AN OVERVIEW OF TREATMENT OF STEEL-MAKING SLAG FOR RECOVERY OF LIME AND PHOSPHORUS VALUES

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ABSTRACT

The steelmaking slag containing high phosphorus (1-3 % P2O5) can not be used in blast furnace, as it increases the refining load. Removal of phosphorus is essential for the recycling of slag which consists of major phases like dicalcium silicate, dicalcium ferrite and wustite. The majority of phosphorus is present in the dicalcium silicate. The objective of this study is to remove this phase selectively to the extent of 90% by different methods. The paper reviews these methods and suggests a methodology for removal of phosphorus.

INTRODUCTION

In the integrated steel plants, 130-200 kg slag is generated from Basic Oxygen furnace (BOF) per tonne of crude steel produced. Possible applications of this slag are in:

1. Iron-making
2. Secondary Steelmaking
3. Road Construction
4. Ballast Material
5. Soil Conditioner

The utilization of BOF slag is limited due to the following reasons:

1. High Phosphorus Content (1-3 % P_2O_5)
2. HighVolume Expansion
3. Undesirable Chemistry
4. Size

The high phosphorus content of BOF slag restricts its use in iron making because under reducing conditions all the phosphorus will revert back to the hot metal. Slag generated in secondary processing of liquid steel is also not suitable for ironmaking because of presence of high alumina content. An attempt has been made to utilize these slags in Ladle Furnace as a partial substitute to lime and fluorspar but its use is restricted due to refractory wear and other problems[1]. The problem of using BOF slag in road and building sector is the free lime content which absorbs moisture and carbon dioxide to form hydroxides and carbon dioxide which lead to volume expansion. However, the BOF slag of size 40-45 mm may serve as an excellent rail ballast material [2].

It has been reported [1,2,6] that less than 50 percent of the BOF slag is utilized, and the remainder is dumped. Possibility exists to use a large portion of the slag if phosphorus can be removed.

The phosphorus rich portion can also find application in agriculture as Soil Conditioner.

The steelmaking slag consists of three major phases [3-5] :

1. Dicalcium silicate
2. Dicalcium ferrite
3. wustite

Amongst these phases, most of the phosphorus is present in the dicalcium silicate. If this phase is separated completely approximately 90% phosphorus would be removed.

OBJECTIVES

- To remove dicalcium silicate selectively
- To use high phosphorus slag as soil conditioner
- To use a good portion of slag in Iron and Steelmaking

LITERATURE SEARCH

Hitoshi Ono et al [3] studied the removal of phosphorus from LD slag by floating separation of Dicalcium Silicate during solidification. On slow cooling from high temperature the slag is separated in two layers, CaO, SiO_2 and P_2O_5 are segregated in the top layer and FeO, Fe_2O_3 and MnO in the bottom layer.

The efficiency of separation depends on following factors:

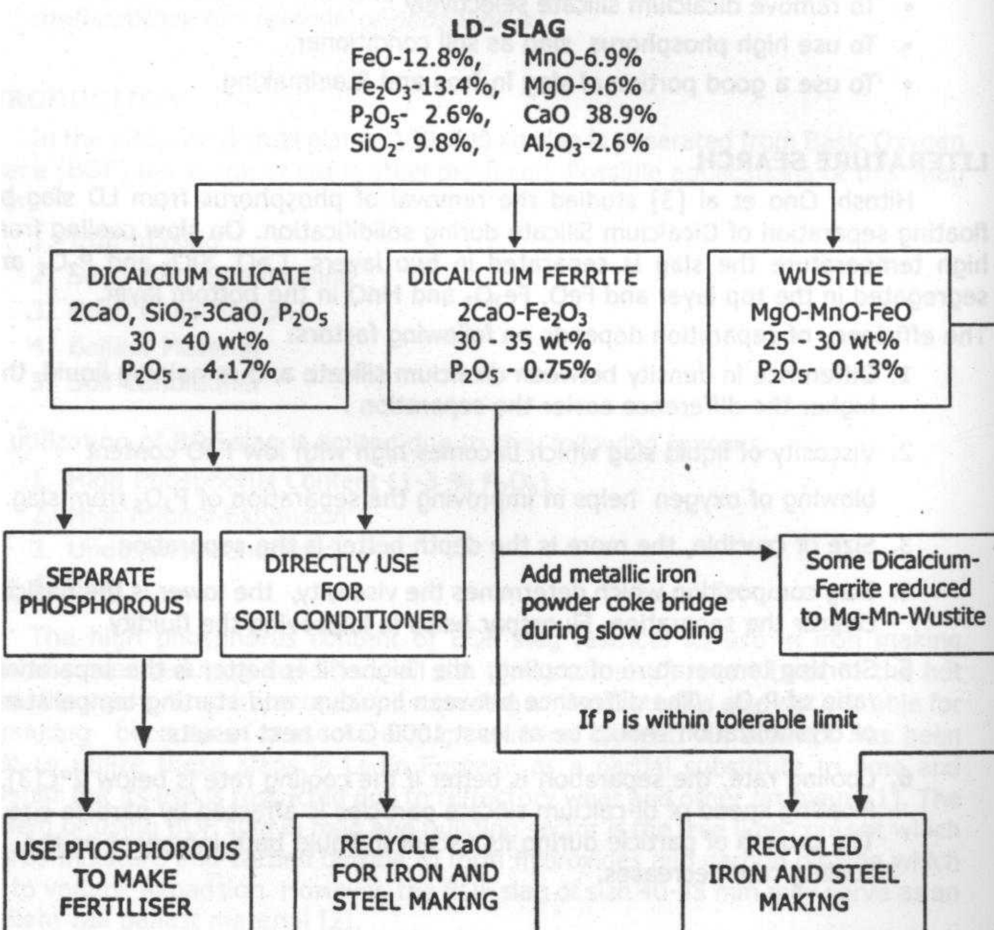
1. Difference in density between dicalcium silicate and remaining liquid, the higher the difference easier the separation .
2. Viscosity of liquid slag which becomes high with low FeO content

   blowing of oxygen helps in improving the separation of P_2O_5 from slag.
3. Size of crucible, the more is the depth better is the separation
4. Slag composition which determines the viscosity, the lower is the basicity clearer the separation. Fluorspar helps in improving the fluidity .
5. Starting temperature of cooling, the higher it is better is the separation ratio of P_2O_5 . The difference between liquidus and starting temperature of crystallization should be at least 1000 C for best results.
6. Cooling rate, the separation is better if the cooling rate is below 2°C[3]. Floating speed of di-calcium silicate particles is affected by particle size. The growth of particle during its ascent in liquid bath increases as the cooling rate decreases.

7. Effect of blowing oxygen, suspended Fe and FeO get oxidized to higher oxides like FeO anf Fe_2O_3. As the oxidation reaction is exothermic, the temperature of slag increases which helps separation of P-rich phase.

An attempt is made to separate dicalcium Silicate using a high gradient magnetic separator (HGMS). To study the separation behavior, mineralogical characteristics of slag samples were examined by SEM/EDAX and X-ray diffraction. The relative proportion of three phases-wustite, dicalcium ferrite and dicalciun silicate in as-received slag is shown in the flow chart. It is apparent that separation of dicalcium silicate from other phases will remove Phosphorus.

FLOW CHART

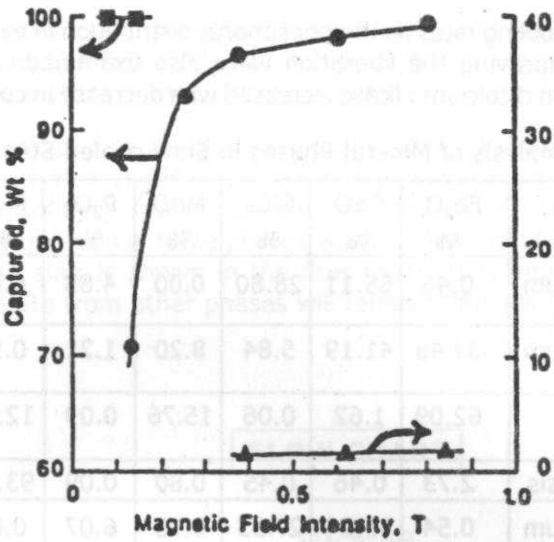


The effect of cooling rates on the phosphorus distribution in each mineral and the grain growth for improving the liberation were also examined. It was found that phosphorus content in dicalcium silicate increased with decrease in cooling rates (Table).

Table : EDS Analysis of Mineral Phases in Slow-cooled Steelmaking Slag

Cooling rate	Phases	Fe_2O_3 %	CaO %	SiO_2 %	MnO %	P_2O_5 %	MgO %	Al_2O_3 %	Wt
1°C/min	Dicalcium Silicate	0.46	65.11	28.80	0.00	4.83	0.00	0.43	50
	Dicalcium Ferrite	37.48	41.19	5.84	8.20	1.21	0.53	3.18	40
	MgMn Ferrite	62.09	1.62	0.06	15.76	0.09	12.82	6.85	40
	Magnesis	2.73	0.46	0.45	0.80	0.09	93.66	1.78	10
0.5°C/min	Dicalcium Silicate	0.54	65.24	27.33	0.13	6.07	0.00	0.21	51
	Dicalcium Ferrite	31.76	41.15	5.56	15.84	1.35	1.01	1.30	39
	MgMn Ferrite	57.58	2.35	0.21	13.17	0.27	17.41	7.69	39
	Magnesis	3.15	0.27	0.28	0.99	0.16	93.03	1.91	10
0.2°C/min	Dicalcium Silicate	0.31	62.13	29.66	0.03	6.80	0.35	0.36	56
	Dicalcium Ferrite	31.63	40.66	7.62	13.15	1.69	1.23	2.89	34
	MgMn Ferrite	52.09	2.30	0.54	11.38	0.32	21.57	10.83	34
	Magnesis	5.58	0.52	0.17	1.54	0.46	88.94	2.15	10
0.1°C/min	Dicalcium Silicate	0.13	52.62	29.36	0.01	6.64	0.20	0.53	60
	Dicalcium Ferrite	30.53	41.08	6.36	14.96	1.47	1.36	2.53	30
	MgMn Ferrite	65.62	1.72	0.00	13.26	0.07	12.03	6.37	30
	Magnesis	5.06	0.62	0.43	1.52	0.44	57.16	4.54	10

The result of magnetic separation of synthetic slag showed that iron rich phase is recovered readily at 0.07 magnetic field intensity (T),intermediate phase dicalcium ferrite is recovered at field intensity (T>0.3) whereas dicalcium silicate will have no effect (Fig). This result was applied on as received and slowly cooled slag. It was found that wustite is converted to Mg-Mn ferrite under oxidizing atmosphere and its close association with dicalcium silicate interfered with magnetic separation.



Magnetic concentration of synthetic dicalcium ferrite, dicalcium silicate and Mg-Mn ferrite by high gradient magnetic seperation [4]
● dicalcium ferrite; ▲ dicalcium silicate; ■ Mg-Mn ferrite

SUGGESTED METHODOLOGY

The suggested methodology is shown in the Flow Chart. The steps to be followed are:

1. Heating of slag to its fusion temperature in a magnesia crucible followed by slow cooling at different rates
2. Separation of dicalcium silicate on the basis of density
3. Study of Separation behavior of dicalcium silicate from simulated synthetic slag by passing through HGMS at different field intensities
4. Separation of dicalcium silicate locked with Mg-Mn ferrite by flotation
5. Use of high phosphorus slag for preparation of bio-fertilser

REFRENCES

1. Das A.K & T. Mukherjee; Utilisation of Steel Plant Slags. Internal Communication, 2000
2. Nayak B.D et al; Challangesof solid waste management in iron and steel industries "Environment and waste Management in Iron & Steel Industries"ISSN:0971-9407,2000pp153-162
3. Ono H et al ; Removal of phosphorus from LD converter by floating of dicalcium silicate during solidification: Trans ISIJ, Vol 21 (1981) pp 136-144
4. Fujita T and Iwaski I; Phosphorus removal in high gradient magnetic separation from steelmaking slags slow cooled in an air atmosphere; "Process Minerology VIII," (1988), D.J.T. Larson and A. H.Vassilou, "The Minerals, Metals and Material Society; pp293-308.
5. Fregeau-Wu E.; "In Situ Grain Size Determination of Slow- Cooled Steelmakingslags; "Process Minerology IX," (1990), "The Minerals, Metals and Material Society; pp429-438 .
6. J. Y. Ryu, R.J. Fruehan and a.T. Morales, "Kinetics of Phosphorus Vaporisation from slag" Transactions, Iron &Steelmakers,26, (1), pp56-68 January1999,