Direct LMF Slag#2 carbonization in saturated by CO_2 aqueous solution.



(a) b) c)

Fig. 7 Optical image of cross section of LMF Slag #2 particle (a), SEM images of the external (b) and near internal surfaces (c) of carbonate layer.

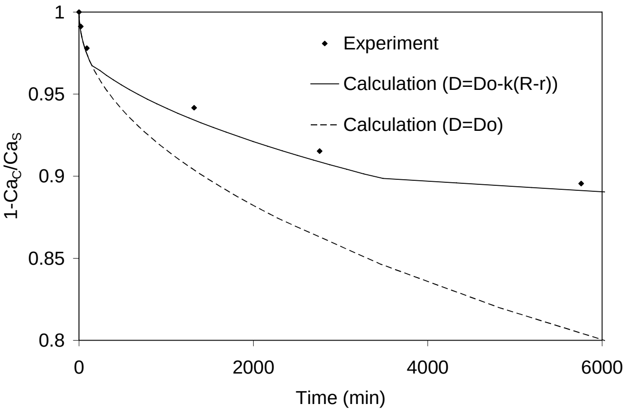


Fig. 8 Comparison of experimental data for slag carbonization with shrinking core model using constant ($D=D_0$) and decreasing ($D=D_0-k(R-r)$) diffusivity of the product layer for 0.5 mm diameter LMF Slag #2.

Finally, data for the rate of Ca leaching was compared to data for the rate of Ca carbonization for the same slag. In both cases some amount of calcium from the slag reacted with the aqueous solution, however, the rate of these reactions significantly differed due to the mechanisms and limiting steps involved. In the slag leaching test, Ca ions dissolved from the slag into the unsaturated aqueous solution. The limiting step was diffusion of calcium ions though developed porous layer. An additional Ca leaching test was performed on Slag #2 (<200 m) that had been preliminary partially carbonized. Fig. 9 shows the percentage of reacted Ca from slag (leached or carbonized) versus reaction time. The comparison illustrates that slag carbonization proceeds slower than Ca leaching. In addition, the calcium carbonate product layer inhibits the Ca leaching process.

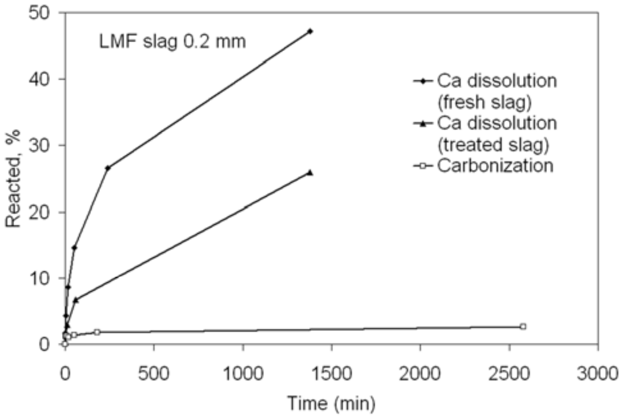


Fig. 9 Comparison of carbonized and leached Ca from fresh and stabilized LMF Slag #2 in aqueous solutions.

4. Reactor Modeling and Experimental Study

The proposed reactor design consists of two vessels connected by a pumped water stream, as shown in Fig. 10. Each reactor vessel operates at ambient pressure and temperature. Water and slag particles are introduced into Reactor 1, wherein calcium ions are leached to form an alkaline

leachate. The aqueous solution is pumped to Reactor 2 through which gaseous CO_2 is bubbled. The CO_2 dissolves into the water to from carbonic acid ions, upon which several competing reactions take place resulting in precipitation of $CaCO_3$. This process scheme allows for several system scenarios two of which were investigated for optimization of CO_2 capture:
Scenario 1: Fresh or recirculated water is supplied into Reactor 1, the leachate containing calcium ions is pumped to Reactor 2 in which calcium carbonate precipitates. The spent leachate (containing residual dissolved CO_2) is discharged or recirculated into Reactor 1 after de-gazing.
Scenario 2: Recirculated solution is supplied to Reactor 2 for saturation with CO_2, the CO_2 saturated water is pumped to Reactor 1 for direct reaction with slag.

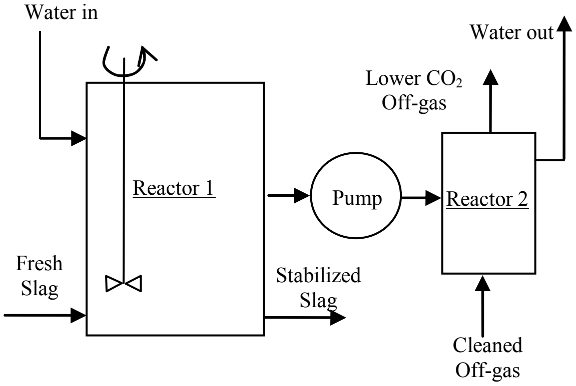


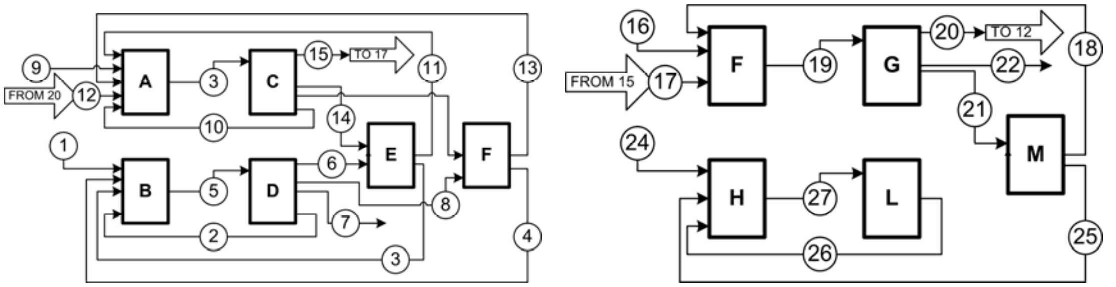
Fig. 10. Flow schematic of proposed apparatus for CO_2 sequestration with steelmaking slag.

An approach developed by Robertson for modeling the heterogeneous reaction kinetics of a non-steady process was used for the scenarios identified for the two-stage reactor system.[14] A block diagram of the METSIM model is shown in Fig. 11. The computer model consists of two blocks, representing Reactor 1 (Fig. 11a) and Reactor 2 (Fig 11b), connected by streams 15/17 and 20/12. In Reactor 1, the amount of slag is defined by Stream 10, which connects the mixer and splitter pair A and C, respectively. In the same manner, the amount of aqueous solution is defined by Stream 2, which connects the mixer and splitter pair B and D, respectively. Slag leaching and direct carbonization reactions occur in splitters E and F, respectively. In Reactor 2, carbon dioxide gas (Stream 16) is mixed with the aqueous stream from Reactor 1 (Stream 12) in Mixer F, while CO_2 dissolution to form carbonic acid ions takes place in Splitter G. Carbonic acid ions react with calcium ions in Splitter M, and any precipitated calcium carbonate accumulates in the loop consisting of the mixer/splitter pair H/L.

This model allows the two scenarios identified to be studied individually. For example, in Scenario 1 fresh water is supplied by Stream 9 to leach the slag in Reactor 1. The leached calcium ions are pumped to Reactor 2 by Stream 15/17 where precipitated calcium carbonate accumulates in Stream 26. The spent aqueous stream is discarded by Stream 22 without flowing back to Reactor 1. Alternatively, in Scenario 2 the aqueous solution is recirculated by streams 15/17 and 12/20 without fresh water input in Reactor 1 or solution discharge from Reactor 2. The model was used to calculate both an unsteady batch type process in Reactor 1 where there is no fresh slag input by Stream 1 and no product discharge by Stream 7, as well as a continuous type process with fresh slag input and carbonate product output.

For application in the METSIM model, the experimental kinetics of the carbonization reaction was approximated to be a function of time (t) as shown in Eq. 5. A factor of n=⅓ resulted in an appropriate fit for the reaction conversion (Ca_C/Ca_S) calculated from Equations 1-4, as well as the experimental data:

$$\ln\left(1-\frac{Ca_C}{Ca_S}\right) = f(t)^n \qquad [6]$$

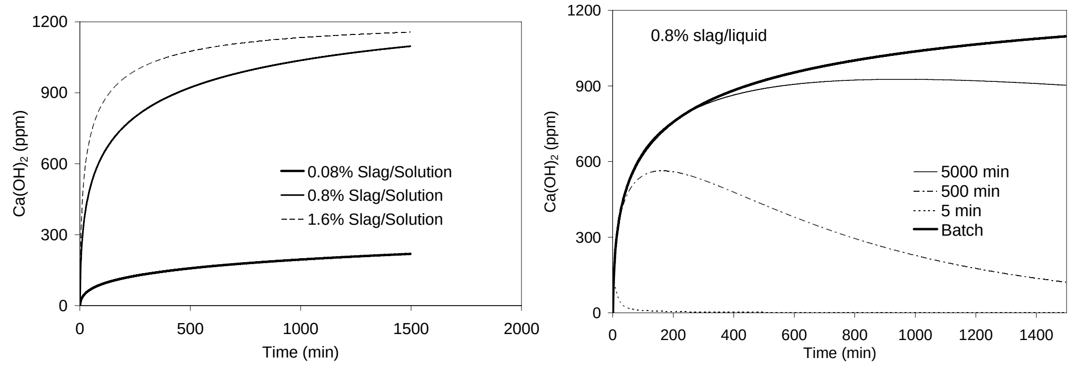


a) b)

Fig. 11—Block diagrams of the METSIM model for Reactor 1 (a) and Reactor 2 (b), which are interconnected by streams 15/17 and 20/12.

Scenario 1 was modeled in which the slag was leached in Reactor 1 and the alkaline liquor was carbonized in Reactor 2. The basis for the model was fresh water feed to Reactor 1 at the same rate the spent liquor was discharged from Reactor 2. No water was recirculated from Reactor 2 to Reactor 1. The goal of this scenario was to analyze the influence of slag/solution ratio and solution residence time in Reactor 1 on the leaching result. The slag used in the model was the 0.2 mm fraction of LMF Slag #2, with 50 wt.% CaO.

The model results show that both increasing the slag/solution ratio and the solution residence time in Reactor 1 produces a higher concentration of calcium ions in solution. Increasing the slag/solution ratio provides a diminishing increase in calcium ions in solution due to saturation of the aqueous phase (Fig. 12a). The fresh water throughput accelerates the leaching rate, which is dependent upon the residence time of Reactor 1 (Fig. 12b). The optimal residence time was defined by the maximum amount of leaching with minimal fresh water input. For slag with 0.2 mm particle diameter and 0.8% slag/solution ratio the optimal residence time was near 1 hour.



a) b)

Fig. 12 METSIM modeling of leaching LMF Slag #2 (0.2 mm diameter) at different slag/solution ratios in batch reactor without fresh water input (a) and increase of Ca leaching by fresh water input into mix-flow type reactor with different solution residence time (b).

Scenario 2 (direct slag carbonization in Reactor 1) was modeled and the results were compared to the experimental data for slag carbonization. Experimental verification was undertaken using a lab-scale apparatus consisting of two connected reactors (plastic tanks). Reactor 1 contained slurry of up to 2 kg of slag and 20 liters of water that was mechanically stirred. The aqueous liquor was pumped at varying rates to Reactor 2, which had a two-liter volume. Bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles, which allowed intimate mixing of the gas and alkaline solution. A multi-channel meter was used to measure the pH level in both reactors. At the completion of each test (20 hours), a sample of the slurry from Reactor 1 was filtered, dried, and analyzed for carbonization.

The prevailing reaction was direct slag particle carbonization in Reactor 1, while a minor amount of residual precipitated carbonates was found in Reactor 2. A similar result was achieved using the METSIM simulation. As the particle size decreased the amount of slag carbonization (i.e. $CaCO_3$ formation) increased as shown in Fig. 13. A 1 mm particle size resulted in 2% $CaCO_3$, while decreasing the particle size by an order of magnitude to 0.1 mm resulted in 8% $CaCO_3$ at the same time. Decreasing the particle size another half order of magnitude to 0.02 mm resulted in 23% $CaCO_3$. The experimental and modeled results were in good agreement.

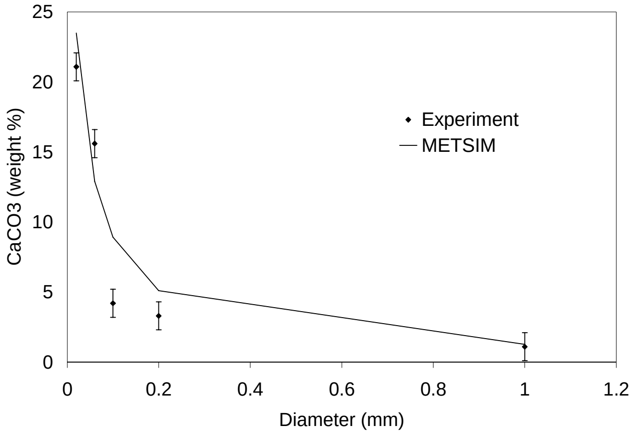


Fig.13 Comparison of METSIM calculated and experimentally measured calcium carbonate content in LMF Slag #2 after 20 hours reaction.

For scale-up to an industrial process of carbon dioxide sequestration, continuous operation of the reactor is desired. For this application the METSIM model was designed to allow continuous feed of fresh slag to Reactor 1 at the same rate as continuous discharge of carbonized product from Reactor 2. Carbon dioxide is introduced into Reactor 2 and the aqueous solution was recirculated from Reactor 2 to Reactor 1. It was assumed as a first approximation that Reactor 1 operated in back-mix mode with the composition of the discharged stream as an average for Reactor 1. Non-steady state model operation was carried out starting with fresh slag. After a specific period of time, the non-steady process became steady. In continuous flow process with the constant rate of slag input, the increase on residence time will increase the required volume of the Reactor 1. Decreasing the slag residence time made it possible to minimize the volume of Reactor 1, however, the result will be a simultaneous decrease in the level of slag carbonization in the discharged product (Fig. 14). An approximate one-week treatment in continuous mode provided nearly half the possible carbonization compared to steady batch type mode.

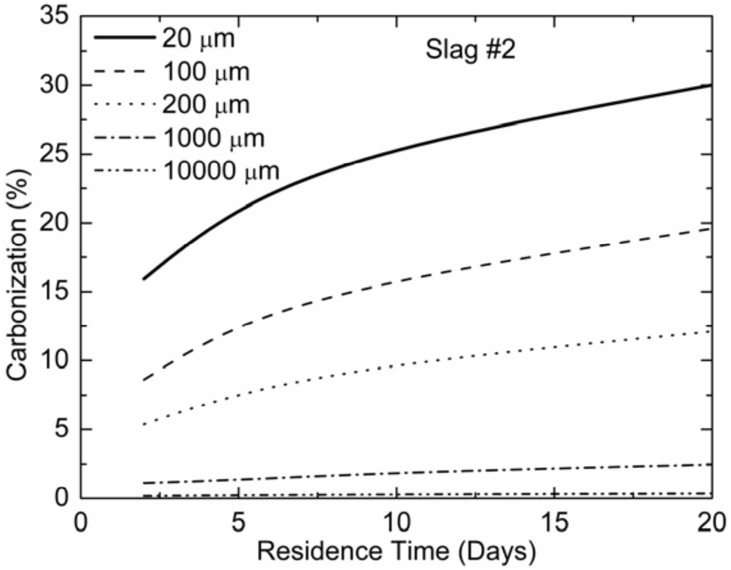


Fig. 14 Scale-up MESTIM modeling of LMF Slag #2 carbonization using varying particle size.

5. Conclusions

1. Carbon dioxide sequestration with steelmaking slag was studied in a two-phase (gas-solid) and three-phase (gas-liquid-solid) systems containing industrial CO_2 gas, water, and slag, at ambient temperature and pressure. The reaction rates of aqueous Ca-leaching and direct carbonization were quantified independently to yield the reaction parameters and rate-limiting mechanisms as listed below.
2. The reaction kinetics was described with modified shrinking core model. The model reflected the morphology of product layer formation. The obtained experimental data and kinetic parameters were used for modeling an industrial prototype reactor.
3. The concept of apparatus consisted of two interconnected reactors was proposed for industrial application of carbon dioxide sequestration by steel making slag. The design allows incorporating the sequestration system into existing streams of slag and off-gasses containing CO_2. METSIM process simulator was used to model of carbon dioxide sequestration using steelmaking slag.
4. A comparison of several scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles and accelerating the reaction kinetics. In addition, this scenario could produce pure calcium carbonate. However, the water requirement in a continuous system is much higher than a recirculated system.
3. To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor without a degassing step. The dissolved carbonic acid results in the formation of a calcium carbonate layer on the slag particles, which inhibits leaching of calcium ions. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly assisted the amount of calcium that could be carbonized. The developed METSIM model can be used for the design of an optimized CO_2 sequestration reactor system based on different slag fractions and compositions.

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American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report - Attachment E

Articles Submitted for Publication

January 2008

Two-Stage Reactor for Geological Sequestration of Carbon Dioxide Using Steelmaking Slag

LEKAKH, S.N., ROBERTSON, D.G.C., RAWLINS, C.H., RICHARDS, V.L., PEASLEE, K.D.

ABSTRACT

Hydrous carbonate sequestration of CO_2 using steelmaking slag was studied using a METSIM process model for analysis of experimental data and determination of reactor design parameters. A two-stage system with water/slag contact in Reactor 1 and alkaline-leachate/CO_2 contact in Reactor 2 was analyzed for several possible operating scenarios including batch versus continuous processing and fresh water versus recirculation. The METSIM leaching and carbonization models were verified with results obtained from previous slag sequestration experiments. Fresh water additions to Reactor 1 allowed the highest leaching efficiency and resulted in excellent carbonization in Reactor 2, however, a continuous system has a high water demand. Recirculation of the spent leachate minimizes the fresh water addition but produces a calcium carbonate product layer on the slag particles in Reactor 1 which inhibits the leaching process. Increasing the slag surface area, slag/solution ratio, or reactor residence time partially overcomes product layer blinding. The optimal residence time was defined for different process parameters and slag particle size.

I. INTRODUCTION

Steelmaking slag contains a high fraction of alkaline-earth oxides which exothermically form carbonates thus rendering this material as an excellent vehicle for capture and sequestration of carbon dioxide. Particulate-based slag is readily available in plentiful quantities at steel mills. This material has been shown to have the potential to sequester 35-45% of the CO_2 generated from EAF production and 6-11% of the CO_2 generated from BOF production.[1] Extraction of CO_2 from steel manufacturing offgas with steelmaking slag for geological sequestration was studied by quantifying the extent and rate of carbonate formation under near-atmospheric aqueous conditions.[2] The natural carbonate formation kinetics are very slow, thus fine grinding to increase slag surface area, increasing pCO_2, increasing temperature, and aqueous catalysis are being investigated to increase the reaction rate suitable for industrial use.[3] The goal of this research is to design a reactor suitable for aqueous-based carbonization of steelmaking slag for geological sequestration of carbon dioxide.

Several research groups have investigated the design of an aqueous reactor system for sequestration of carbon dioxide using steelmaking slag. Huijgen et al.[4], Eloneva et al.[5], and Stolaroff et al.[6] have worked with leaching and carbonization of steelmaking slag under various conditions. They each found that the rate and extent of aqueous leaching and carbonization was inversely related to particle size the primary factor, while pH, temperature and CO_2 partial pressure had milder effects on Ca-conversion. In comparison with naturally occurring wollastonite ($CaSiO_3$), steel slag was able to sequester 11 times more CO_2 at ambient temperature. Other consortiums have actively researched methods of large-scale mineral-based sequestration of carbon dioxide. O'Connor et al. conducted research to optimize the process conditions for direct aqueous carbonation of silicate minerals.[7-9] Activation of the minerals (serpentine or olivine) through attrition grinding or heat-treatment was necessary to achieve high levels of carbonization. Additions of $NaHCO_3$ and NaCl to the suspension were found to catalyze the reaction significantly. Park et al. investigated carbonization of olivine and serpentine similar to the work of O'Connor et al.[10] Aqueous carbonation studies revealed that increasing the reactor temperature, pCO_2, and $NaHCO_3$/NaCl concentration increased the carbonization rate. Fernandez et al. found the reactivity of magnesite slurries for carbonization increases with decreasing particle size and increase with pCO_2, temperature, and solid-liquid ratio.[11]

The current study capitalizes on the findings from many of these researchers as well as current experimental work to model the design of a reactor for aqueous-based sequestration of carbon dioxide with steelmaking slag. The current process uses a two-stage system in order to decouple the competing leaching and carbonization mechanisms that occur simultaneously. The reaction rate of calcium leaching from slag into water and the direct carbonation of slag particles were investigated separately to understand the limiting mechanisms for the overall sequestration process. Areas modeled in this investigation to understand the reaction rate include particle size, reactor vessel residence time, reaction time, and reactor flow sequencing.

II. REACTOR DESIGN AND MODELING PROCEDURE

A. *CO_2 Sequestration Reactor Design*

Carbon sequestration through the aqueous-based reaction of CO_2-containing offgas with lime-bearing steelmaking slag allows for several possible reactions to take place. A list of the key competing reactions considered is given in Table 1. For simplification the calcium containing phases are all designated as CaO.

The process design consists of two vessels connected by a pumped water stream, as shown in Figure 1. Each reactor vessel operates at ambient pressure and temperature. Water and slag particles are introduced into Reactor 1, wherein calcium ions are dissolved to form an alkaline leachate. The leachate is pumped to Reactor 2 through which gaseous CO_2 is bubbled. The CO_2 dissolves into the water to from carbonic acid ions, upon which several competing reactions take place resulting in precipitation of $CaCO_3$. This process design allows for several system scenarios to be investigated for optimization of CO_2 capture.

- Scenario 1: Fresh water is supplied into Reactor 1 and the leachate containing calcium ions is pumped to Reactor 2 where calcium carbonate precipitates. The spent leachate (containing residual dissolved CO_2) is discharged.
- Scenario 2: The same design as Scenario 1 except that the water supplied to Reactor 1 is recirculated from Reactor 2 after complete degassing.
- Scenario 3: Fresh water is supplied to Reactor 2 for saturation with CO_2 then the CO_2 saturated water is pumped to Reactor 1 for direct reaction with slag. The spent water (containing residual dissolved CO_2) is discarded.
- Scenario 4: The water supplied to Reactor 1 is recirculated from Reactor 2 without degassing.

Experimental verification of the different scenarios was undertaken using lab-scale apparatus consisting of two connected reactors (tanks). Recirculation of the aqueous stream took place both with and without partial degassing by argon bubbling. Reactor 1 contained mechanically stirred slurry of 2 kg of slag in 20 liters of water. The aqueous leachate was pumped at varying rates to Reactor 2, which had a two-liter volume. Bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles to allow intimate mixing of the gas and alkaline solution. A multi-channel pH meter was used to directly measure the pH level in both reactors. At the completion of each test, a sample of the slurry from Reactor 1 was filtered, dried, and analyzed for fraction carbonization as described in the previous work.[3] Kinetic data from this previous work was used in the studied scenarios, while METSIM process simulation software was used to perform the modeling calculations.[13]

B. *METSIM Modeling Procedure*

An approach developed by Robertson for modeling heterogeneous reaction kinetics of a non-steady-state process was used for the two-stage reactor system.[14] A block diagram of the METSIM model is shown in Figure 2. The computer model consists of two blocks, representing Reactor 1 (Figure 2a) and Reactor 2 (Figure 2b), connected by streams 15/17 and 20/12. In Reactor 1, the amount of input slag is defined by Stream 10 which connects the mixer and splitter pair A and C, respectively. In the same manner, the amount of aqueous solution is defined by Stream 2 which connects the mixer and splitter pair B and D, respectively. Slag leaching and direct carbonization reactions occur in splitters E and F, respectively. In Reactor 2, carbon dioxide gas (Stream 16) is mixed with the aqueous stream from Reactor 1 (Stream 12) in Mixer F, while CO_2 dissolution to form carbonic acid ions takes place in Splitter G. Carbonic acid ions react with calcium ions in Splitter M, and any precipitated calcium carbonate accumulates in the loop consisting of the mixer/splitter pair H/L.

This model allows the flexibility of studying each of the four scenarios individually. For example, in Scenario 1 fresh water is supplied by Stream 9 to leach the slag in Reactor 1. The leached calcium ions are pumped to Reactor 2 by Stream 15/17 where precipitated calcium carbonate accumulates in Stream 26. The spent aqueous stream is discarded by Stream 22 without flowing back to Reactor 1. Alternatively, in Scenario 4 the aqueous solution is recirculated by streams 15/17 and 12/20 without fresh water input in Reactor 1 or solution discharge from Reactor 2. The model was used to calculate both a non-steady-state batch type process in Reactor 1 with no fresh slag input by Stream 1 and no product discharge by Stream 7, as well as a steady-state continuous type process with fresh slag input and carbonate product output.

C. *Experimental Reaction Kinetics for METSIM Modeling*

In the METSIM model, the reaction rate F is defined by Equation 1. The rate constant *K* is defined by the mass flow rate ($m_i/\Delta t$) from the mixer/splitter to the phase splitter where the reaction occurs with the particular value of reaction extent (*RE*) at each time step (Δt). The experimentally measured kinetic parameters from earlier work for leaching and carbonization were used to evaluate the factors listed in Equation 1.[3]

$$F = K \times (RE) \qquad [1]$$

Carbonization. Heterogeneous direct aqueous carbonization of slag particles was modeled for the batch case of Scenario 4 in order to validate the results with the experimental data. In this scenario, the reaction rate is limited by mass transfer through the carbonate product layer, and the reaction rate decreases with time as a result of increasing thickness and density of carbonate layer.[3] The reaction rate expression increases in complexity because the porosity of the product layer decreases simultaneously along with shrinking of the core of unreacted slag (with radius r_c) in each particle (with initial radius *R*). Therefore, a modified shrinking core model was used with the assumption that diffusivity (*D*) decreases as the reaction proceeded. This model is defined by Equations 2-5, where J_A (moles/m^2·s) is the flux of component *A*, dN_A/dt (moles/s) is the reaction rate, ρ_m (moles/m^3) is the molar density, and the parameter *k* (m/s) was chosen to fit the experimental data.[4]

$$-\frac{dN_A}{dt} = -4\pi r^2 J_A \qquad [2]$$

$$J_A = -D\frac{dC_A}{dr} \qquad [3]$$

$$dN_A = 4\pi\rho_m r_c^2 dr_c \qquad [4]$$

$$D = D_0 - k(R - r_c) \qquad [5]$$

In this system, Equation 2 is the reaction rate as a function of surface area and flux, Equation 3 is the diffusion flux as a function of diffusivity and concentration gradient, and Equation 4 is the mass balance of component A.[15] Equation 5 is the diffusivity as a function of carbonized layer thickness. This system of equations was solved numerically for three incremental time steps, each with changing diffusivity, in order to fit the experimental data for carbonization of an Al-killed LMF slag with 49.9 wt.% CaO (Slag #2, 420-590 µm).[3] Comparison of the experimental results and those calculated from the modified shrinking core model using constant and decreasing diffusivity are shown in Figure 3. The terms Ca_C and Ca_S are the fractions of calcium carbonized and calcium initial present in the slag, respectively.

For application in the METSIM model, the experimental kinetics of the carbonization reaction was approximated to be a function of time (*t*) as shown in Equation 6. A factor of n=⅓ resulted in an appropriate fit for the reaction conversion (Ca_C/Ca_S) calculated from Equations 2-5, as well as the experimental data.

$$\ln\left(1 - \frac{Ca_C}{Ca_S}\right) = f(t)^n \qquad [6]$$

For direct carbonization of slag particles (Figure 4) the experimental data was fit to Equations 7 and 8. In these equations *d* is the particle diameter (mm), *t* is time (min) and coefficient A=0.0012 was taken from correlated experimental data (Figure 4b). The first derivative (Equation 8) represents the reaction rate *F* and was used in the METSIM model.

$$Ca_C = Ca_S\left(1 - \exp\left(-\frac{A}{d}t^{1/3}\right)\right) \qquad [7]$$

$$F = \frac{dCa_C}{dt} = \frac{ACa_S}{3d}t^{-2/3}\exp\left(-\frac{A}{d}t^{1/3}\right) \qquad [8]$$

Leaching. A similar analysis of the calcium leaching process was undertaken, with a set of reactions that corresponds to Scenario 1. The reaction rate changes during the leaching process because the initial chemical reaction limited mechanism is overtaken by slower diffusion through the porous surface layer developed during treatment.[3] The difference in Equation 9 for leaching when compared to carbonization (Equation 8) follows from the necessity, due to batch test procedure, of taking into account the solution volume V (cm^3), the calcium saturation level C_{sat} (wt. %) for solution in equilibrium with solid Ca(OH)$_2$, and the total surface area S= 6$W/\rho d$ (cm^2) of slag particles with diameter d (cm), density ρ (g/cm^3), and weight W (g) In Equation 9, C_D is the concentration of dissolved calcium in solution (wt. %) and the coefficient A=0.0004 was taken from a correlation of experimental data shown in Figure 5.

$$F = \frac{dC_D}{dt} = \tfrac{1}{3}VAC_{sat}St^{-2/3}\exp\left(-ASt^{1/3}\right) \qquad [9]$$

The extent of calcium leaching from slag depends on the slag particle size and the particle surface conditions. Calcium from fresh slag leached twice as fast when compared to the same slag in carbonized condition.[3] Because leaching and carbonization may occur simultaneously in Scenario 4 in the designed apparatus, the leaching reaction rate (Equation 9) was linked to the current slag carbonization level during each calculation step.

III. RESULTS AND DISCUSSION

A. *Model Validation With Batch Reactor*

The METSIM model was first validated by comparing the calculated results with the experimental data obtained from the batch reactor tests of the previous work.[3]

Leaching. The calcium leaching experiments were performed in a batch type reactor under protective argon atmosphere with unsaturated aqueous solutions, which corresponds to Scenario 1 for Reactor 1. The METSIM modeling of a batch type reactor was done by disconnecting Reactor 1 from Reactor 2 and disregarding the feed streams. Figure 6 shows the comparison of calculated and experimental results for the concentration of calcium leached (C_D) from LMF Slag #2 (49.9 wt.% CaO) at two average particle sizes (60 µm and 200 µm). The calculated leaching results were in good agreement with the experimental data.

Carbonization. Direct carbonization of the same slag was studied in a batch type reactor using aqueous solution saturated by carbonic acid under CO_2 at one atmosphere pressure.[3] This process was modeled using batch type Reactor 1 connected to Reactor 2 with continuously flowing CO_2 gas saturating the aqueous solution. The transport of calcium ions from Reactor 1 to Reactor 2 was prohibited. This approach modeled the experimental conditions of Scenario 3. Figure 7 shows the experimental results for the amount of calcium carbonized (Ca_C) were in good agreement compared to that predicted by the METSIM model for two different average particle sizes of LMF Slag #2 (60 µm and 2800 µm).

B. *Model Validation with Experimental Two-Stage Reactor*

The METSIM model was further validated by comparing the calculated results with the experimental data obtained from the two-stage reactor tests of the previous work.[3] Scenario 4 was modeled (batch amount of slag with recirculated, un-degassed water) and the results compared to the experimental data for slag carbonization. In the experimental work, both Ca leaching and direct slag particle carbonization were monitored simultaneously in both reactors. Reactor 1 contained 200 g LMF slag (<3.2 mm) in 20 liters of water, while Reactor 2 contained two liters of solution through which 1.5 g/min CO_2 was bubbled. A solution exchange rate of one liter per minute was used to transfer the fluid between the two reactors. The experimental procedure included preliminary soaking of slag in Reactor 1 for 20 minutes with solution recirculation but without CO_2 input in Reactor 2. During this time, the pH increased in both reactors as $Ca(OH)_2$ was formed. Shortly after introducing CO_2 into Reactor 2, the concentration of calcium ions in solution decreased while concentration of carbonic acid increased. The rate of decrease in pH (Figure 8) depended on the solution residence time in Reactor 1 (20 minutes) and Reactor 2 (2 min).

The reaction was allowed to proceed for 20 hours, after which the product was dried, sieved, and analyzed for calcium carbonization. The prevailing reaction was direct slag particle carbonization in Reactor 1, while a minor amount of residual precipitated carbonates was found in Reactor 2. A similar result was achieved using the

METSIM simulation. The model predicted carbonate precipitation in Reactor 2 during a short period of time immediately after introducing CO_2, after which direct carbonization of the slag in Reactor 1 took predominance. As the particle size decreased the amount of slag carbonization (i.e. $CaCO_3$ formation) increased as shown in the model results in Figure 9a. A 1000 µm particle size resulted in 2% $CaCO_3$ at 20 hours (1200 min), while decreasing the particle size by an order of magnitude to 100 µm resulted in 8% $CaCO_3$ at the same time. Decreasing the particle size another half order of magnitude to 20 µm resulted in 23% $CaCO_3$. A comparison of the experimental (Figure 9b) and modeled (Figure 9a) results for five particle sizes shows good agreement.

C. *Industrial Process Modeling*

The validated METSIM process model was used to study the four scenarios defined for the purpose of reactor flow schematic optimization.

Scenario 1: Continuous and Batch Operation. The goal of this scenario was to analyze the influence of slag/solution ratio and solution residence time in Reactor 1 on the extent of leaching only. In this model, slag was leached in Reactor 1 and the alkaline leachate was carbonized in Reactor 2. The slag used was LMF Slag #2 with 49.9 wt.% CaO and a monosize 200 µm distribution. During continuous operation, fresh water was input into Reactor 1, which contained a fixed amount of slag, while at the same rate the spent leachate was discharged from Reactor 2, with no water recirculated to Reactor 1. For comparison, batch operation was studied in which there was no water flow in or out of Reactor 1, only a fixed starting volume of water and slag was used.

The results of this model are presented in Figure 10 and show that both increasing the slag/solution ratio and the solution residence time in Reactor 1 resulted in a higher concentration of calcium ions in solution. Increasing the slag/solution ratio with zero water throughput (i.e. batch mode) provided a diminishing increase in calcium ions in solution due to saturation of the aqueous phase (Figure 10a). For example, increasing the slag solution ratio by an order of magnitude from 0.08% to 0.8% results in an increase of $Ca(OH)_2$ from 150 PPM to 950 PPM at 10 hours, while a further doubling of the slag/solution ratio to 1.6% results in a corresponding increase to 1100 PPM at the same time. To overcome saturation of the aqueous phase, the feed water throughput in Reactor 1 can be increased, which corresponds to decreasing the residence time (Figure 10b). At a fixed slag/solution ratio of 0.8%, 5000 minute residence time approaches a batch system, which has a theoretical infinite residence time. As the residence time decreases the resulting solution becomes less saturated and at five minutes the leachate is very under-saturated. While minimizing the solution saturation provides increased driving force for Ca dissolution, it also requires a significant increase in feed water. The total fraction of calcium leached from the slag (y-axis of Figure 10c) is equal to the concentration of calcium in solution multiplied by the solution volume. The optimal residence time is therefore a balance between maximizing the amount leached with minimizing fresh water input. For slag with 200 µm particle diameter (monosize) and 0.8% slag/solution ratio, the optimal residence time is near 1 hour (Figure 10c).

Scenario 2: This scenario minimizes fresh water input into the system by recirculating the leachate from Reactor 2 to Reactor 1. However, for this scenario to work properly the recirculated leachate must be fully degassed to prevent carbonic acid from reporting to Reactor 1. Preliminary experiments with degassing the leachate by argon bubbling showed that full leachate degassing is difficult to achieve and the residual content of carbonic acid will provide direct carbonization of the slag particles in Reactor 1. This scenario is therefore covered by the study of Scenario 4.

Scenario 3: This scenario inputs fresh water into Reactor 2 for saturation with CO_2, then the CO_2 saturated water is pumped to Reactor 1 for direct reaction with slag. As this scenario requires a significant quantity of fresh water input, it was not modeled in this analysis.

Scenario 4: Steady-State Continuous Operation. For scale-up to an industrial process of carbon dioxide sequestration, continuous processing of slag through the system is desired. To meet this criteria a steady-state METSIM model was setup to allow continuous feed of fresh slag to Reactor 1 at the same rate carbonized product was discharged from Reactor 2. Carbon dioxide was introduced into Reactor 2 and the aqueous solution was recirculated from Reactor 2 to Reactor 1. As a first approximation, Reactor 1 was assumed to operate in back-mix mode with the composition of the discharged stream as an average for Reactor 1. The steady-state model was compared to a batch processing model, and both cases used fresh slag (LMF Slag #2 with 49.9 wt.% CaO).

In batch processing mode, the amount of slag carbonization achieved increased steadily with reaction time, as shown in Figure 11a. At seven days (10,800 min.) of processing in batch mode, ~8% carbonization was achieved using a 200 µm particle. In steady-state processing mode, with a constant amount of slag throughput, the overall amount of carbonization was dependent upon Reactor 1 slag residence time and particle size (Figure 11b). A 200 µm particle at seven days residence time achieved ~8% carbonization, while a 20 µm particle achieved ~22.5% carbonization. The particle size is critical as a 1 mm particle achieved only ~2% carbonization at the same residence time. Increasing the slag residence time of Reactor 1 results in a higher amount of carbonization achieved. For a 200 μm particle, two day residence time gave ~5% carbonization, while twenty day residence time gave ~12% carbonization. While increasing the slag residence time in Reactor 1 results in a higher amount of carbonization, it also requires a larger reactor volume. Decreasing the slag residence time makes it possible to minimize the volume of Reactor 1, but result in a simultaneous decrease in the level of slag carbonization in the discharged product. A balance can be realized between particle size and reactor residence time (volume). To achieve a specific amount of carbonization, reducing the slag particle size allows for reduction in reactor residence time (e.g. volume).

IV. CONCLUSIONS

METSIM process simulation software was used to model several reactor design scenarios for hydrous carbonate sequestration of CO_2 using steelmaking slag. A two-stage reactor design was modeled in batch and continuous mode. The process allowed introducing water and slag into the first reactor and carbon dioxide into the second reactor, with the possibility of recirculation of the solution. A comparison of the scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles, which could reduce the leaching efficiency. However, the water requirement in a continuous system is much higher than a recirculated system. To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor. The drawback to this system is that the residual absorbed CO_2 in the recirculated water results in the formation of a calcium carbonate later on the slag particles, which inhibits leaching of calcium ions. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly assisted the amount of calcium that could be carbonized. It was shown that the METSIM model is a useful tool for designing and optimizing CO_2 sequestration reactor systems based on different slag fractions and compositions.

V. ACKNOWLEDGEMENTS

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Table I. Reactions Occurring During Aqueous Slag-CO_2 Sequestration[4,12]

Description	Reaction
Ca leaching	$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2(OH^-)$
CO_2 dissolution	$CO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + CO^{2-}_{3(aq)}$
Carbonate precipitation	$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(s)}$
Ca direct carbonization	$CaO_{(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} = CaCO_{3(s)} + 2OH^-$
Water dissociation	$2(OH^-) + 2H^+ \rightarrow 2H_2O_{(l)}$

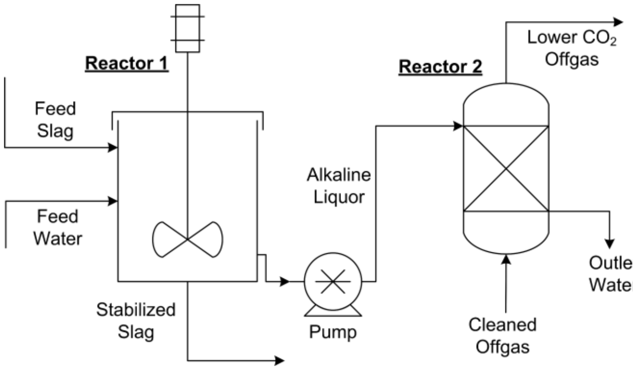
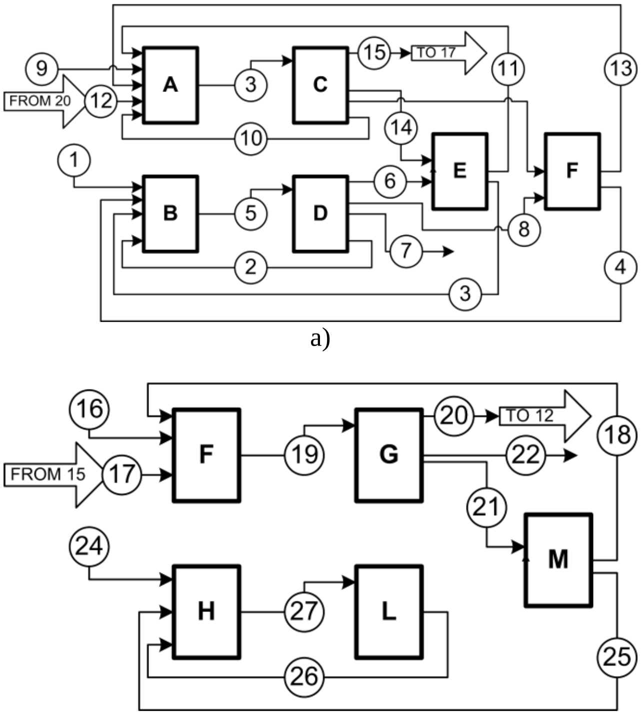


Fig. 1—Flow schematic of system for CO_2 sequestration with steelmaking slag.



a)

b)

Fig. 2—Block diagrams of the METSIM model for Reactor 1 (a) and Reactor 2 (b) which are interconnected by streams 15/17 and 20/12.

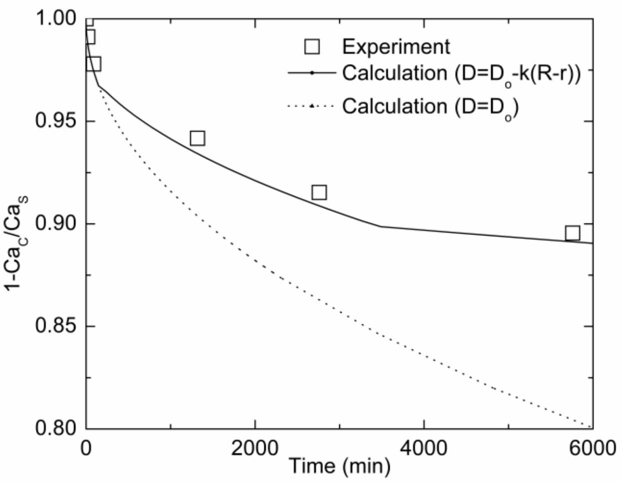
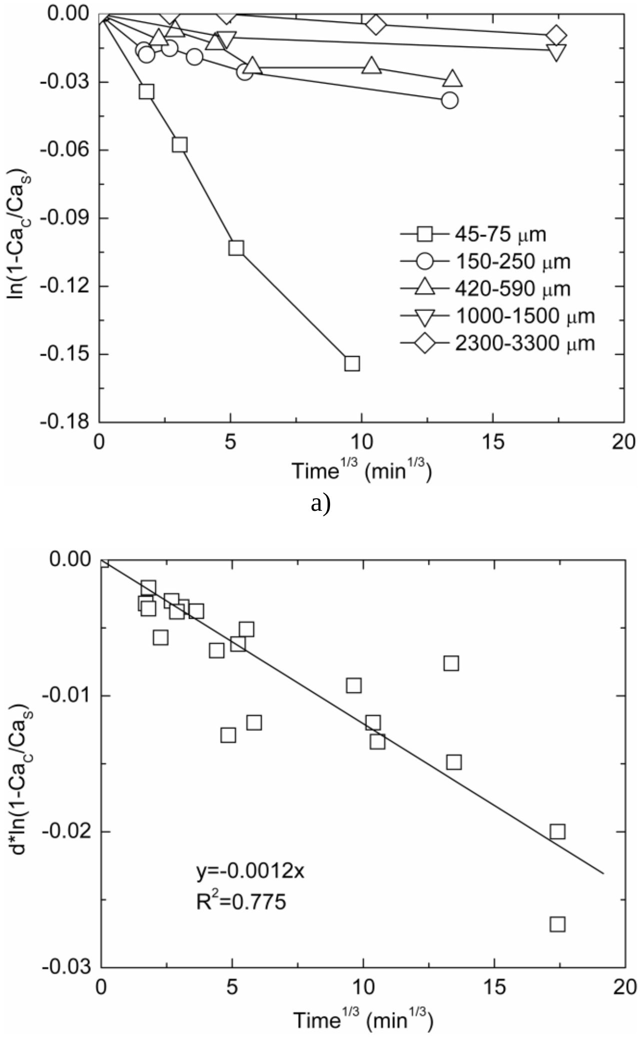


Fig. 3—Comparison of experimental data for slag carbonization with shrinking core model using constant ($D=D_0$) and decreasing ($D=D_0-k(R-r)$) diffusivity of the product layer for slag with 49.9 wt.% CaO and 420-590 µm particle size.



a)

b)

Fig. 4—Comparison of experimental data for slag carbonization with the parameters ln(1-Ca_C/Ca_S) (a) and d*ln(1-Ca_C/Ca_S) (b) versus time$^{1/3}$.

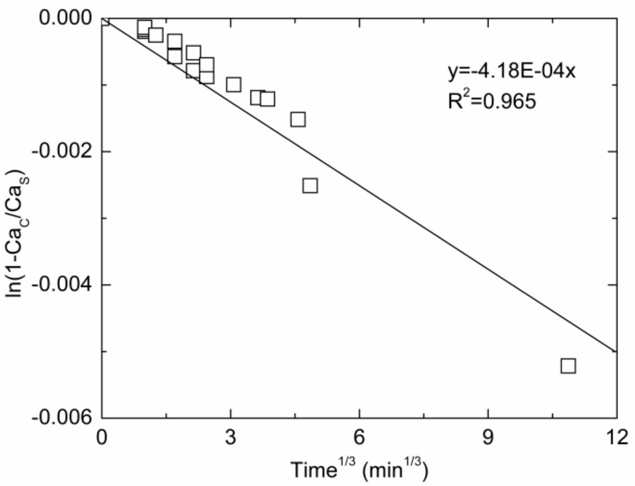
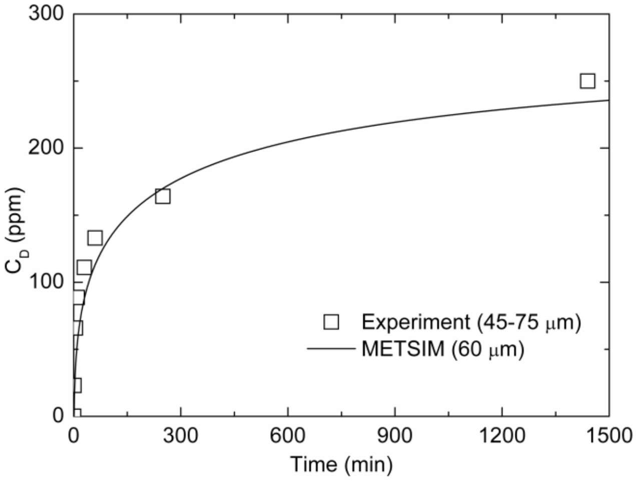
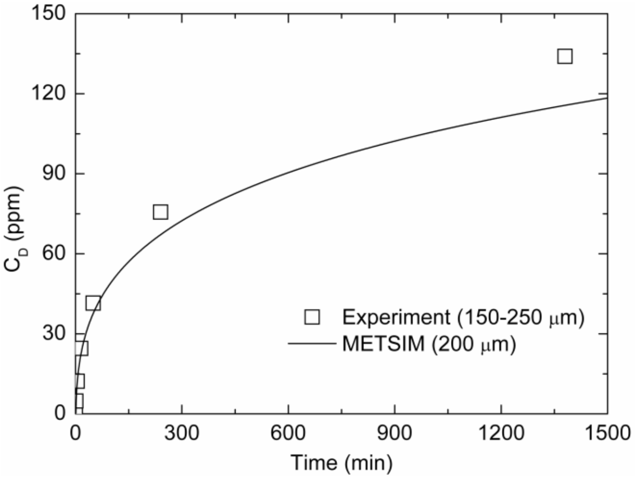


Fig. 5— Comparison of experimental data for slag leaching with the parameter $(1/S)*\ln(1-C_D/C_{sat})$ versus time$^{1/3}$.

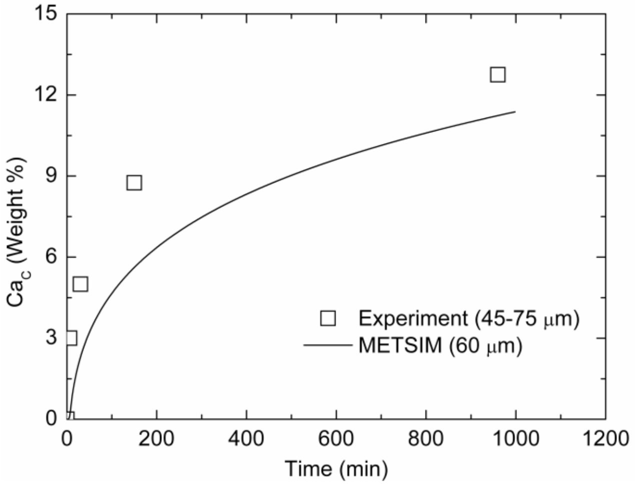


a)

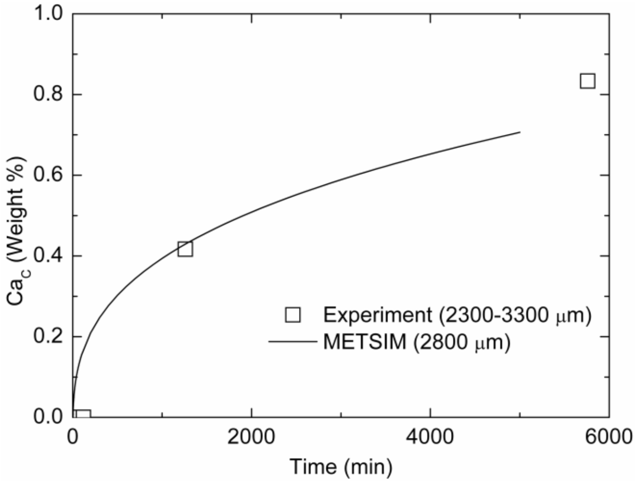


b)

Fig. 6—Comparison of experimental concentration of leached calcium (C_D) to calculated results from METSIM model for slag particles with 60 µm (a) and 200 µm (b) average diameter.



a)



b)

Fig. 7—Comparison of experimental results for calcium carbonization (*Ca_C*) in slag to calculated results from METSIM model for slag particles with 60 µm (a) and 2800 µm (b) average diameter.

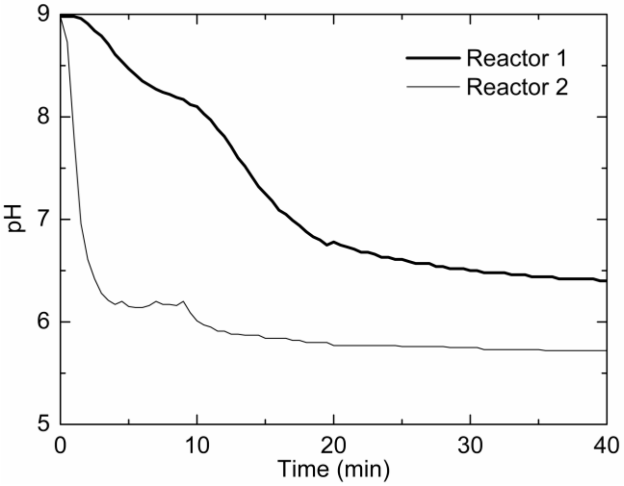
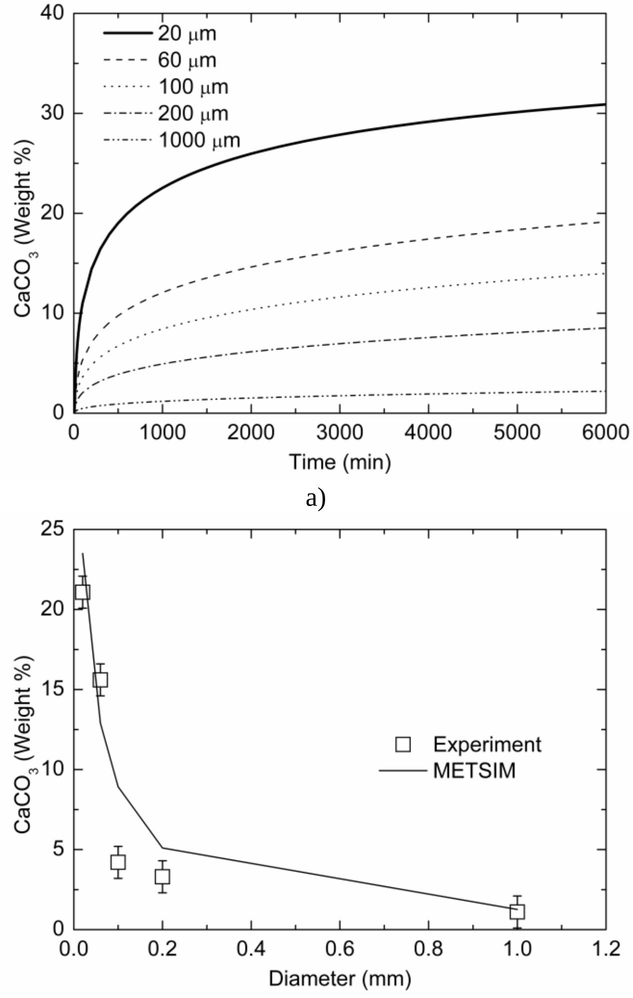


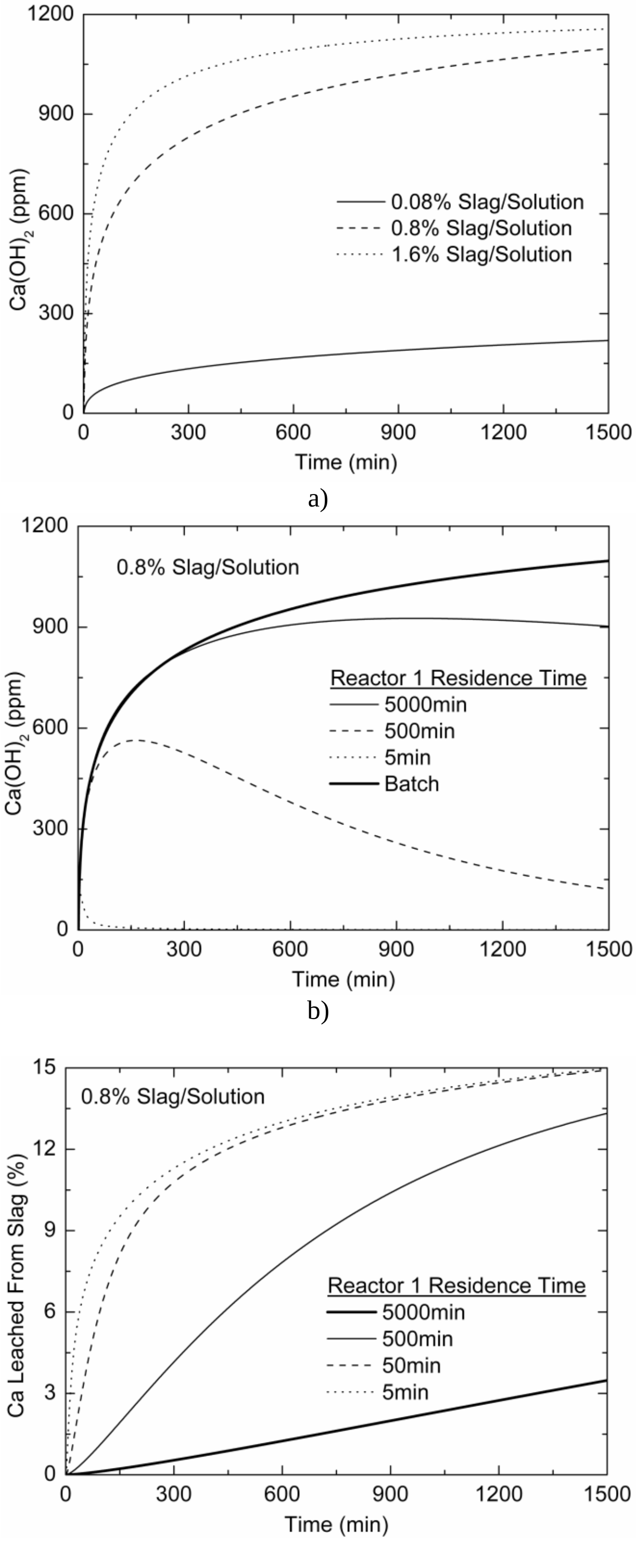
Fig. 8—Changing pH of aqueous solutions in reactors during carbonization (200 g of crushed <3.2 mm LMF Slag #2, 1.5 g/min flow rate CO_2) based on start of CO_2 flow.



a)

b)

Fig.9—METSIM calculated kinetics of LMF slag carbonization for several particle sizes (a) and comparison of calculated and experimentally measured calcium carbonate content after 20 hours reaction (b).

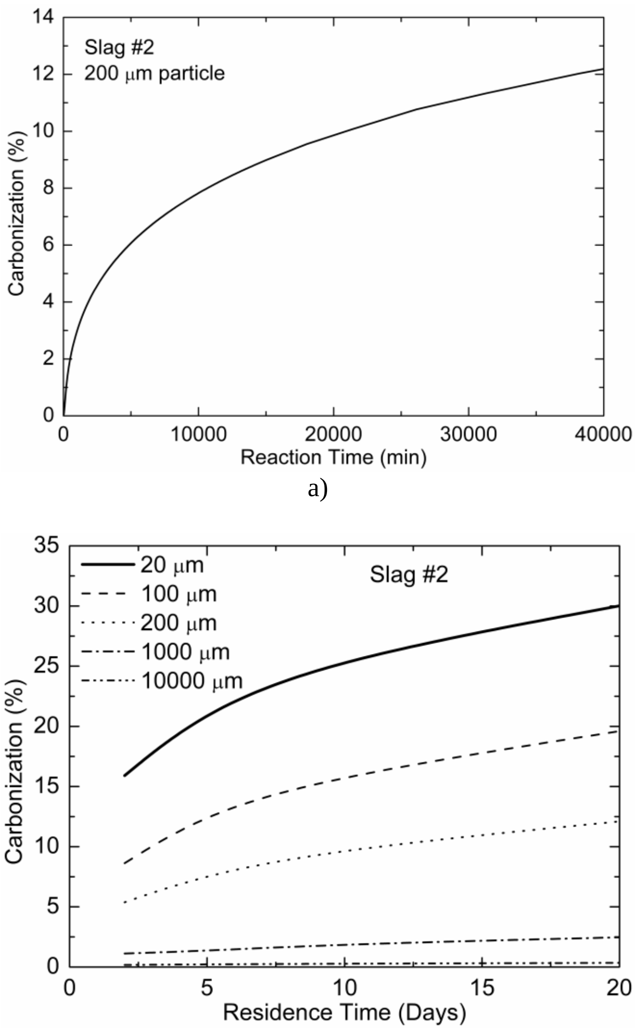


a)

b)

c)

Fig. 10—Results of METSIM model for leaching LMF Slag #2 (200 μm diameter) at different slag/solution ratios in batch mode (a) and increase of Ca leaching by fresh water input into mix-flow type Reactor 1 with different residence times (b, c).



a)

b)

Fig. 11—Comparison of batch carbonization a 200 μm particle (a) and steady-state continuous carbonization (b) using varying particle size of LMF Slag #2 in Reactor 1.

Carbon Dioxide Sequestration with Steelmaking Slag: Process Feasibility and Reactor Design

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Keywords: Steelmaking Slag, CO_2, Sequestration, Metal Recovery, Reactor

ABSTRACT

The goal of this research is to develop a functional sequestration process using steelmaking slag for permanent capture of carbon dioxide emitted from steelmaking offgas. A parallel benefit of this process is rapid chemical stabilization of the slag minerals with reducing swelling or leaching potential. This paper summarizes the results of the project including mineralogical features of carbonate formation in steelmaking slag, study of the reaction mechanisms, thermogravimetric analysis of the reaction between solid-state slag and CO_2, design and testing of a two-stage lab scale reactor system, METSIM modeling of possible reactor designs, and exploration of the economic feasibility of the process based on operating costs, metals recovery and credit for CO_2 sequestration.

INTRODUCTION

Extraction of CO_2 from steel manufacturing offgas with steelmaking slag is being studied by quantifying the extent and rate of carbonate formation under near-atmospheric aqueous conditions.[1-3] Basic oxygen furnace (BOF) and electric arc furnace (EAF) slags typically average 30-50 wt.% CaO and 10-12 wt.% MgO and ladle metallurgy furnace (LMF) slags typically contain 50-60 wt.% CaO and 10-12 wt.% MgO. Slag production per ton is typically 75-150 kg for BOFs, 65-80 kg for EAFs, and 15-20 kg for LMFs. Production of a ton of steel generates on the average 519 kg CO_2 carbon equivalent (CE) for BOFs and 119 kg CO_2 CE for EAFs Assuming full stoichiometric conversion of CaO and MgO to carbonate, steelmaking slag has the potential to sequester 6-11% of the CO_2 generated from BOF production and 35-45% of the CO_2 generated from EAF production[2].

The use of slag as an agent for capturing CO_2 emissions has the potential of increasing the application and value of slag. Due to its high alkaline earth oxide content and immediate availability at the steel mill, steelmaking slag can serve as a unique source-point mitigation for CO_2 sequestration. In order to achieve suitable efficiency for industrial-scale CO_2 sequestration, the slag must be finely ground in order to provide sufficient surface area for rapid leaching of the alkaline-earth components and subsequent conversion to carbonates. Because mineral comminution is energy intensive, there are concerns that the energy required to grind the slag could exceed the CO_2 sequestration benefit in both direct cost and indirect CO_2 generation (e.g. CO_2 emitted from the electric generation source). To characterize the comminution energy for steelmaking slag accurately, a separate study was conducted that determined the grindability of this slag using the Bond Work Index method.[4] Work index is the comminution parameter that expresses the resistance of a mineral to crushing or grinding. This parameter permits calculation of the power expended in mineral crushing and grinding unit processes. The study also included size-by-size separation of the liberated magnetic fraction from the ground product. The results of the grindability study were used to develop a valuation model of the overall sequestration process.

This paper summarizes the mineralogical features of carbonate formation in steelmaking slag, reaction mechanisms, thermogravimetric analysis of the reaction between solid-state slag and CO_2, design and testing of a two-stage lab scale reactor system, METSIM modeling of several possible reactor designs, and exploration of the economic feasibility of the process based on process operating costs, metals recovery and credit for CO_2 sequestration.

SLAG CHARACTERIZATION

Table I lists the chemical composition of several industrial slags as obtained by x-ray fluorescence (XRF). EAF slag #1 contained 32.1% CaO while LMF Slags #2 and #3 contained higher, but nearly equal, percentage of CaO plus an Al_2O_3/SiO_2 amount that reflects their respective steel deoxidation practice.

Table I. Steelmaking slag compositions (Wt Pct)

Sample	*#1*	*#2*	*#3*
Type	EAF	LMF Al-Killed	LMF Si-Killed
CaO	32.1	49.9	51.3
SiO_2	19.4	4.5	28.3
Al_2O_3	8.6	32.3	4.9
TiO_2	0.4	0.3	0.3
MgO	9.4	4.3	4.3
MnO	6.8	0.8	1.3
Fe_xO_y	26.4	6.3	5.5
SO_3	0.6	1.0	1.6

X-ray diffraction (XRD) showed that the three slags listed in Table I contained primarily dicalcium silicate (Ca_2SiO_4) and tricalcium silicate (Ca_3SiO_5) with lesser amounts of akermanite ($Ca_2MgSi_2O_7$), $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$), clinoenstatite ($MgSiO_3$), and magnesio-wustite ($MgFeO_2$). Only a minor amount of free periclase (MgO) and lime (CaO) were present showing the alkaline earth metal oxides are primarily tied up as silicates, aluminates, and ferrites. As the slag-CO_2 reaction may be governed by particle surface area, the specific surface area (m^2/g) was determined for several fractions of the crushed slag samples using the Brunauer-Emmett-Teller (BET) gas sorption method. The measured specific surface area (m^2/g) of slag particles was significantly larger than the area calculated for hypothetical uniform spheres indicating an angular shape and open internal porosity.

CO_2 SEQUESTRATION THERMODYNAMICS AND KINETICS

The thermodynamic potential of specific phases in steelmaking slag to sequester carbon dioxide as carbonates is shown in Figure 1. The area above each corresponding phase line shows the carbonate stability region. As temperature or partial pressure of CO_2 (pCO_2) increases, the carbonate stability region for each phase shrinks. From the phase stability chart, the operating region for a slag-CO_2 reactor, based on temperature or pCO_2, can be identified. The shaded section in Figure 1 shows the pCO_2 operating region produced within the stack offgas (11 vol.% CO_2 max), which is approximately 200-300°C considering dicalcium silicate as the predominant phase.[1] At ambient conditions (~350 ppm CO_2), all phases listed on Figure1 are stable as carbonates thus the slag will spontaneously react to sequester CO_2.

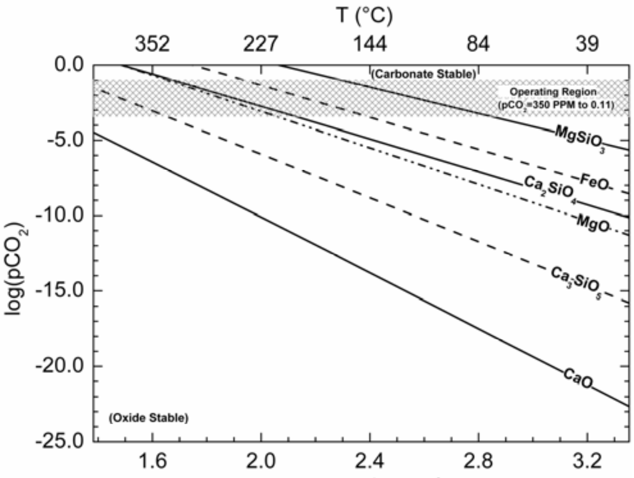


Figure 1. Carbonate stability diagram for alkaline earth metal oxide phases found in steelmaking slag (data generated from FactSage™ 5.4)

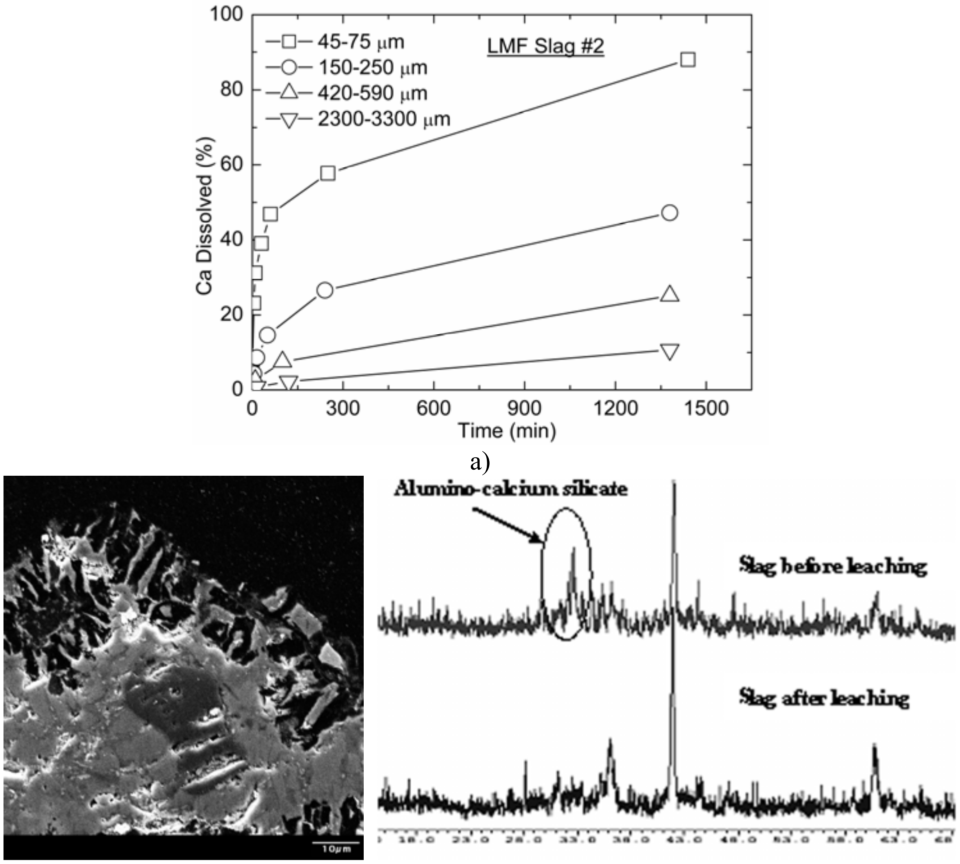
The primary obstacle to industrial-scale slag sequestration is the extremely slow solid-gas reaction rate at ambient pressure and temperature. Aqueous based processing has been found to accelerate the reaction kinetics. During aqueous based sequestration between CO_2-containing offgas with CaO-bearing slag, there are several possible competing reactions (see Table II). For simplification, the calcium containing phases are all designated as CaO. The reaction kinetics of both calcium dissolution from slag and direct carbonation of slag were studied in a slurry (aqueous) reactor at atmospheric pressure.

Table II. Reactions occurring during aqueous slag-CO_2 sequestration[5,6]

Description	*Reaction*
Ca leaching	$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2(OH^-)$
CO_2 dissolution	$CO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + CO^{2-}_{3(aq)}$
Carbonate precipitation	$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(s)}$
Ca direct carbonization	$CaO_{(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} = CaCO_{3(s)} + 2OH^-$
Water dissociation	$2(OH^-) + 2H^+ \rightarrow 2H_2O_{(l)}$

Calcium Leaching

Calcium leaching from slag was performed using a batch-type reactor containing deionized water and a buffer to maintain the pH between 7.0-7.5[7]. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to measure the Ca^{2+} concentration in slag samples leached with water. Figure 2a shows the effect of particle size on the extraction rate of Ca^{2+} from LMF slag #2. The particle size (i.e. surface area) had a significant influence on the amount of calcium leached. Leaching of Ca^{2+} from the slag particle starts at the slag surface, which includes many deep interconnected pores throughout the slag particle. Figure 2b shows a scanning electron microscope (SEM) image of the porous layer developed during leaching. XRD analysis showed that selective dissolution of the calcium containing phases takes place during aqueous leaching (Figure 2c).



a)

b)

c)

Figure 2. Calcium leaching from slag in aqueous solution (a) from different size fractions of LMF slag, (b) selective phase dissolution leaving a porous structure and (c) XRD spectra before and after aqueous leaching

The shrinking core model was used for analysis of heterogeneous (particulate) solid-fluid reactions to determine the rate-limiting mechanism.[8] Analysis of experimental data showed that multiple mechanisms were involved with Ca leaching from steelmaking slag. During the initial stage (see Figure 3), the reaction time follows the chemical reaction controlled model whereby solid CaO dissolves into Ca^{2+} ions in the water. As the dissolution reaction progresses a porous surface structure develops, as shown in Figure 2b, resulting in a tortuous path for the ions to travel. Subsequent diffusion through this structure became the rate-limiting step as indicated by the reaction rate change in Figure 3 at around 10 minutes when the data more closely fits diffusion using the shrinking core model.

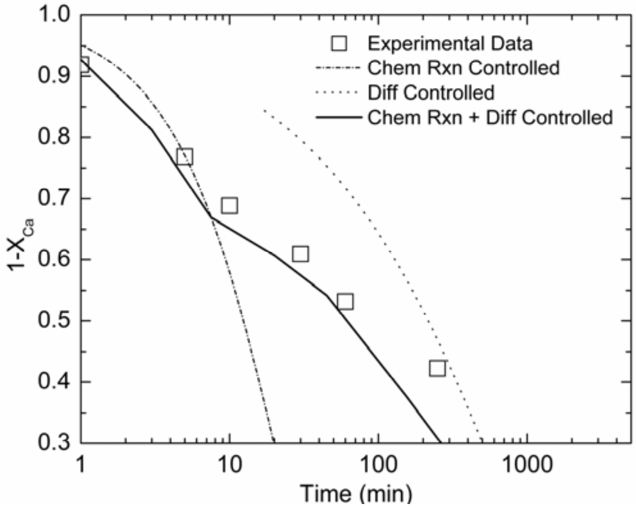


Figure 3. Comparison of experimental data for Ca leaching from slag #2
(45-75 µm particle size) with chemical and diffusion reaction control mechanisms

Direct Slag Carbonization

Direct carbonization was performed in a batch-type reactor using slag mixed with deionized water through which CO_2 was continuously bubbled. The degree of carbonization versus time for four size fractions of LMF slag #2 is shown in Figure 4. Particle size has a significant controlling influence on the resultant amount of carbonization, with a particle size <100 µm needed to achieve any appreciable level of reaction.

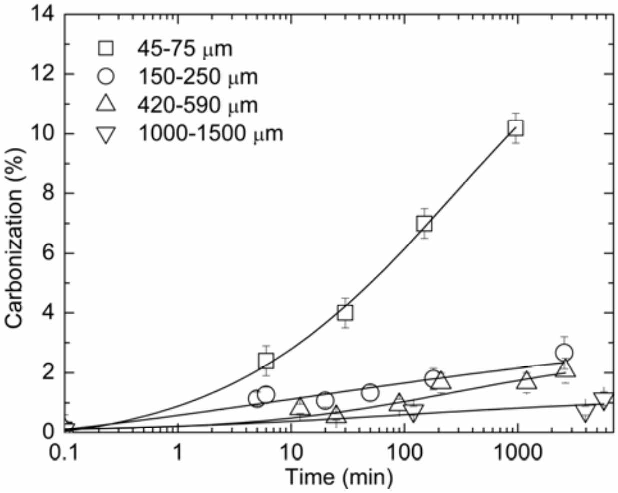
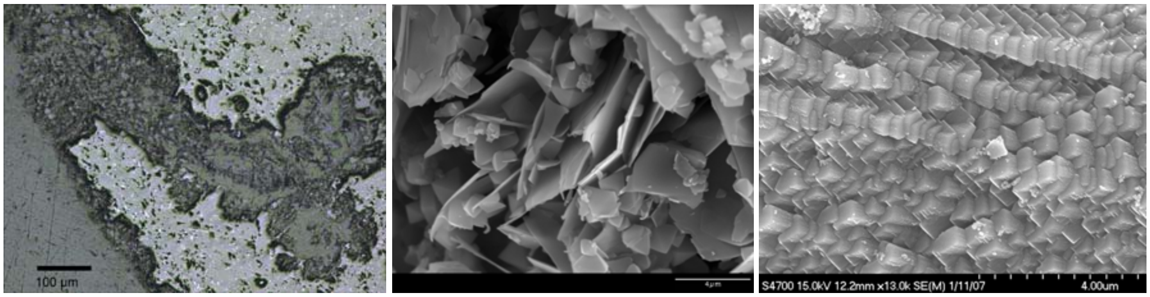


Figure 4. Direct carbonization of LMF slag#2 in CO_2 saturated aqueous solution

Morphological and chemical analysis of the carbonate layer formed on the slag particle surface is shown in Figure 5. Because slag particles exhibit a porous structure, interconnected channels allow surface reactions to take place deep inside the slag particle, as shown in Figure 5a which shows a 700 µm deep pore containing calcium carbonate product. The carbonate layer on the external surface consisted of plate-like crystals in a random high-porosity structure (Figure 5b), while the product layer contained in the pores consisted of overlapping plates packed very close together, with a higher bulk density (Figure 5c).

Slag carbonization data was analyzed in a similar manner to that of the calcium leaching results to determine the controlling reaction mechanism. Conversion (i.e. $CaO \rightarrow CaCO_3$) was strongly dependent on particle size with product layer diffusion determined as the rate-controlling step.[3] The layer of calcium carbonate formed on the particle surface retarded the diffusion of carbonic acid ions into the slag particle. This effect of increasing product layer density was incorporated into the shrinking core model by introducing a variable diffusivity (D) as a function of product layer thickness. A comparison of the experimental results with those calculated from the modified shrinking core model using constant and decreasing diffusivity is shown in Figure 6. The terms Ca_C and Ca_S are the fractions of calcium carbonized and calcium initially present in the slag, respectively. Constant diffusivity resulted in a deviation from the experimental data, while changing the diffusivity based on thickness resulted in good correlation over the entire range tested.



(a) (b) (c)

Figure 5. LMF slag #2 particle (a) reflective light microscopy cross section, SEM images of the (b) external and (c) near internal surfaces of product carbonate layer

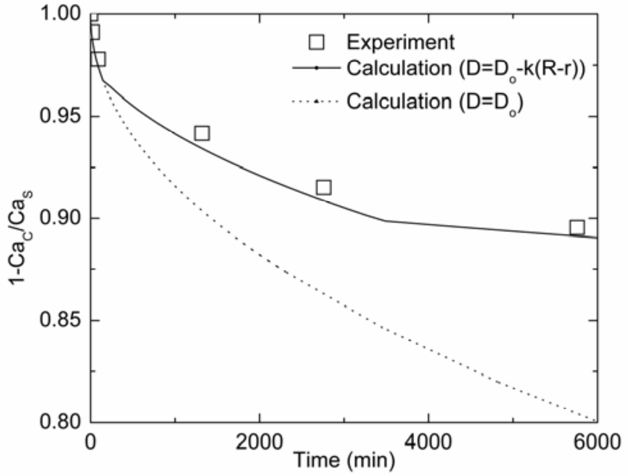


Figure 6. Comparison of experimental data for slag carbonization with shrinking core model using constant ($D=D_0$) and decreasing ($D=D_0-k(R-r)$) diffusivity of the product layer for 0.5 mm diameter LMF slag #2

Finally, the rate of Ca leaching was compared to the rate of Ca carbonization. In both cases, some amount of calcium reacted, however, the rate of these reactions significantly differed due to the mechanisms and limiting steps involved. In the leaching test, Ca ions dissolved from the slag into the unsaturated aqueous solution was rate limited by diffusion of calcium ions though the growing porous layer. An additional Ca leaching test was performed on slag #2 (<200 μm) that had been previously partially carbonized resulting in an even lower rate of reaction than fresh, unreacted slag (see Figure 7). This figure also shows that the rate of slag carbonization is much slower than Ca leaching because the calcium carbonate product layer inhibits the Ca leaching process.

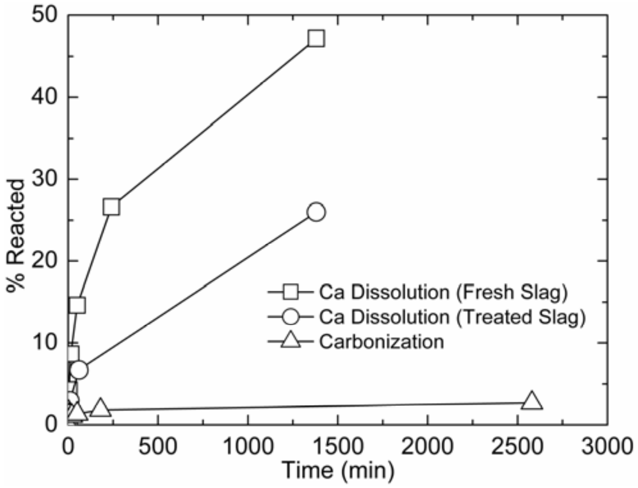


Figure 7. Comparison of carbonized and leached Ca from fresh and treated LMF slag #2 in aqueous solution

REACTOR MODELING

Industrial scale-up of the sequestration process requires a reactor scheme to contact the offgas with the slag particles. The proposed reactor design consists of two vessels connected by a pumped water stream as shown in Figure 8. Each reactor vessel operates at ambient pressure and temperature. Water and slag particles are introduced into Reactor 1 where the calcium ions are leached to form an alkaline leachate. The leachate is pumped to Reactor 2 through which gaseous CO_2 is bubbled. The CO_2 dissolves in the water forming carbonic acid, which then reacts with calcium ions to precipitate $CaCO_3$. This process scheme allows for the setup of several system scenarios, two of which were investigated for optimization of CO_2 capture. In Scenario 1, fresh or recirculated water is supplied into Reactor 1, while the leachate containing calcium ions is pumped to Reactor 2 to form calcium carbonate precipitates. The spent leachate (containing residual dissolved CO_2) is discharged or recirculated into Reactor 1 after degassing. In Scenario 2, recirculated water is supplied to Reactor 2 for saturation with CO_2, while the CO_2 saturated water is pumped to Reactor 1 for direct reaction with slag. These two scenarios were investigated using metallurgical simulation modeling software, METSIM, incorporating results from the leaching and carbonization tests.

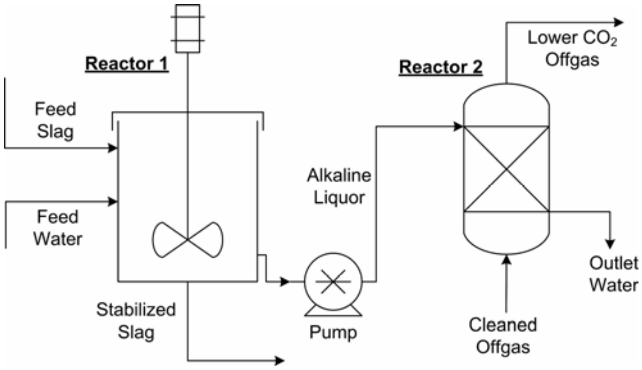
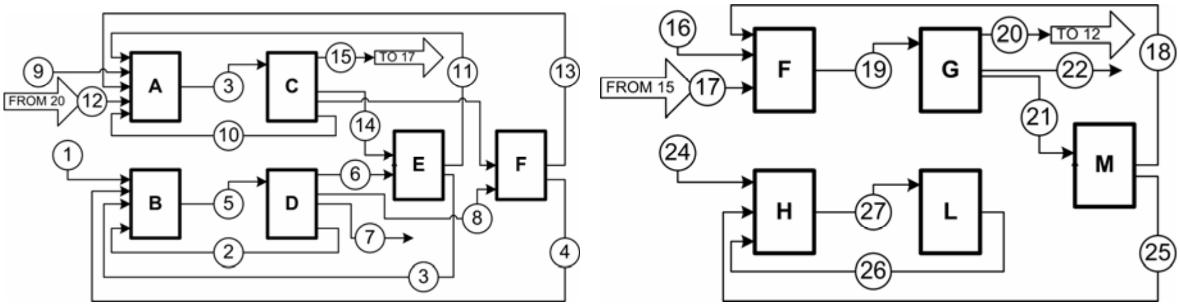


Figure 8. Flow schematic of the reactor design for CO_2 sequestration with steelmaking slag

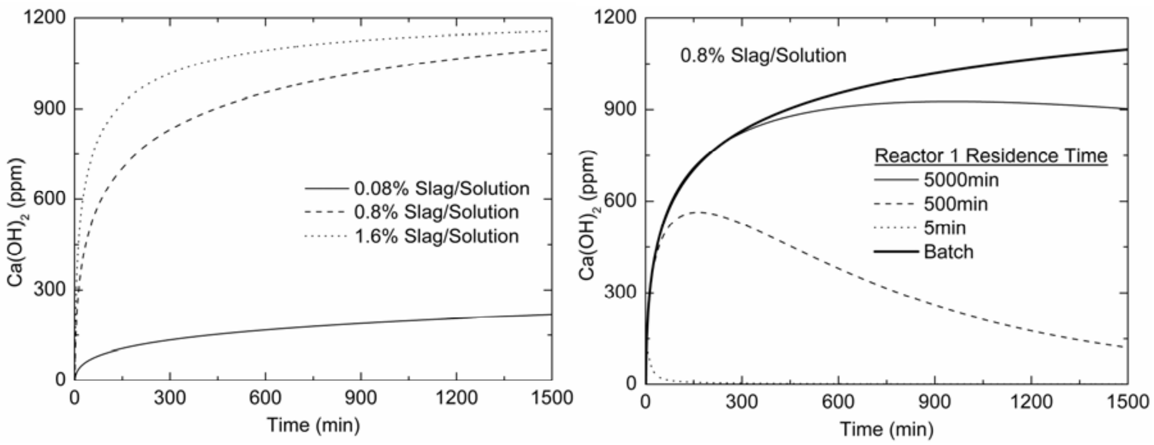
An approach developed by Robertson for modeling heterogeneous reaction kinetics of a non steady-state process was used for the scenarios identified for the two-stage reactor system.[9] A block diagram of the METSIM model is shown in Figure 9. The computer model consists of two blocks, representing Reactor 1 (Figure 9a) and Reactor 2 (Figure 9b) interconnected by solution streams. In Reactor 1, slag leaching and direct carbonization reactions occur in splitters E and F, respectively. In Reactor 2, carbon dioxide gas is mixed with the aqueous stream from Reactor 1 in Mixer F, while CO_2 dissolution to form carbonic acid ions takes place in Splitter G. Carbonic acid ions react with calcium ions in Splitter M, and any precipitated calcium carbonate accumulates in the loop consisting of the mixer/splitter pair H/L. This model allows for consideration of the two scenarios individually. For example, in Scenario 1, fresh water is supplied by Stream 9 to leach the slag in Reactor 1. The leached calcium ions are pumped to Reactor 2 by Stream 15/17 where precipitated calcium carbonate accumulates in Stream 26. The spent aqueous stream is discarded by Stream 22 without flowing back to Reactor 1. Alternatively, in Scenario 2 the aqueous solution is recirculated by streams 15/17 and 12/20 without fresh water input in Reactor 1 or solution discharge from Reactor 2. The model was used to calculate both an unsteady batch type process in Reactor 1 where there is no fresh slag input by Stream 1 and no product discharge by Stream 7, as well as a continuous type process with fresh slag input and carbonate product output. For application in the METSIM model, the experimental kinetics of the carbonization reaction was approximated to be a function of time, $(t)^n$. A factor of n=⅓ resulted in an appropriate fit for the reaction conversion (Ca_C/Ca_S) calculated from modified shrinking core model, as well as the experimental data.



a) b)

Figure 9. Block diagrams of the METSIM model for interconnected (a) Reactor 1 and (b) Reactor 2

Investigation of Scenario 1 included slag leaching in Reactor 1 and calcium carbonate precipitation in Reactor 2. In this model, fresh water was supplied in Reactor 1 while the leachate solution was pumped to Reactor 2. No water was recirculated from Reactor 2 to Reactor 1. The goal of this scenario was to analyze the influence of slag/solution ratio and solution residence time in Reactor 1 on the leaching result. The model used 200 µm particles of LMF slag #2 that contained 50 wt.% CaO. The results of the investigation (Figure 10) show that both increasing the slag/solution ratio and the solution residence time in Reactor 1 produces a higher concentration of calcium ions in solution. Increasing the slag/solution ratio provides a diminishing increase in calcium ions in solution due to saturation of the aqueous phase, as shown in Figure 10a. Fresh water throughput accelerates the leaching rate, which is dependent upon the residence time of Reactor 1 (Figure 10b). The optimum residence time was defined by the maximum amount of leaching with minimal fresh water input.



a) b)

Figure 10. METSIM model results of leaching slag at (a) different slag/solution ratios in batch reactor without fresh water input and (b) in mix-flow type reactor with fresh water input at different solution residence times

The results of Scenario 2 (direct slag carbonization in Reactor 1) were experimentally verified using a lab-scale apparatus consisting of two connected reactors (plastic tanks). Reactor 1 contained up to 2 kg of slag in 20 liters of water that was mechanically stirred. The aqueous liquor was pumped at varying rates to Reactor 2, which had a two-liter volume. Bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles, which allowed intimate mixing of the gas and alkaline solution. A multi-channel meter was used to measure the pH level in both reactors. At the completion of each test (20 hours), a sample of the slurry from Reactor 1 was filtered, dried, and analyzed for carbonization. The prevailing reaction was direct slag particle carbonization in Reactor 1, while a minor amount of residual precipitated carbonates was found in Reactor 2. Figure 11 shows that the METSIM model results are in good agreement with the experimental results and that the amount of slag carbonization increased with decreasing particle size. The amount of carbonate formation greatly increased at particle sizes smaller than 200 µm, indicating a certain minimal amount of grinding may be necessary to achieve practical carbonation rates.

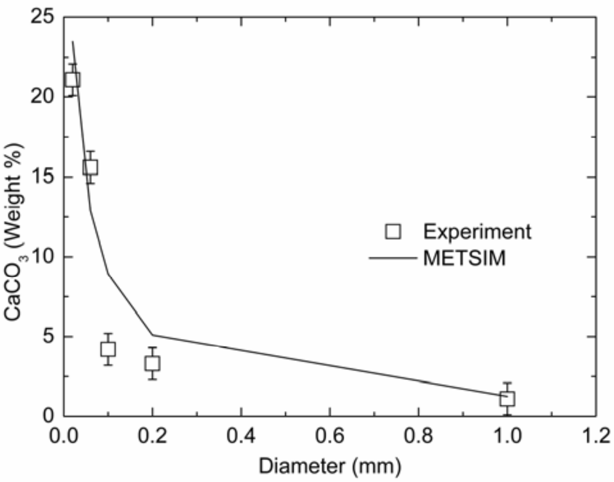


Figure 11. Comparison of calculated (METSIM) and measured calcium carbonate content in slag from direct carbonization tests

Effective scale-up to an industrial process for carbon dioxide sequestration requires continuous reactor operation. For this application, the METSIM model was designed to allow continuous feed of fresh slag to Reactor 1 and discharge of carbonized product at the same rate. It was assumed as a first approximation that Reactor 1 operated in back-mix mode with the composition of the discharged stream as an average for Reactor 1. In this case, the volume of the Reactor 1 depends on the slag residence time and slag input flow rate. Decreasing the slag residence time made it possible to minimize the volume of Reactor 1, however, the result will be a simultaneous decrease in the level of slag carbonization in the discharged product (Figure 12).

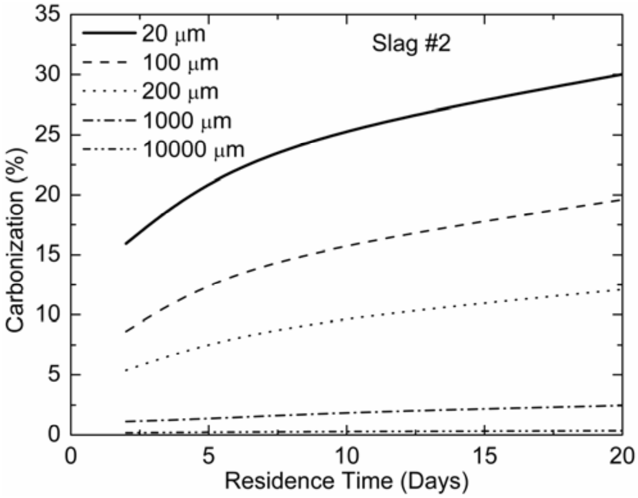


Figure 12. Reactor residence time dependence upon particle size from MESTIM model of slag carbonization

SLAG COMMINUTION AND METAL RECOVERY.

The results of the calcium dissolution and slag carbonation tests show that particle size is a controlling factor to achieve reasonable carbonization rates. Slag comminution promotes carbonate conversion at a rate sufficient for industrial-scale sequestration; however, the overall merit of the process is determined by a balance of the grinding costs (i.e. direct energy and indirect CO_2 generation) and benefits (i.e. improved CO_2 sequestration and metal recovery). Because detailed comminution data for steelmaking slag by type was not available, grindability measurements were conducted using EAF, BOF, and LMF slag.[4] Bond Work Index values (W_i) were obtained for each of the slags using a laboratory ball mill.

The work required for comminution(W), in kilowatt-hours per short ton (st) of crushed slag, is a function of the Bond Work Index (W_i) and particle diameter in microns at which 80% passes in the product (P_{80}) and feed (F_{80})[10]. The W_i value has high portability as a standard for comparing comminution of minerals, and for use in mineral processing sizing and simulation programs. Based on observations from slag characterization and sequestration analysis, a target grind size (P_{80}) for the work index test was determined. Scanning electron microscopy (SEM)/backscatter electron (BSE) analysis of steelmaking slag samples indicated that a grind size of ~100 μm should be sufficient to liberate most of the metal particles and give sufficient slag reaction time. Furthermore, CO_2 sequestration kinetic analysis and modeling showed that a particle size of 200 μm or less gives significantly improved reaction time for an industrial scale reactor. Based on these observations, the target grind size for the Bond Work Index test was chosen at 106 µm (150 Tyler mesh). Size-by-size analysis of the ground material subsequently found that more than 90% of the metallic fraction is >106 µm.

The results of the grindability experiment enabled development of a METSIM model for estimating the comminution power requirement. The total comminution power required at each target grind size is shown in Figure 13. This data is shown based on normalized mass throughput in which the total power is divided by mass throughput. For this model, EAF and BOF slags are processed at four times the rate of LMF slag (i.e. 100,000 mt/yr vs. 25,000 mt/yr). All slag types show increasing comminution power with decreasing P_{80}, which increases sharply a particle sizes smaller than 200 µm.

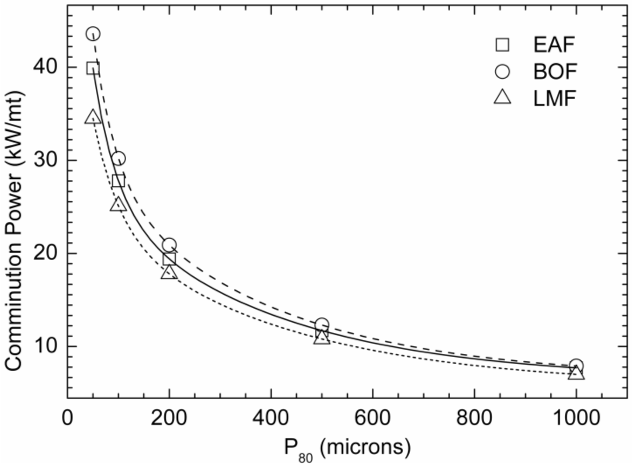


Figure 13. Normalized comminution power (crushing plus grinding) versus P_{80} for three slag types

The metal content of steelmaking slag was measured in the crushed product feeding the grindability test and in the ground product from the final period after the grindability test. As preparation for the grindability test, all slags were crushed (jaw/roll) to pass a 3.36 mm sieve. Magnetic material liberated from crushing (>3.36 mm) was separated and set aside for subsequent analysis. After conducting each grindability test, the magnetic fraction was separated on a size-by-size basis of 10 fractions from 106-3360 µm, plus the <106 µm fraction as a whole. Figure 14 shows the particle size distribution of the magnetic fraction and Table III shows the total quantity of magnetic material in each slag. Overall, ~90% of the magnetic particles were >106 µm, which aids in liberation and magnetic separation. From the magnetic fraction separated after crushing and after grinding, the amount of steel trapped in the slag was determined by melt separation.[4] Quantitative analysis (Table III) was performed only on the total magnetic fraction separated after crushing (>3.36 mm) and the total magnetic fraction separated after grinding (<3.36 mm). This data was used for calculation metal recovery (kg/mt) versus target grind size (Figure 15).

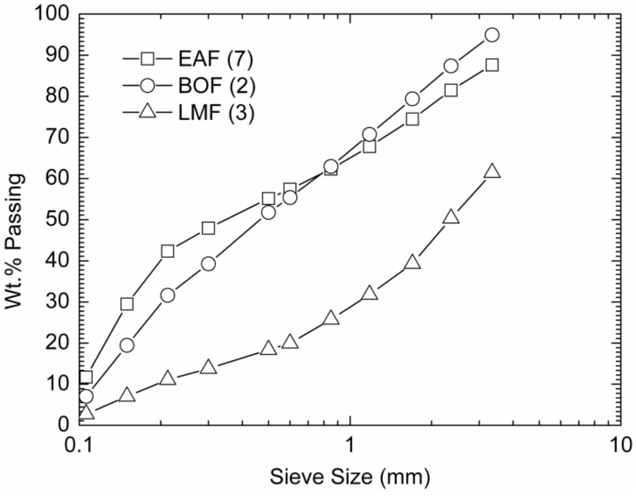


Figure 14. Particle size distribution of magnetic fraction in three types of steelmaking slags

Table III. Quantity and quality of magnetic material in steelmaking slag

Wt.% Magnetic	*EAF*	*BOF*	*LMF*
>106 µm	8.61	8.81	5.92
<106 µm	1.14	0.67	0.17
Total	9.75	9.48	6.09
Wt.% Metallic			
>3.36 mm	86.1	88.1	95.5
<3.36 mm	60.7	71.9	72.0

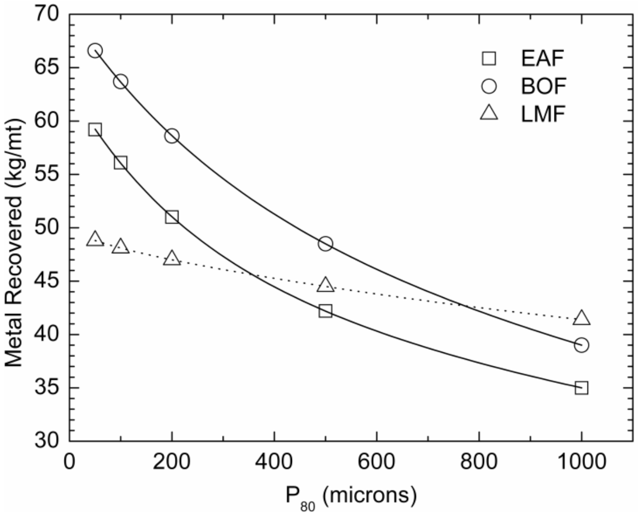
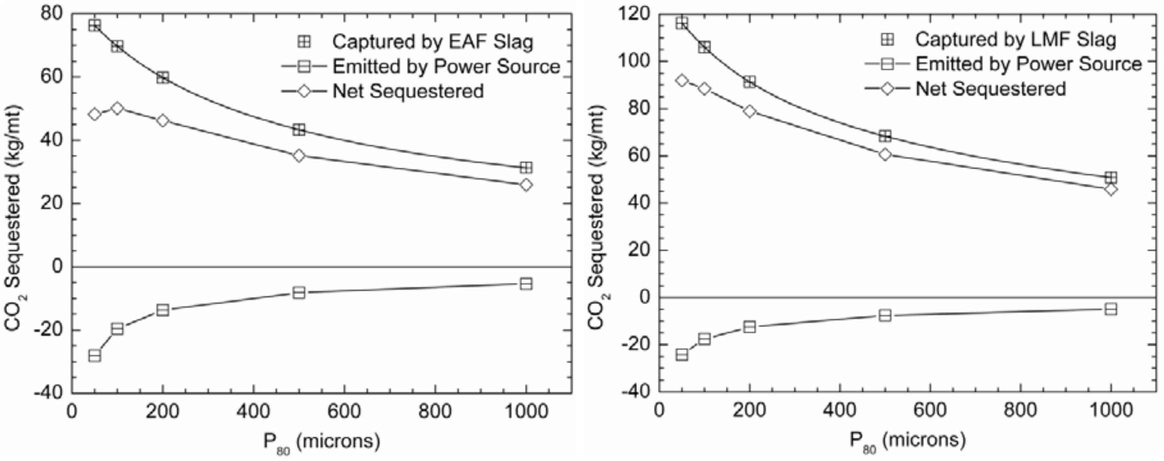


Figure 15. Amount of recovered metal liberated from steelmaking slag by target grind P_{80}

VALUATION ANALYSIS OF COMPLEX SLAG PROCESSING

The primary concern with slag grinding has been the issue of power (electric) consumption of the mill and corresponding CO_2 generation (emission) at the electric supply source. Both terms can be quantified as input into an overall valuation model. The amount of CO_2 captured by EAF and LMF slags for each P_{80} value was calculated from sequestration reactor modeling data. Figure 16 shows the resulting CO_2 balance. Each graph shows the amount of CO_2 captured by that slag, the amount of CO_2 emitted by the electric supply source (as a negative sequestration value calculated from the comminution data), and the net CO_2 sequestered, at each grind size (P_{80}). The amount of CO_2 captured by the slag and the amount released by the power source both increase with decreasing P_{80}. The amount released by the power supplier is 15-40% of the amount captured depending on the slag type and size, resulting in a net positive amount of CO_2 sequestered at all sizes.



a) b)

Figure 16. Net CO_2 sequestered (slag capture-power source emission) for (a) EAF and (b) LMF slags versus grind size

Valuation of the slag grinding process is determined through a cost analysis model. Operating cost (\$/hr) for each slag type is determined from power consumption (kWh) multiplied by electric cost (\$/kWh) plus CO_2 generation amount (mt/hr) multiplied by CO_2 cost (\$/mt) from which metal recovery (mt/hr) times scrap price (\$/mt) is subtracted. The operating cost is then normalized by dividing by each slags respective mass flow rate (mt/hr). A negative operating cost is equivalent to a positive net value for the process. Equipment capital costs are not factored into this analysis. An example of the cost analysis are presented in Figure 17, which shows net value, normalized to \$/mt, versus grind size (P_{80}). EAF and BOF slags show similar curves, with BOF slag at a ~15% higher net value than EAF slag. Both show similar peak P_{80} sizes (112 versus 122 μm); indicating maximum value comes from grinding both slags to similar sizes. LMF slag has a peak at 369 μm, and shows much less sensitivity to grind size. In terms of magnitude, the most significant factor in valuation is metal recovery, which accounts for 76-90% of the cost as P_{80} increases from 50-1000 μm. The peak P_{80} value shifts to lower values with increasing scrap price or decreasing electricity cost. Carbon dioxide credit/value is not a critical term regarding direct economic valuation of the process as detailed, however, for environmental assessment this process does provide a net positive sequestration that may have benefits besides financial impact. Future emission regulations may change the magnitude of the CO_2 sequestration term significantly.

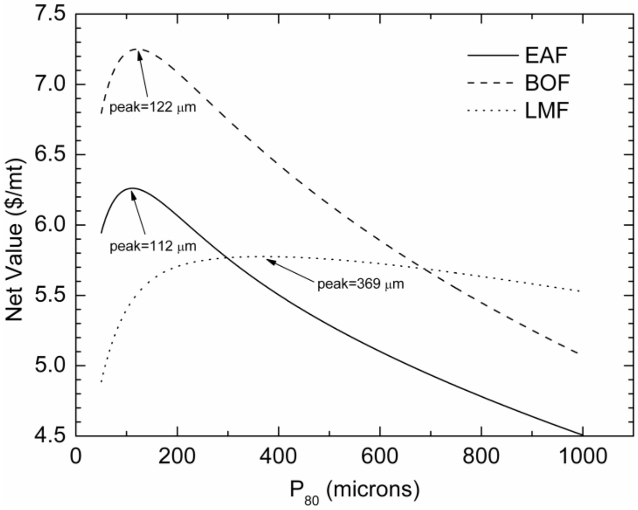


Figure 17. Net value from grinding versus P_{80} for steelmaking slags based on power consumption, CO_2 sequestration, and metal recovery. (Basis: electric cost - \$0.06207/kWh, CO_2 emission - 0.704 kg/kWh, CO_2 cost - \$1.90/mt, metal value - \$141.17/mt)

CONCLUSIONS

1. Carbon dioxide sequestration with steelmaking slag was studied in a three-phase (gas-liquid-solid) system containing industrial slag, CO_2, and water at ambient temperature and pressure. The reaction rates of aqueous Ca-leaching and direct carbonization were quantified independently to yield the reaction parameters and rate-limiting mechanisms. The reaction kinetics were then described by a modified shrinking core model. The morphology of the product layer was incorporated into this model. The kinetic parameters obtained from experimental data were used for modeling an industrial prototype reactor.

2. A slag-CO_2 sequestration process prototype consisting of two interconnected reactors was proposed for industrial scale-up. This design allows for simplified retrofit into existing slag and off-gas processing facilities METSIM process simulator was used to model both calcium leaching and direct carbonization, which allowed investigation of multiple scenarios for the process scheme. A comparison of several scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles and accelerating the reaction kinetics. However, the water requirement in a continuous system is much higher than a recirculated system. To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor without degassing. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor.

3. The feasibility of grinding steelmaking slag was investigated based on metal recovery and CO_2 sequestration. Each step of the process, including slag comminution power consumption, associated CO_2 generation from the power supply source, CO_2 sequestration by the comminuted slag, and metal recovery from the comminuted slag was evaluated over a range of grind size P_{80} values. Valuation analysis, using published commodity index data resulted in peak curves for all slags. In terms of fraction of the overall value, metal recovery is the most significant factor. However, for environmental assessment this process will provide net positive CO_2 sequestration that may have benefits besides direct economic impact. Future emission regulations may change the magnitude of the CO_2 sequestration term significantly.

ACKNOWLEDGEMENTS

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American Iron and Steel Institute
Technology Roadmap Program

CO_2 Breakthrough Program Phase I: Geological Sequestration of CO_2 by Hydrous Carbonate Formation with Reclaimed Slag

Final Report - Attachment F

Industrial Reactor Modeling Report

January 2008

Carbon Dioxide Sequestration by Steel Making Slag - Industrial Process Modeling

1. REACTOR DESIGN AND MODELING PROCEDURE

1.1 CO_2 Sequestration Reactor Design

Carbon sequestration through the aqueous-based reaction of CO_2-containing offgas with lime-bearing steelmaking slag allows for several possible reactions to take place. A list of the key competing reactions is given in Table 1. For simplification the calcium containing phases are all designated as CaO.

Table I. Reactions Occurring During Aqueous Slag-CO_2 Sequestration

Description	Reaction
Ca leaching	$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2(OH^-)$
CO_2 dissolution	$CO_{2(g)} + H_2O_{(l)} \rightarrow 2H^+ + CO^{2-}_{3(aq)}$
Carbonate precipitation	$Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \rightarrow CaCO_{3(s)}$
Ca direct carbonization	$CaO_{(s)} + CO^{2-}_{3(aq)} + H_2O_{(l)} = CaCO_{3(s)} + 2OH^-$
Water dissociation	$2(OH^-) + 2H^+ \rightarrow 2H_2O_{(l)}$

The reactor design consists of two vessels connected by a pumped water stream, as shown in Fig. 1. Each reactor vessel operates at ambient pressure and temperature. Water and slag particles are introduced into Reactor 1, wherein calcium ions are leached to form an alkaline leachate. The aqueous solution is pumped to Reactor 2 through which gaseous CO_2 is bubbled. The CO_2 dissolves into the water to from carbonic acid ions, upon which several competing reactions take place resulting in precipitation of $CaCO_3$. This process scheme allows for several system scenarios to be investigated for optimization of CO_2 capture.

- Scenario 1: Fresh water is supplied into Reactor 1, the leachate containing calcium ions is pumped to Reactor 2 in which calcium carbonate precipitates. The spent leachate (containing residual dissolved CO_2) is discharged.
- Scenario 2: The same design as Scenario 1 except that the water supplied to Reactor 1 is recirculated from Reactor 2 after (complete or partial) degassing.
- Scenario 3: Fresh water is supplied to Reactor 2 for saturation with CO_2, the CO_2 saturated water is pumped to Reactor 1 for direct reaction with slag, after which the water (containing residual dissolved CO_2) is discarded.
- Scenario 4: The water supplied to Reactor 1 is recirculated from Reactor 2 without degassing.

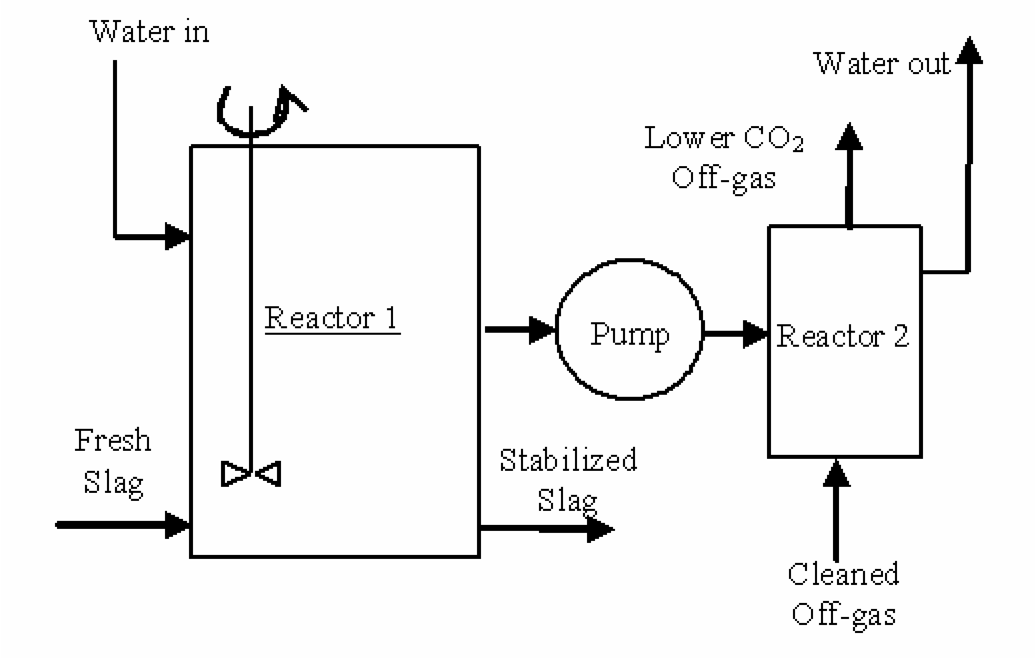
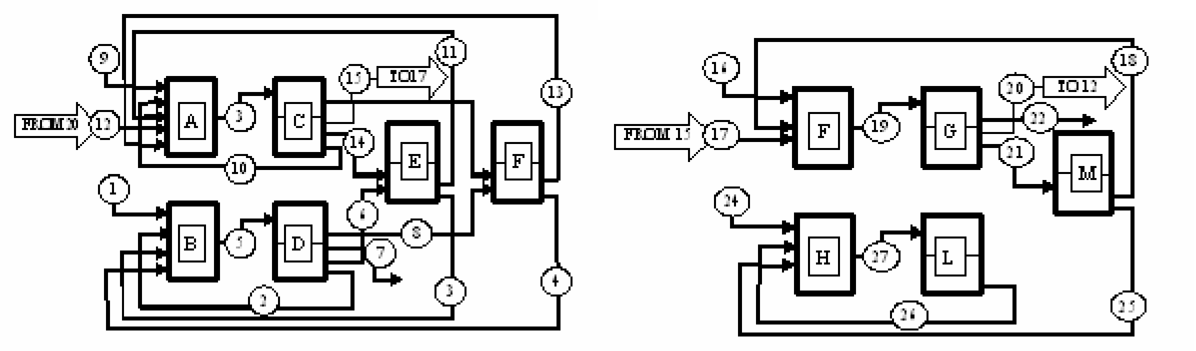


Fig. 1 Flow schematic of apparatus for CO_2 sequestration with steelmaking slag.

Experimental verification of the different scenarios was undertaken using a lab-scale apparatus consisting of two connected reactors (plastic tanks). Recirculation of the aqueous stream took place both with and without partial degassing by argon bubbling. Reactor 1 contained slurry of up to 2 kg of slag and 20 liters of water that was mechanically stirred. The aqueous liquor was pumped at varying rates to Reactor 2, which had a two-liter volume. Bottle grade CO_2 was bubbled through a diffuser in the bottom of Reactor 2 to generate a distribution of fine gas bubbles which allowed intimate mixing of the gas and alkaline solution. A multi-channel pH meter was used to measure the pH level in both reactors. At the completion of each test, a sample of the slurry from Reactor 1 was filtered, dried, and analyzed for carbonization as described in the previous work. Kinetic data from previous work were used in the various scenarios. METSIM process simulation software was used to perform calculations.

1.2 METSIM Modeling Procedure

An approach developed by Robertson for modeling heterogeneous reaction kinetics of a non-steady process was used for the studies of the two-stage reactor system. A block diagram of the METSIM model is shown in Figure 2. The computer model consists of two blocks, representing Reactor 1 (Fig. 2a) and Reactor 2 (Fig. 2b), connected by streams 15/17 and 20/12. In Reactor 1, the amount of slag is defined by Stream 10 which connects the mixer and splitter pair A and C, respectively. In the same manner, the amount of aqueous solution is defined by Stream 2 which connects the mixer and splitter pair B and D, respectively. Slag leaching and direct carbonization reactions occur in splitters E and F, respectively. In Reactor 2, carbon dioxide gas (Stream 16) is mixed with the aqueous stream from Reactor 1 (Stream 12) in Mixer F, while CO_2 dissolution to form carbonic acid ions takes place in Splitter G. Carbonic acid ions react with calcium ions in Splitter M, and any precipitated calcium carbonate accumulates in the loop consisting of the mixer/splitter pair H/L.



a) b)

Fig. 2 Block diagrams of the METSIM model for a) Reactor 1 and b) Reactor 2 which are interconnected by streams 15/17 and 20/12.

This model allows the flexibility of studying each of the four scenarios individually. For example, in Scenario 1 fresh water is supplied by Stream 9 to leach the slag in Reactor 1. The leached calcium ions are pumped to Reactor 2 by Stream 15/17 where precipitated calcium carbonate accumulates in Stream 26. The spent aqueous stream is discarded by Stream 22 without flowing back to Reactor 1. Alternatively, in Scenario 4 the aqueous solution is recirculated by streams 15/17 and 12/20 without fresh water input in Reactor 1 or solution discharge from Reactor 2. The model was used to calculate both an unsteady batch type process in Reactor 1 where there is no fresh slag input by Stream 1 and no product discharge by Stream 7, as well as a continuous type process with fresh slag input and carbonate product output.

1.3 Experimental Reaction Kinetics for METSIM Modeling

Procedure of using experimental kinetic data for METSIN modeling was described in article "Two-Stage Reactor for Aqueous Leaching and Carbonization of Steelmaking Slag for Geological Sequestration of Carbon Dioxide" LEKAKH, S.N., ROBERTSON, D.G.C., RAWLINS, C.H., RICHARDS, V.L., PEASLEE, K.D. submitted in Metallurgical and Materials Transaction. Briefly ,in the METSIM model, the reaction rate F is defined by Equation 1. In this equation the rate constant K is defined by the mass flow rate ($m_i/\Delta t$) from the mixer/splitter to the phase splitter where the reaction occurs with the particular value of reaction extent (RE) at each time step (Δt). The experimentally measured kinetic parameters from earlier work for leaching and carbonization were used to evaluate the factors listed in Eq. 1:

$$F = K \times (RE) \qquad [1]$$

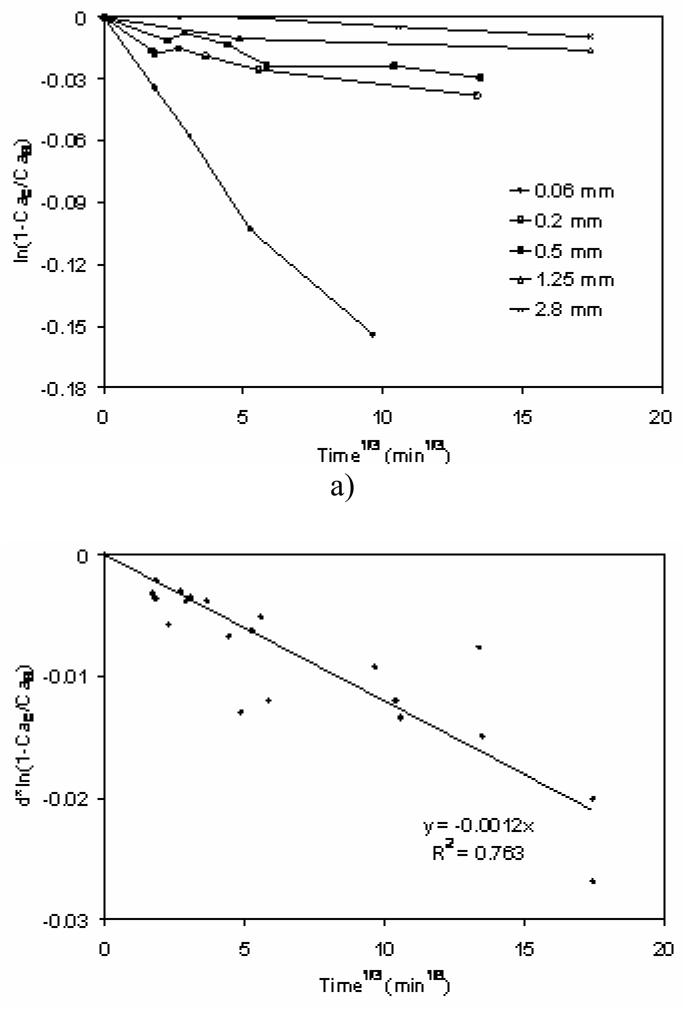
Carbonization. For application in the METSIM model, the experimental kinetics of the carbonization reaction was approximated to be a function of time (t) as shown in Eq. 2. A factor of n=⅓ resulted in an appropriate fit for the reaction conversion (Ca_C/Ca_S) calculated from shrinking core model as well as the experimental data:

$$\ln\left(1 - \frac{Ca_C}{Ca_S}\right) = f(t)^n \qquad [2]$$

For direct carbonization of slag particles (Fig. 3) the experimental data was fit to Eq. 3 and Eq. 4. In these equations *d* is the particle diameter (mm), *t* is time (min) and coefficient *A*=0.0012 was taken from correlated experimental data . The first derivative (Eq. 3) represents the reaction rate *F* and was used in the METSIM model.

$$Ca_C = Ca_S\left(1-\exp\left(-\frac{A}{d}t^{1/3}\right)\right) \tag{3}$$

$$F = \frac{dCa_C}{dt} = \frac{ACa_S}{3d}t^{-2/3}\exp\left(-\frac{A}{d}t^{1/3}\right) \tag{4}$$



a)

b)

Fig. 3 Comparison of experimental data for slag carbonization for parameters ln(1-Ca_C/Ca_S) (a) and d*ln(1-Ca_C/Ca_S) (b) versus time$^{1/3}$.

Leaching. A similar analysis of the calcium leaching process was undertaken, in which this set of reactions corresponds to Scenario 1. The reaction rate changes during the leaching process because the initial chemical reaction limited mechanism is overtaken by slower diffusion through the porous surface layer developed during treatment. The difference in Eq. 5 for leaching when compared to carbonization (Eq. 4) follows from the necessity, due to batch test procedure, of taking into account the solution volume V (cm^3), the calcium saturation level C_{sat} (wt. %) for solution in equilibrium with solid $Ca(OH)_2$, and the total surface area $S = 6W/\rho d$ (cm^2) of slag particles with diameter d (cm), density ρ (g/cm^3), and weight W (g) In Equation 9, C_D is the concentration of dissolved calcium in solution (wt. %) and the coefficient A=0.0004 was taken from correlated experimental data shown in Fig. 4:

$$F = \frac{dC_D}{dt} = \tfrac{1}{3} VAC_{sat} St^{-\frac{2}{3}} \exp\left(-ASt^{\frac{1}{3}}\right) \qquad [5]$$

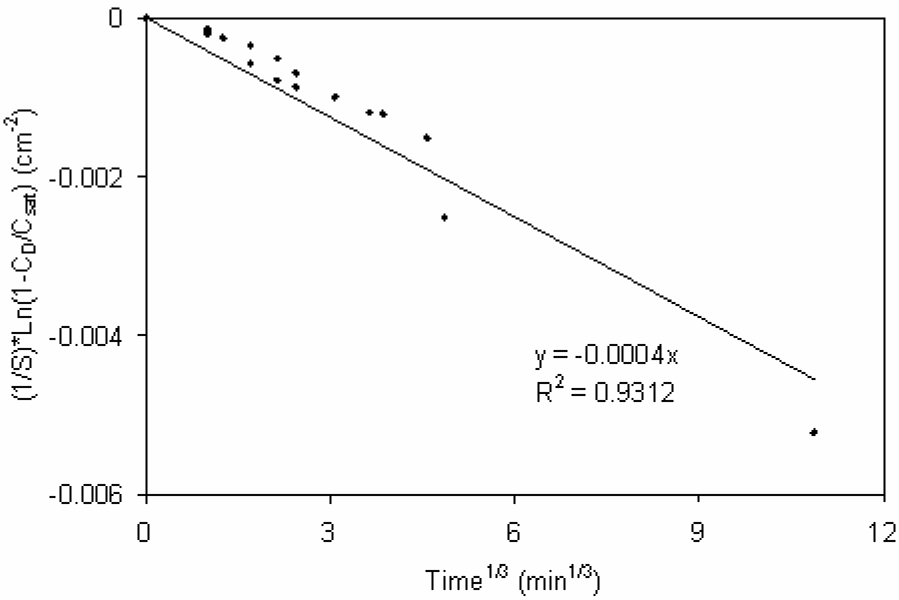
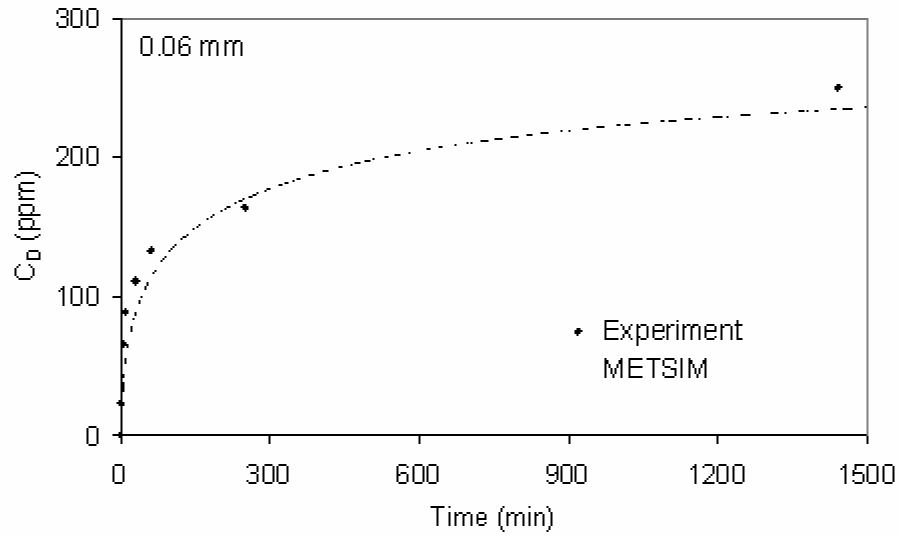


Fig. 4 Comparison of experimental data for slag leaching for the parameter $(1/S)*\ln(1-C_D/C_{sat})$ versus time$^{1/3}$.

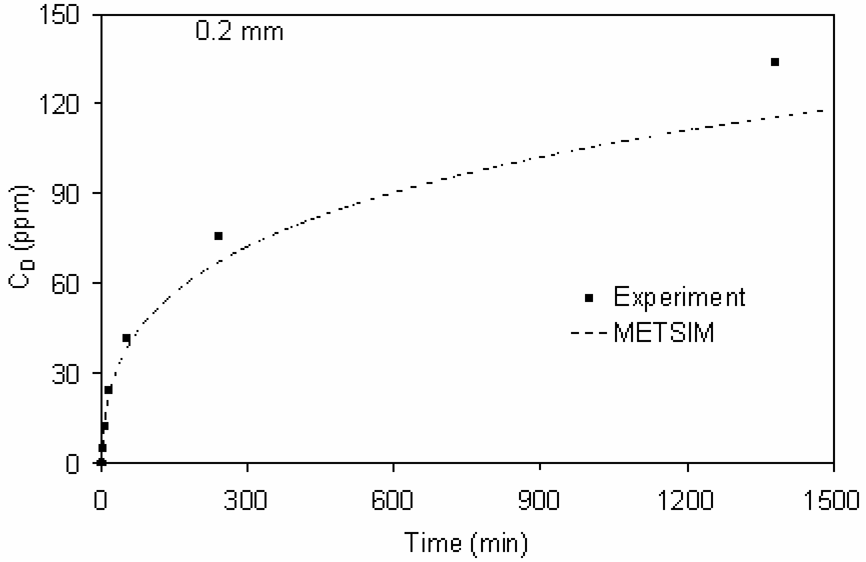
The extent of calcium leaching from slag depends on the slag particle size and the particle surface conditions. Calcium from fresh slag leached twice as fast when compared to the same slag in carbonized condition. Because leaching and carbonization may occur simultaneously in Scenario 4 in the designed apparatus, the leaching reaction rate (Eq. 5) was linked to the current slag carbonization level during each calculation step.

2. MODEL VERIFICATION

The METSIM model was verified by comparing the calculated results with the experimental data obtained from the previous work. The calcium leaching experiments were performed in a batch type reactor under protective argon atmosphere with unsaturated aqueous solutions (e.g. Scenario 1 for Reactor 1). The METSIM modeling of a batch type reactor was done by disconnecting Reactor 1 from Reactor 2 and disregarding the feed streams. Fig. 5 shows the comparison of calculated and experimental results for the concentration of calcium leached (C_D) from LMF slag (50 wt.% CaO) at two particle sizes (0.06 mm and 0.2 mm). The calculated leaching results were in good agreement with the experimental data.



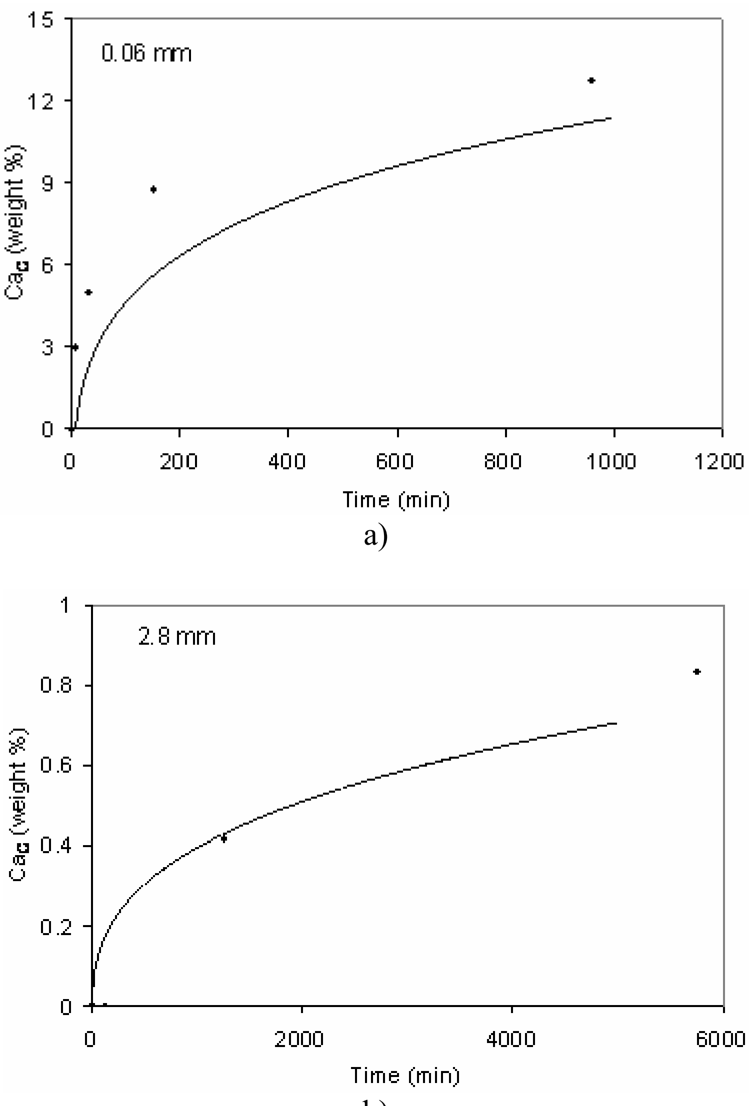
a)



b)

Fig. 5 Comparison of experimental concentration of leached calcium (C_D) to calculated results from METSIM model for slag particles 0.06mm (a) and 0.2 mm diameter (b).

Direct carbonization of the same slag was studied in a batch type reactor using aqueous solution saturated by carbonic acid under CO_2 at one atmosphere pressure. This process was modeled using batch type Reactor 1 connected to Reactor 2 with continuously flowing CO_2 gas saturating the aqueous solution. The transport of calcium ions from Reactor 1 to Reactor 2 was prohibited. This approach modeled the experimental conditions of Scenario 3. Fig. 6 shows the experimental results for the amount of calcium carbonized (Ca_C) compared to that predicted by the METSIM model for two different particle sizes of LMF slag with average particle sizes 0.06 mm and 2.8 mm.



a)

b)

Fig. 6 Comparison of experimental results for calcium carbonization (*Ca_C*) in slag to calculated results from METSIM model for slag with average particle sizes 0.06 mm (a) and 2.8 mm (b) diameter.

Scenario 4 was modeled (water recirculation without degassing) and the results compared to the experimental data for slag carbonization. In the experimental work, both Ca leaching and direct slag particle carbonization were monitored simultaneously in both reactors. Reactor 1 contained 200 g LMF slag (<3.2 mm) in 20 liters of water, while Reactor 2 contained two liters of solution through which 1.5 g/min CO_2 was bubbled. A solution exchange rate of one liter per minute was used to transfer the fluid between the two reactors. The experimental procedure included preliminary soaking of slag in Reactor 1 for 20 minutes, with solution recirculation but without CO_2 input in Reactor 2. During this time, the pH increased in both reactors as $Ca(OH)_2$ was formed. Shortly after introducing CO_2 into Reactor 2, the concentration of calcium ions in solution decreased while concentration of carbonic acid increased. The rate of decrease in pH (Fig. 7) depended on the solution residence time in Reactor 1 (20 minutes) and Reactor 2 (2 min).

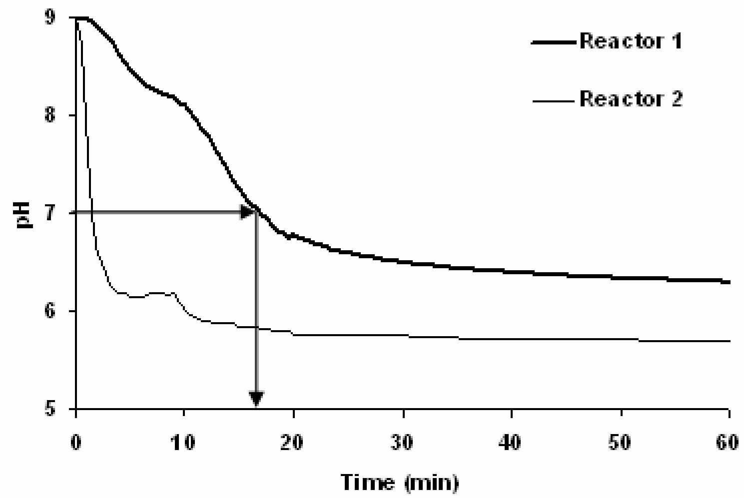
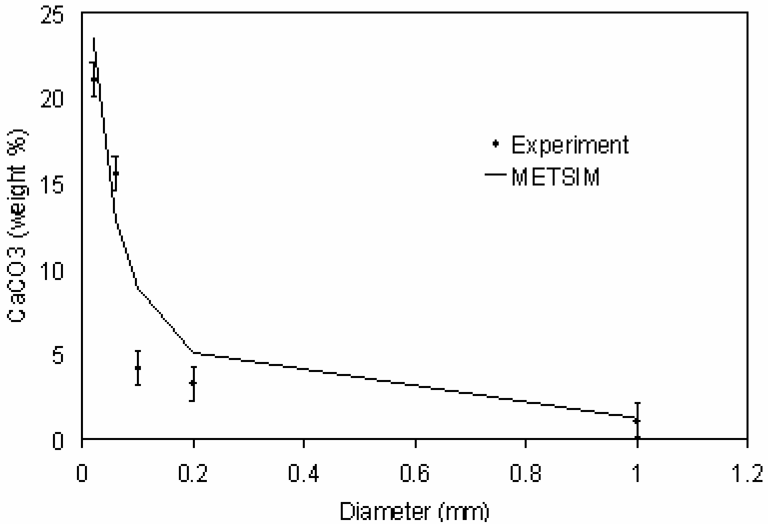


Fig. 7 Changing pH of aqueous solutions in reactors during carbonization (200 g of crushed <3.2 mm LMF slag, 1.5 g/min flow rate CO_2) based on start of CO_2 flow.

The reaction was allowed to proceed for 20 hours, after which the product was dried, sieved, and analyzed for calcium carbonization. The prevailing reaction was direct slag particle carbonization in Reactor 1, while a minor amount of residual precipitated carbonates was found in Reactor 2. A similar result was achieved using the METSIM simulation. The model predicted carbonate precipitation in Reactor 2 during the short period of time immediately after introducing CO_2, after which direct carbonization of the slag in Reactor 1 took predominance. As the particle size decreased the amount of slag carbonization (i.e. $CaCO_3$ formation) increased. A 1 mm particle size resulted in 2% $CaCO_3$ at 20 hours, while decreasing the particle size by an order of magnitude to 0.1 mm resulted in 8% $CaCO_3$ at the same time. Decreasing the particle size another half order of magnitude to 0.02 mm resulted in 23% $CaCO_3$. A comparison of the experimental and modeled results (Fig. 8) for five particle sizes shows good agreement.



b)

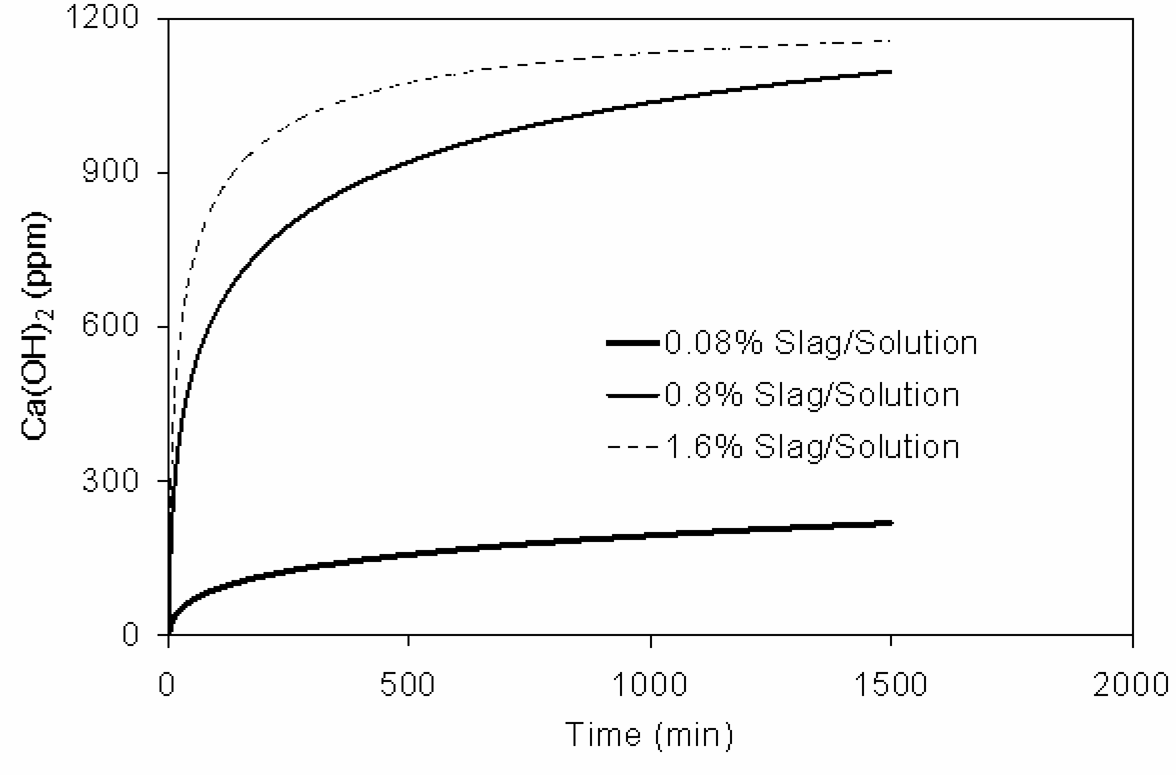
Fig. 8 Comparison of calculated METSIM and experimentally measured calcium carbonate content after 20 hours reaction.

3. INDUSTRIAL PROCESSES MODELLING.

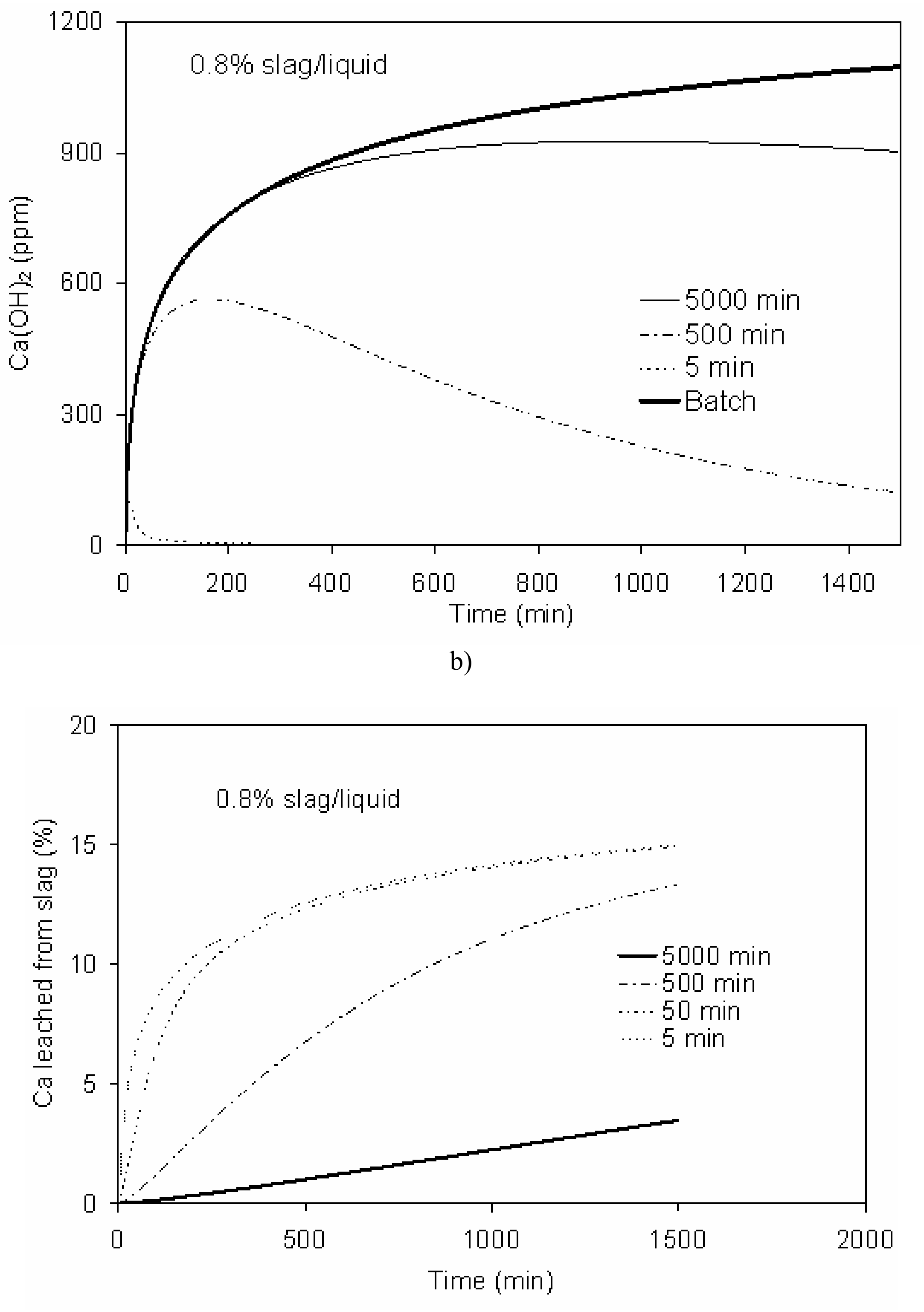
3.1 Leaching Process Modeling (Scenario 1).

The process was modeled in which the slag was leached in Reactor 1 and the alkaline liquor was carbonized in Reactor 2. The basis for the model was fresh water feed to Reactor 1 at the same rate the spent liquor was discharged from Reactor 2. No water was recirculated from Reactor 2 to Reactor 1. The goal of this scenario was to analyze the influence of slag/solution ratio and solution residence time in Reactor 1 on the leaching result. The slag used in the model was the 0.2 mm fraction of LMF slag with 50 wt.% CaO.

The model results show that both increasing the slag/solution ratio and the solution residence time in Reactor 1 produces a higher concentration of calcium ions in solution. Increasing the slag/solution ratio provides a diminishing increase in calcium ions in solution due to saturation of the aqueous phase (Fig. 9a). The fresh water throughput accelerates the leaching rate, which is dependent upon the residence time of Reactor 1 (Fig. 9b). The total amount of calcium leached (y-axis of Fig. 9c) is equal to the concentration of calcium in solution multiplied by the solution volume. The optimal residence time is defined by the maximum amount of leaching with minimal fresh water input. For slag with 0.2 mm particle diameter and 0.8% slag/solution ratio the optimal residence time is near 1 hour (Fig. 9c).



a)



b)

c)

Fig. 9 METSIM modeling of leaching LMF slag with average 0.2 mm diameter at different slag/solution ratios in batch type reactor without fresh water input (a) and increase of Ca leaching by fresh water input into mix-flow type reactor with different solution residence time (b, c)

3.2 Direct Slag Carbonization (Scenario 4).

For scale-up to an industrial process of carbon dioxide sequestration, slag continuous operation of the reactor is desired. For this application, the METSIM model was designed to allow continuous feed of fresh slag to Reactor 1 at the same rate as continuous discharge of carbonized product from Reactor 2. Carbon dioxide was introduced into Reactor 2 and the aqueous solution was recirculated from Reactor 2 to Reactor 1. It was assumed as a first approximation that Reactor 1 operated in back-mix mode with the composition of the discharged stream as an average for Reactor 1. A non-steady state operational model was used starting with fresh slag. After a specific period of time, the non-steady process became steady-state. The modeled industrial process parameters are given in Table 2 for mini-mill equipped EAF with 1 million ton annual steel production. CO_2

Table 2. Industrial process parameters.

Steel (t/year)	Slag (kg/t steel)	Slag treatment (day)	Solution Residence in Reactor 1 (hour)	Solution Residence time in Reactor 1 (hour)	CO_2 (kg/t steel)
1000000	70	2-30	1-24	0.1-3	50-400

Decreasing the slag residence time made it possible to minimize the volume of Reactor 1, but resulted in a simultaneous decrease in the level of slag carbonization in the discharged product (Fig. 10). A one-week treatment in continuous mode provided approximately 50% of the possible carbonization of a steady batch type model. The effect of slag residence time in continuous flow steady process is shown in Fig. 11.

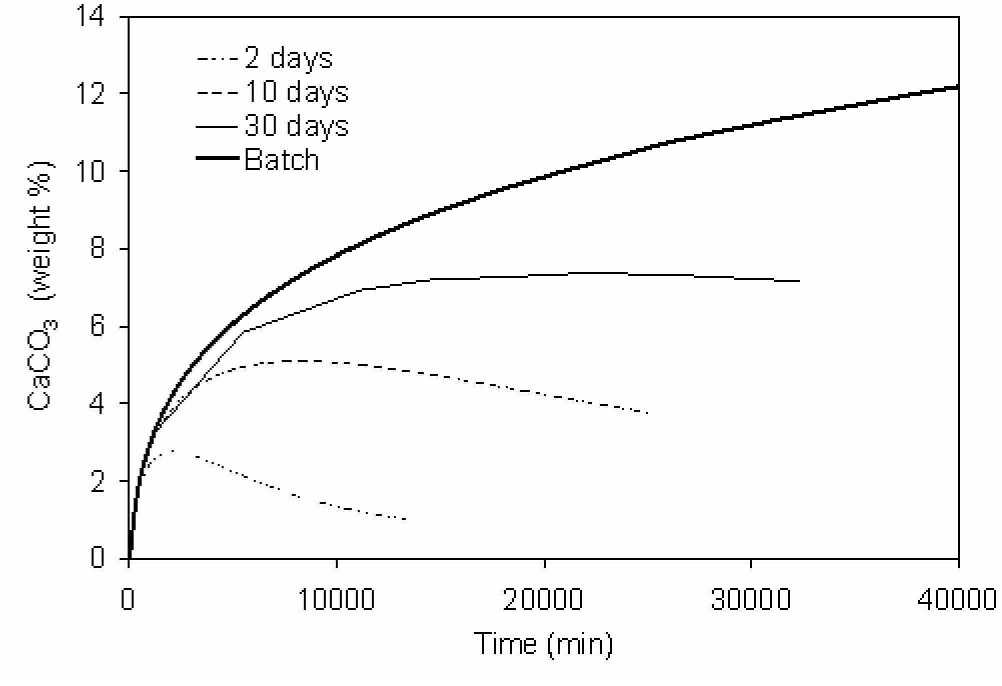


Fig. 10 Comparison of batch and continuous carbonization of LMF slag with average diameter 0.2 mm at different slag residence times.

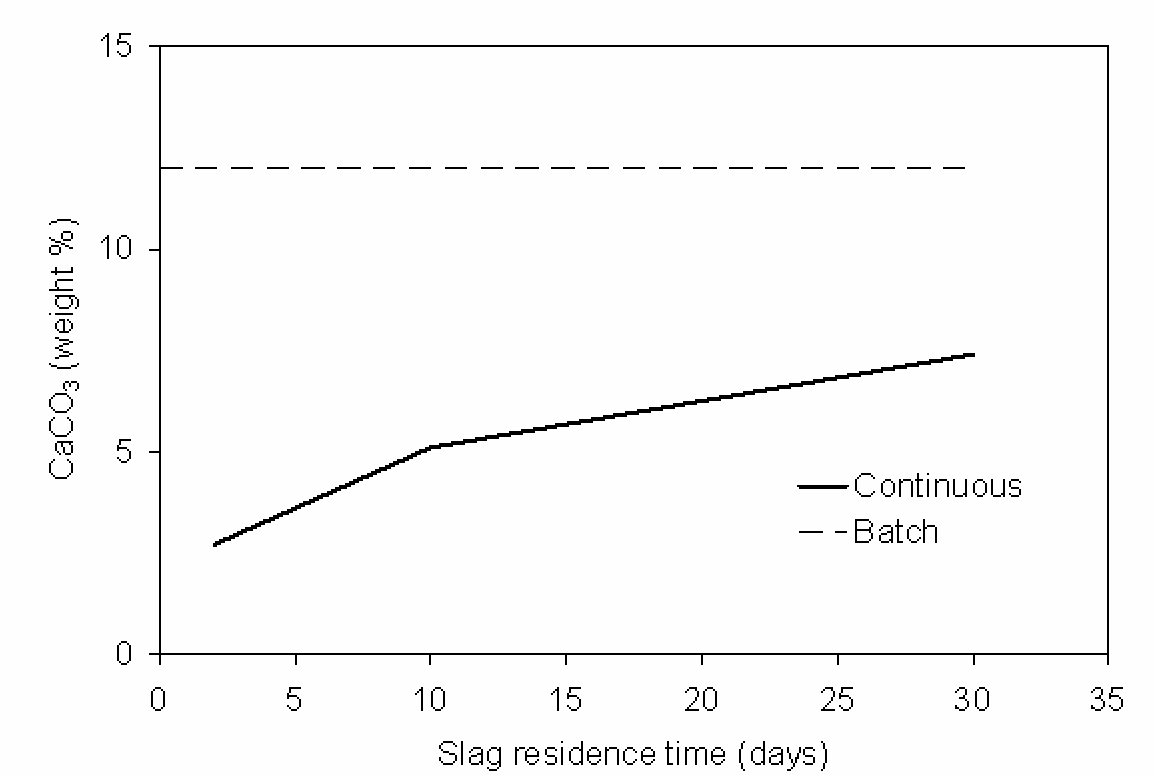


Fig. 11. Influence slag residence time on $CaCO_3$ in slag in steady continuous and batch regimes.

The effect of particle sizes on slag carbonization for continuous flow process at constant slag residence time (20 days) is shown in Fig. 12a. The time was given from the moment when process started. The near steady regime was achieved after 10-15 days treatment. In these calculations the discharged slag had an average content of calcium carbonate. The effect of particle size on carbonate content at near steady condition is given in Fig 12 b. The rate (Ton CO_2/min) of carbon dioxide sequestered for these conditions in given in Fig. 13.

The other process variables had less influence on the final result of slag carbonization. For example, increasing solution exchange rate between reactors (or decreasing solution residence time) accelerated carbonization process. The optimal solution residence time in Reactor 1 is 6-12 hours.

Described above results were achieved for mono particle sizes. In the real slag processing, slag could be crushed for particular sizes and after magnetic metal separation treated in suggested process. For slag with any size distribution, the process parameters could be evaluated with taking into account the amount of different slag particle fractions. Below two examples is given for as-received and additionally crushed slags from different mini-mills. The particle size distribution of as-received slags is given in Fig. 13. These slags were additionally crushed with using lab jaw crusher after passing 3.3 mm (Fig. 14).

The calculation procedure included:

- approximation of the achieved slag carbonization versus fraction for particular process parameter conditions. For example, the approximation for conditions depictured in Fig.12 (20 days slag average residence time and 1 day solution residence time in Reactor 1) gives equation:

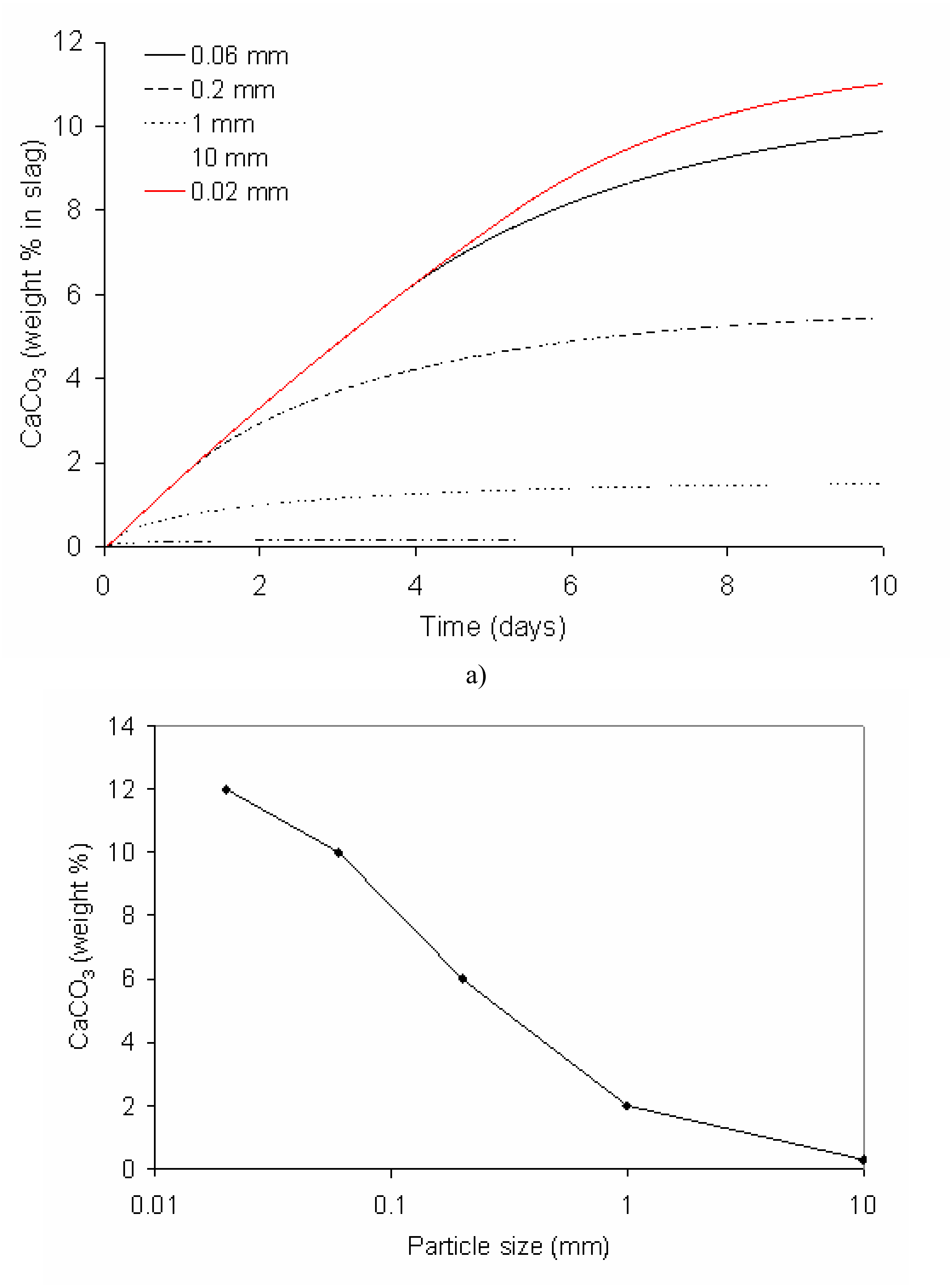
$$CaCO_3 = 1.6128d^{-0.6098} \qquad [6]$$

- calculation of degree carbonization with taken into account different particle sizes in slag,
- calculation of an average equivalent diameter and an average degree of carbonization with using Equation [6].
-

An example of these calculations is given in Table 3 for two types of described above industrial slag conditions and process parameters.

Table 3. Slag carbonization as-received and additionally crushed slag.

Diameter mm	$CaCO_3$ %	As-received		Crushing (-3mm)	
		Fraction (F)	$FxCaCO_3$	Fraction (F)	$FXCaCO_3$
10	0.40	0.68	0.27		
1	1.61	0.15	0.24	0.7	1.13
0.2	4.30	0.1	0.43	0.15	0.65
0.06	8.97	0.05	0.45	0.1	0.90
0.02	17.52	0.02	0.35	0.05	0.88
Total $CaCO_3$ (%)			1.74		3.55
Equivalent diameter, mm			0.88		0.28



a)

b)

Fig. 12 Slag carbonization in continuous regime with 20 days average residence time (a) and effect of particle size on slag carbonization in continuous process with 20 days slag residence slag and 1 day solution residence time at near steady condition (b).

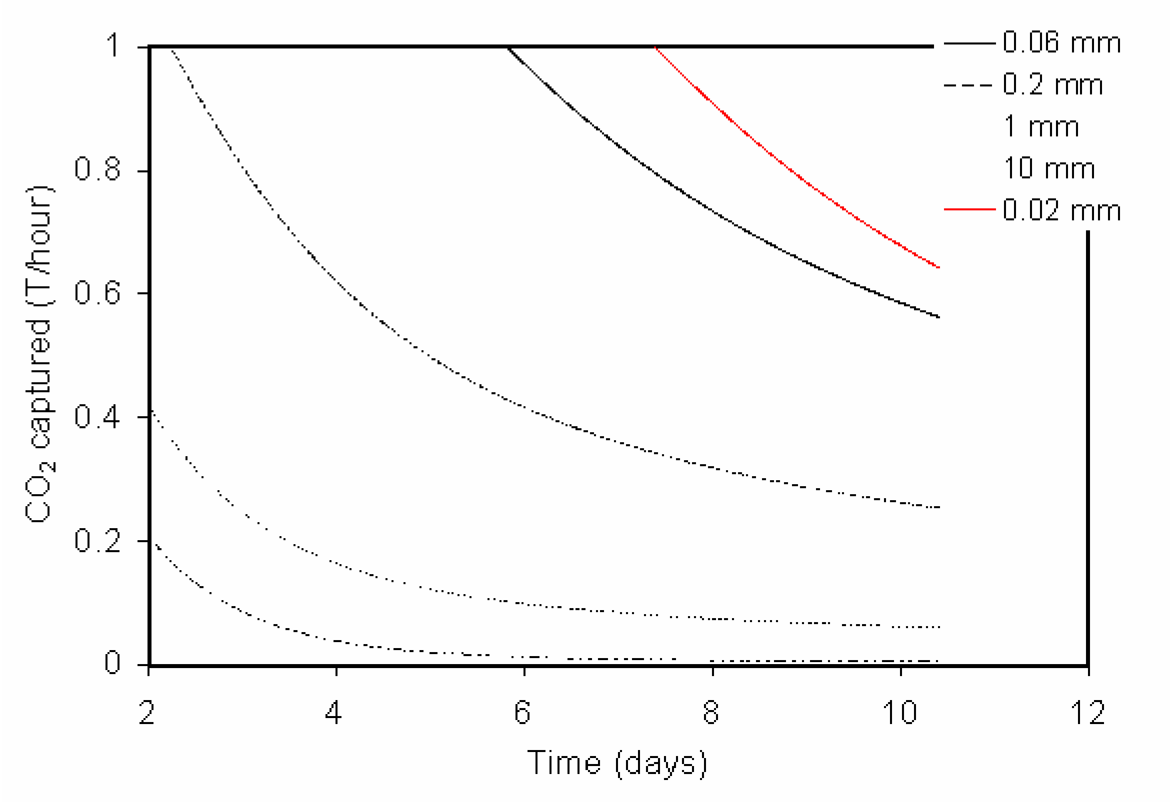


Fig. 13 Rate of CO2 sequestered in continuous regime with 20 days slag residence time

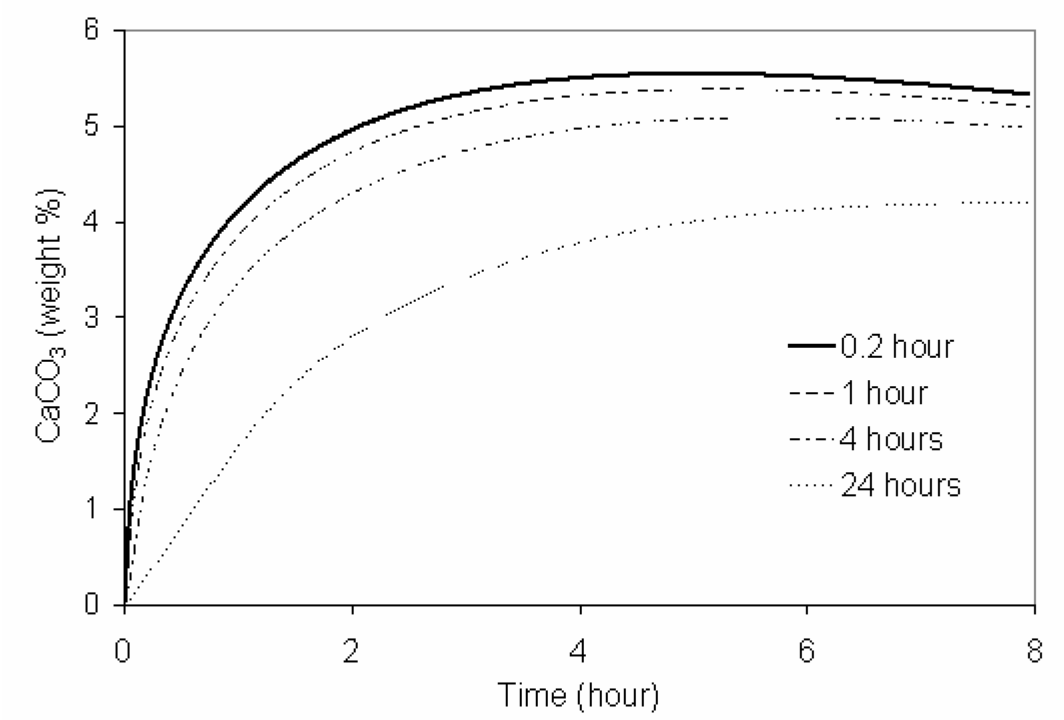


Fig 14. Effect of solution residence time in Reactor 1 on slag (0.2 mm) carbonization in continuous process with 10 days slag residence time

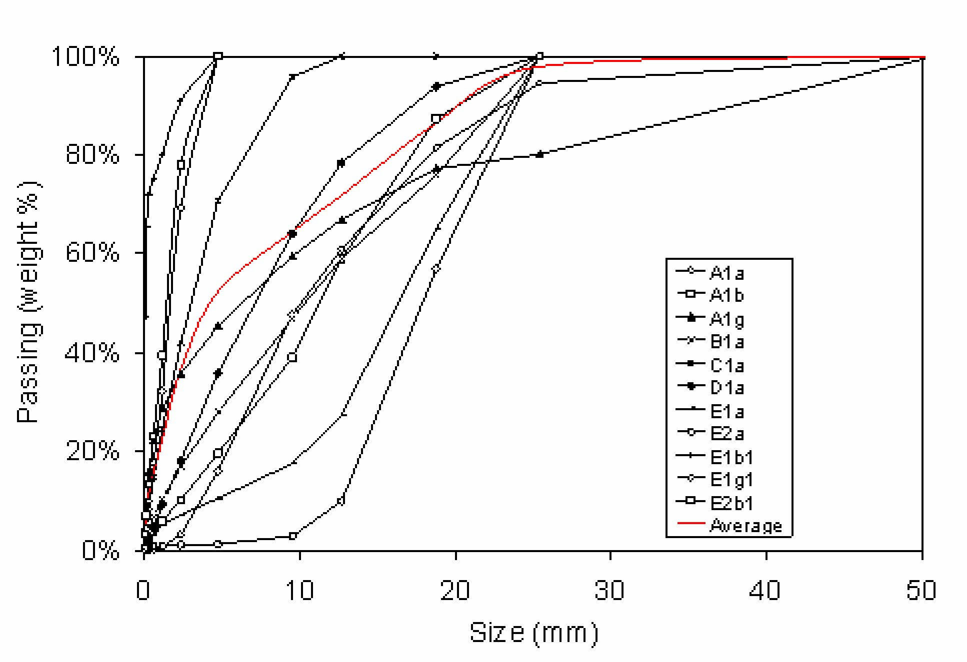


Fig. 15. Particle size distribution in as-received slags from different mini-mills

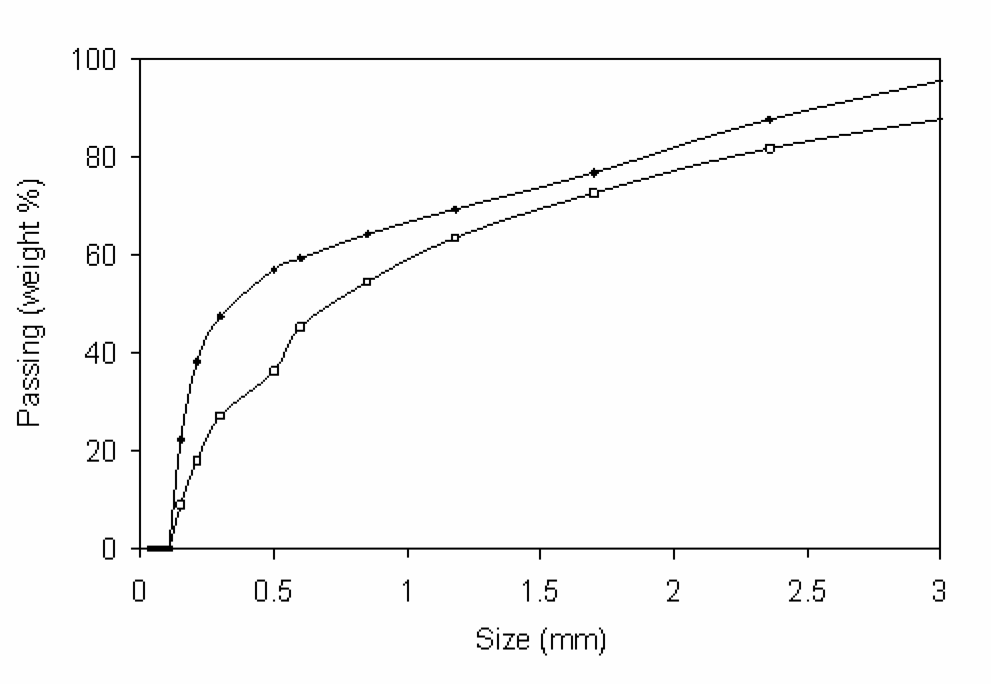


Fig 16. Slag particle size distribution after jaw crushing (- 3mm)

CONCLUSIONS

- METSIM process simulation software was used to model several reactor scenarios for hydrous carbonate sequestration of CO_2 using steelmaking slag. A two-stage reactor design was modeled. The process allowed introducing water and slag into the first reactor and carbon dioxide into the second reactor, with the possibility of recirculation of solution. A comparison of the scenarios shows that continuous calcium leaching by fresh water in the first reactor has the advantage of preventing the formation of a carbonate product layer on the slag particles, which could reduce the leaching efficiency. However, the water requirement in a continuous system is much higher than a recirculated system.
- To minimize the fresh water make-up, the spent aqueous liquor from the second reactor could be recirculated to the first reactor. The drawback to this system is that the residual absorbed CO_2 in the recirculated water results in the direct formation of a calcium carbonate later on the slag particles, which inhibits leaching of calcium ions. The product layer blinding effect could be partially overcome by increasing the slag surface area (i.e. decreasing the particle size), and increasing the residence time in the first reactor. The METSIM model showed that these two factors greatly assisted the amount of calcium that could be carbonized.
- It was shown that the METSIM model is a useful tool for designing and optimizing CO_2 sequestration reactor systems based on different slag fractions and compositions. The industrial carbon dioxide sequestration process by steel making slag was modeled for one industrial case (1 million tons of EAF steel production) with different process parameters and slag conditions.