

ASSESSMENT OF ENERGY RECOVERY FROM CARBONATION PROCESS USING MASS AND ENERGY BALANCE

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ABSTRACT

Mineral carbonation technology, one of the carbon capture and storage (CCS) technologies, is mainly concerned with the reduction of harmful emissions of carbon dioxides (CO₂) to the atmosphere. However, carbonation system requires extra energy for pretreatment of the feed stocks including mining, transport, grinding and activation (when necessary), disposal of carbonates and byproducts, etc. This extra energy is called energy penalty. Despite this energy penalty there is a growing interest in carbonation technology because of its several benefits (such as abundance of metal oxide bearing material, exothermic reaction, safe storage of CO₂ in a stable solid form, etc) over other CCS technologies. In this study the mass and energy balance analysis of the carbonation system using Matlab/Simulink software is presented and discussed in order to assess the energy recovery from the carbonation products and reduction of CO₂ emissions. Energy gain from the carbonation reaction is calculated with an aim that it will contribute to the self-sufficiency of energy requirement of the carbonation system. This may improve the overall efficiency of the power plant too. It is found from this study that at carbonation temperature below 423.15° K (150 °C), the carbonation system is energy self-sufficient with exothermic heat gain and no heat recovery is needed from the carbonation products. However, the energy recovery from the products is required when carbonation occurs at above 423.15° K.

Key words: CCS, Carbonation technology, implementation, Energy, heat, efficiency, self-sufficient, Matlab.

INTRODUCTION

The contributors to greenhouse effects are carbon dioxide (CO₂), chlorofluorocarbons (CFCs), methane (CH₄), and nitrous oxide (N₂O). The contribution of each gas to the greenhouse effects is CO₂ - 55%, CFCs - 24%, CH₄ - 15%, and N₂O - 6% [1]. Figure 1 shows the trend of CO₂ emissions over the years [2]. Fossil-fuel electric power generation industries are the main contributor of CO₂ emission and specially coal power generation industries. About 46% of the world's power

generation is based on coal combustion and it is estimated that combustion of coal for power generation will be responsible for about 41% of the world's CO₂ emissions by 2025 [3]. In Australia 75% of the total electricity is produced from coal fired power plants, so coal fired power plants have a great impact on the Australian economy [4]. Therefore, there is a growing demand to identify an appropriate technology to reduce CO₂ emission from coal power plant. The control of CO₂ emission to the atmosphere is one of the most challenging environmental issues for today's world. The global scientific communities are continuing their research to control CO₂ emissions from various CO₂ contributing sectors to mitigate the problem of global climate change.

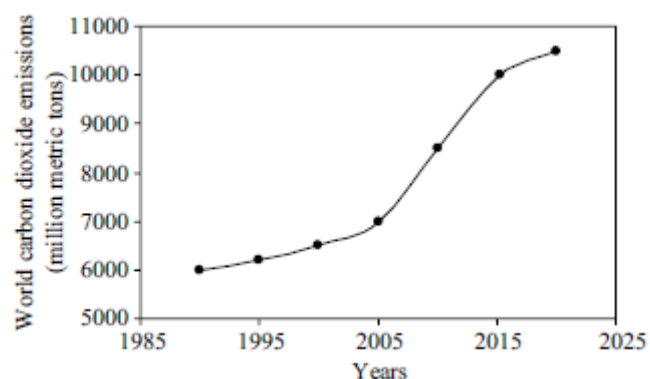


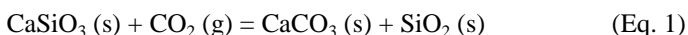
Figure 1 World CO₂ emissions between 1990 and 2020

[2]

Carbon capture and storage (CCS) technologies are viewed as viable option to mitigate this environmental problem. It has been observed that all CCS technologies are energy and cost consuming process. The mineral carbonation technology which is the main focus of this study requires extra energy for pretreatment of the feed stocks including mining, transport, grinding and activation (when necessary), carbonation reaction, recycling the additives and the disposal of carbonates and byproducts. This extra energy is termed as energy penalty.

Despite this energy penalty there is a growing interest in carbonation technology considering its different benefits over other sequestration technologies. For example, the benefit includes abundance of metal oxide bearing material; carbonation process is an exothermic reaction which can make this process self energy sufficient, and safe storage of CO₂ in a stable solid form. However, mineral carbonation is still in Research and Development phase [5]. A limited number of studies are available on the development of this technology for reducing CO₂ emission.

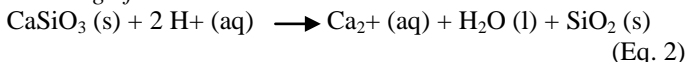
There are mainly two types of carbonation system available; they are dry and wet carbonation. It has been found from the literature that the aqueous carbonation route is the most favourable route of carbonation process [6, 7]. In this process water is used as an additive which enhances the carbonation rate and a major portion of water can be recycled after the carbonation process. The idea of aqueous mineral carbonation comes from the natural weathering process where CO₂ slowly reacts with natural silicate minerals. In nature such a reaction is known as silicate weathering process. For industrial application carbonation reaction is enhanced by raising the temperature. The overall reaction of the carbonation process with wollastonite mineral (CaSiO₃) is as below [6].



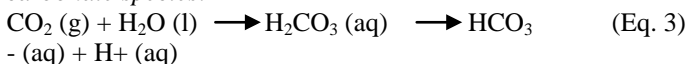
$$\Delta H (\text{Enthalpy of reaction}) = -87 \text{ kJ/mol}$$

The carbonation reaction of wollastonite occurs in three steps: (a) Ca leaching from the CaSiO₃ matrix (b) Dissolution of CO₂ and (c) CaCO₃ nucleation and growth. They are defined below:

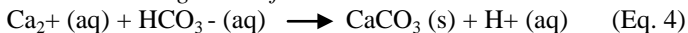
Leaching of Ca:



Dissolution of CO₂ and subsequent conversion of (bi) carbonate species:



Nucleation and growth of calcium carbonate:



Limited information has been found from the literature relating to the energy recovery opportunities from carbonation reaction. Some possibilities for energy integration by carbonation technology have been identified by Brent and Petrie, these are listed in Table 1, which shows various energy sinks and sources [8].

In this study mass and energy balances of aqueous carbonation system are presented and discussed for the coal fired power plant to evaluate the performance of this technology using Matlab/simulink software.

Table 1 Possible Energy sinks and energy sources [8]

| Energy Sinks (recovered energy utilization area) | Energy Sources (for energy recovery) |
|--|--|
| Mineral comminution energy CO ₂ compression duty | Compressed CO ₂ product stream Dehydroxylation reaction products |
| Serpentine activation Carbonation reagent slurry preheating | Carbonation reaction products |

POWER PLANT WITH CARBONATION TECHNOLOGY

Figure 2 shows a simplified schematic diagram of electricity production from burning coal [9], though a real plant is much more complex with its operational characteristics. A typical pulverized coal (PC) combustion power plant is equipped with three units, boiler block, generator block and flue gas clean up block. The flue gas clean up block mainly consists of selective catalytic reduction (SCR) for NO_x (Nitrogen Oxide) removal, electrostatic precipitation (ESP) for particulate matter removal, and wet flue gas desulphurisation (FGD) or wet lime scrubbing to remove SO_x and mercury. To incorporate carbonation unit in existing power plant just prior to the flue gas stack would require some modification of the plant. It has been observed that efficiency of the carbonation process would be increased by achieving faster reaction rates with higher concentration of CO₂ [10]. So CO₂ capture devices can be introduced after flue gas clean up block to separate CO₂ from other component of the flue gas steam to make pure CO₂ stream for carbonation reaction. Figure 3 shows a general flow diagram of carbonation unit which is the future work of this study to incorporate this technology into power plant. In this paper only carbonation reactor has been considered for mass and energy balance and wollastonite feed stock has been used for carbonation reaction with power plant flue gas.

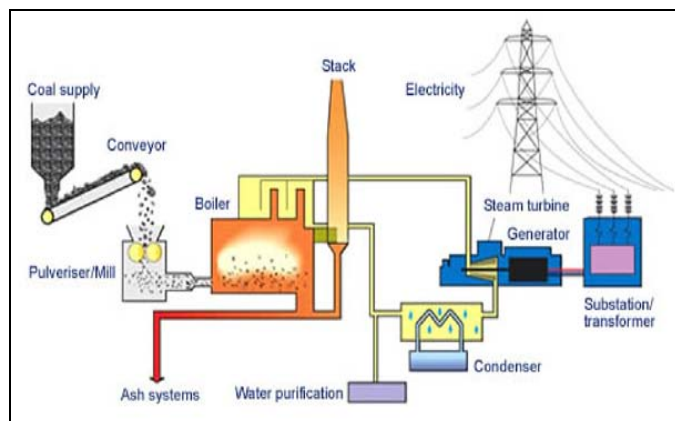


Figure 2 schematic diagram of a coal fired power plant [9]

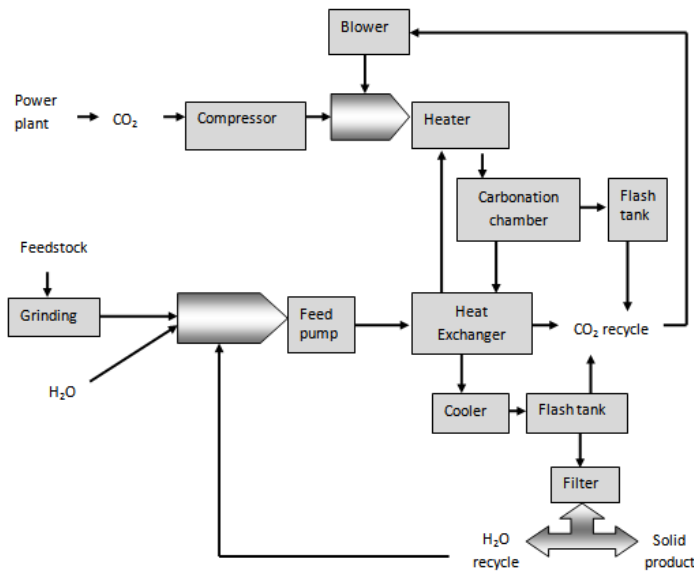


Figure 3 General Flow diagram of Carbonation unit [11]

At first wollastonite is grounded into a specific particle size in a grinder and mixed with water at a specific liquid/solid ratio to form slurry which is then pumped by a feed pump to the reactor pressure. Subsequently this slurry is heated by a heat exchanger below the reactor temperature and CO₂ is added directly into the slurry through a compressor. Before carbonation, this mixture is heated in a heater and the reactor is heated to a specific reaction temperature. Then, carbonation takes place in the reactor between compressed CO₂ and the slurry of wollastonite. After carbonation, non reacted CO₂ is recycled to the carbonation chamber through a blower and the product slurry is cooled by a heat exchanger and a cooler. Solid products of the carbonation reaction are separated by a filter. Released CO₂ and H₂O are recycled to the carbonation chamber. There are several process variables which affect the carbonation reaction, such as reaction time, reaction temperature, CO₂ partial pressure (P_{CO_2}), particle size of wollastonite feedstock, liquid-to-solid ratio (L/S) and stirring rate [5]. It has been reported in the literature that the maximum conversion of wollastonite in carbonation reaction is 75% at 200 °C, 20 bar CO₂ partial pressure with particle size of <38 μm [11].

MASS AND ENERGY BALANCES OF CARBONATION PROCESS

Mass and energy balances are essential and valuable tools for investigating the general performance of a process plant. Mass and energy balance of the carbonation process has

been calculated based on literature data, reference book and coal fired power plant real data. A few assumptions were made to calculate mass and energy balances.

Mass Balance

The mass balance of the carbonation unit with power plant flue gas was carried out by an analysis of the feed material using the following input data: composition of wollastonite, composition of power plant flue gas, liquid and solid ratio and atomic mass of the feed material. For modelling purposes, general operating conditions were sourced from local coal fired power stations, which are given below.

| | |
|----------------------------------|----------------|
| Total capacity: | 1400 MW |
| Annual CO ₂ Emission: | 9,665,819 tons |
| Intensity: | 1,051 kg/MWh |
| Annual electricity production: | 8,352,934 MWh |
| Actual operating capacity: | 1,049.86 MWh |

The overall efficiency of the plant was taken as 45%. This is a typical operating efficiency for generators of a supercritical plant [11]. The following assumptions were made to calculate the mass and energy balance of carbonation reactor.

| | |
|--|----------------------------|
| Compositions of the wollastonite | CaSiO ₃ – 84.3% |
| | CaCO ₃ – 1.8% |
| | SiO ₂ – 13.9% |
| Composition of flue gas | 86% – N ₂ |
| | 14% – CO ₂ |
| Conversion efficiency of CaSiO ₃ | 69% |
| Liquid solid ratio | 2:1 |
| H ₂ O acts as an additive and 90% H ₂ O can be recycled after reaction | |
| Water recycle rate | 90% |
| Make up water | 10% |
| CO ₂ Conversion efficiency | 90% |

CaCO₃, SiO₂ and N₂ remain inert in this reaction. Only CaSiO₃ of wollastonite takes part in the carbonation reaction [11]. Conversion rate of the carbonation reaction (eq.1) is 2.6394 kg CaSiO₃ / kg CO₂. Mass balances of input materials and output product have been calculated based on this conversion rate using Matlab/Simulink. Figures 4, 5 and 6 show the sub systems of mass balance of flue gas, wollastonite and products respectively in Simulink block diagram. Table 1 indicates the summary of mass balance of feed stream and exit stream.

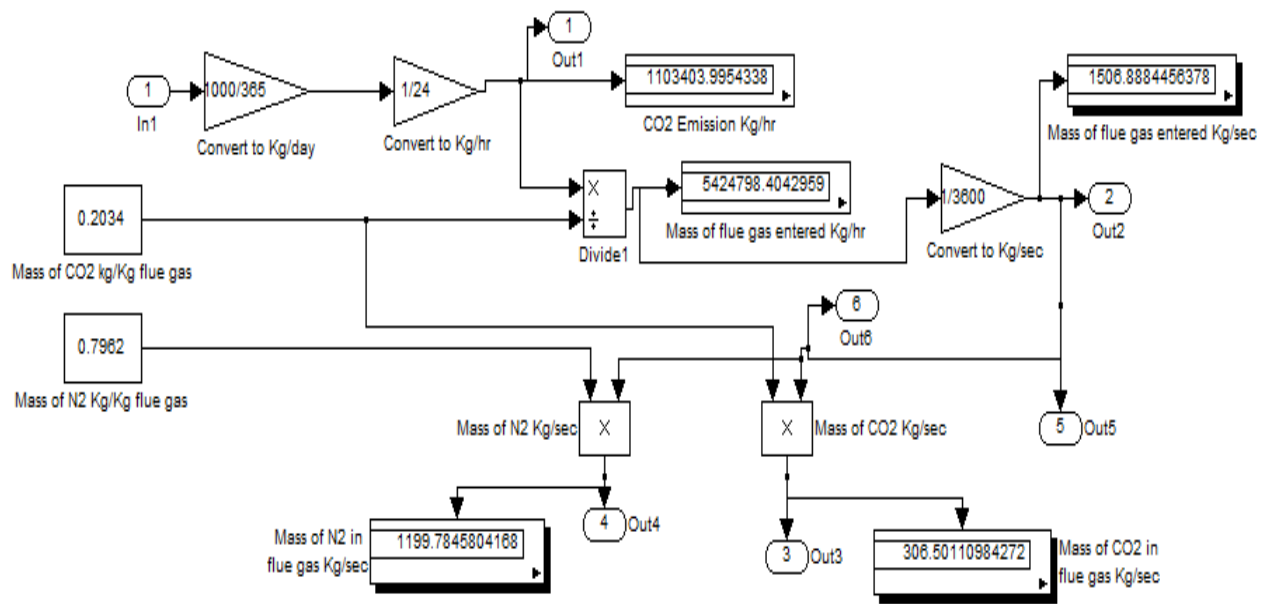


Figure 4 Subsystem for mass of Flue gas

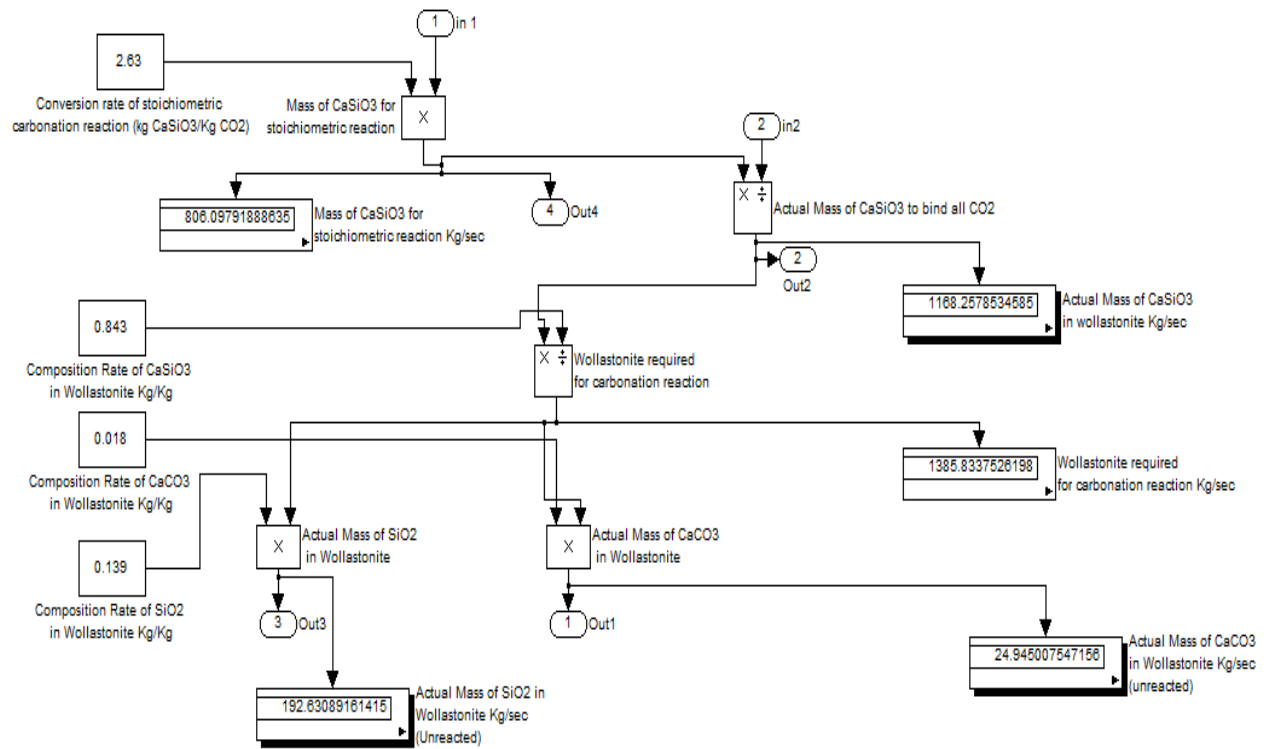


Figure 5 Subsystem for mass of Wollastonite

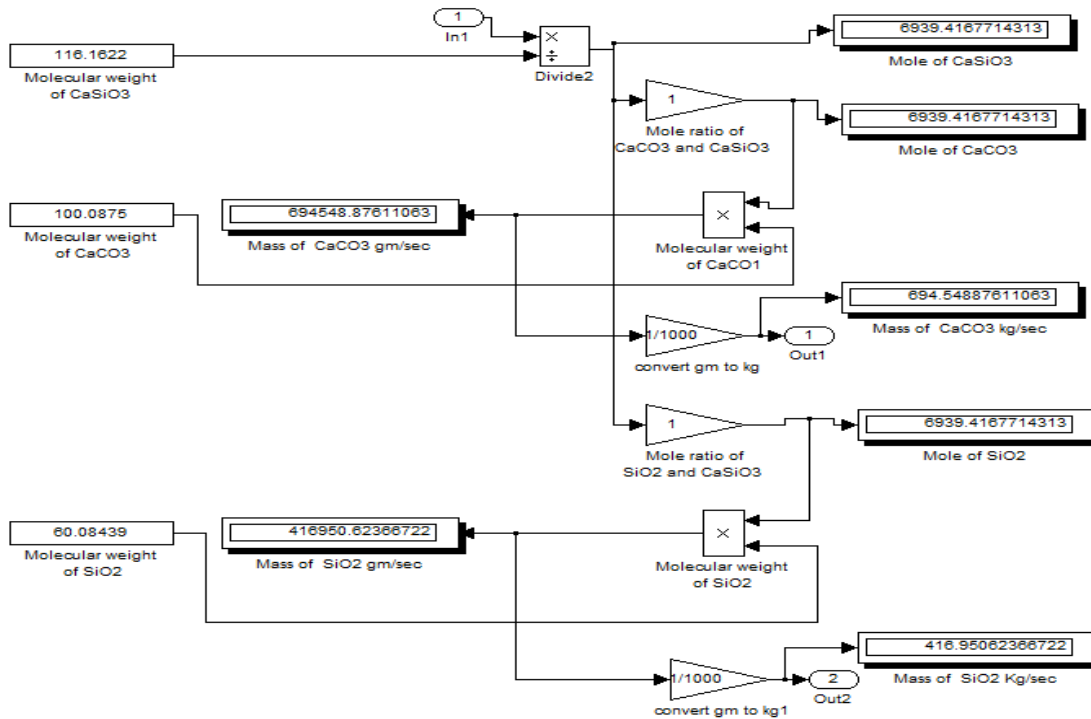


Figure 6 Subsystem for mass of product

Energy Balance

Following the completion of the mass balance models, the energy balance models were developed. For effective implementation of carbonation system into an existing power plant, it would be preferred that it does not reduce the existing power plant operating efficiency. Therefore this paper investigated the heat recoveries needed from the carbonation reaction to ensure that the carbonation system is energy self-sufficient. In this model, the solid reactant wollastonite and the flue are introduced into the carbonation system at an ambient temperature (25 °C). Recycled CO₂ and H₂O also enter the carbonation system at 298.15 °K (25 °C). The models have been run with the carbonation temperatures ranging from 323.15 °K (50°C) up to the maximum carbonation temperature of 523.15°K (250°C) for wollastonite feed stock [11]. It has been found from the literature that the maximum conversion of wollastonite in carbonation reaction is 75% at 200 °C, 20 bar CO₂ partial pressure with particle size of <38 μm [11].

The sensible energy of a process can be defined by $Q = mC_pT$ where m is the mass flow rate in kg/sec., C_p is the specific heat capacity in kJ/kgK & T is the temperature in °K . It is to be noted that C_p is a function of temperature, and can be defined by the polynomial equation, $C_p = 2 \times 10^{-9}T^3 + 5 \times 10^{-6}T^2 + 0.004T - 0.0785$ (Figure 7).

Figure 8 indicates the energy input required for heating the reactants to the desired carbonation temperature. In this study it was assumed that 85% of heat energy can be recovered from the output products. It was found from the modelling that

1171.1 MW of heat energy is required to heat the reactants and 995.4023 MW of heat energy can be recovered from the products at maximum carbonation temperature of 523.15°K (250°C) (Figure 9).

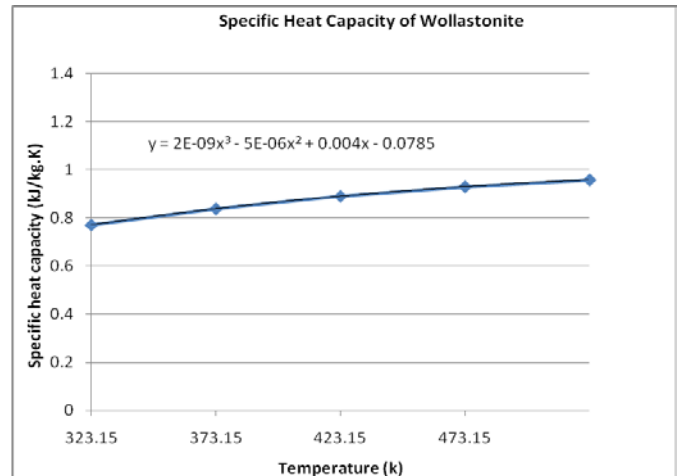


Figure 7 Specific heat capacity of Wollastonite

Figure 10 shows the total recoverable energy from the carbonation reaction based on the exothermic gain (Figure 11) and energy recovered from the products. The exothermic gain for wollastonite carbonation is 87 kJ/mole [6]. The exothermic

nature of the carbonation reactions increases the feasibility of introducing such a system into existing power plants. If the total (100%) heat energy from the exothermic gain can be captured within the continuous carbonation system that will increase the overall efficiency. At temperature of 323.15°K, the recoverable energy is 706.6 MW and this recoverable energy increases as temperature increases. Figure 10 indicates also the energy recovery needed from the products of the wollastonite carbonation reaction to maintain the existing power plant efficiency (produce an energy self-sufficient carbonation system). It can be seen from Figure 10 that at temperatures below 423.15°K (150°C) the carbonation system is self-sufficient as the exothermic gain produced by the carbonation reaction is sufficient enough to heat the system.

The remaining 482.7 MW (323.15 K) and 222.13 MW (373.15 K) exothermic energy and the recoverable energy from product can be utilized to improve the energy efficiency of the other part of the carbonation plant and power plant. However,

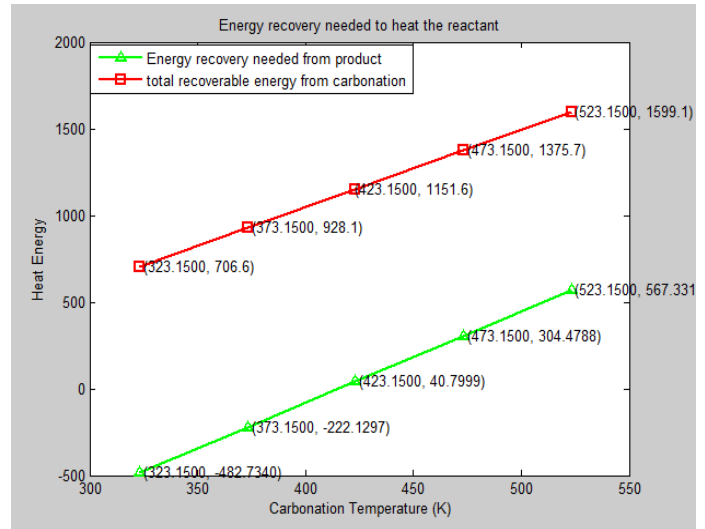


Figure 10 Energy recovery needed to heat the reactants at various carbonation temperatures

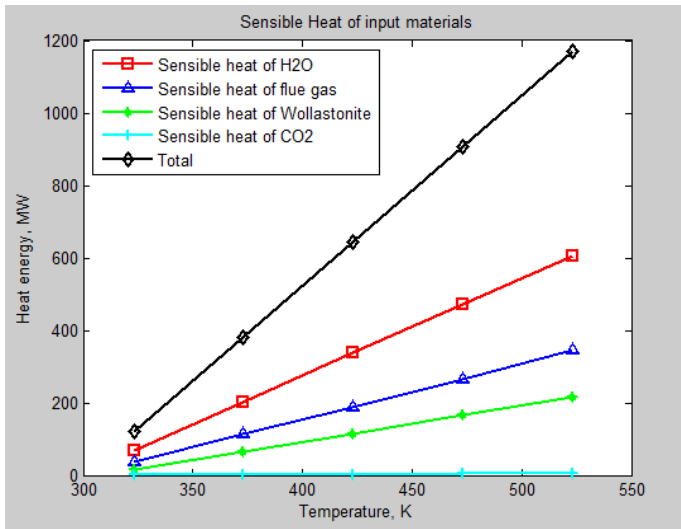


Figure 8 Sensible heats of input materials

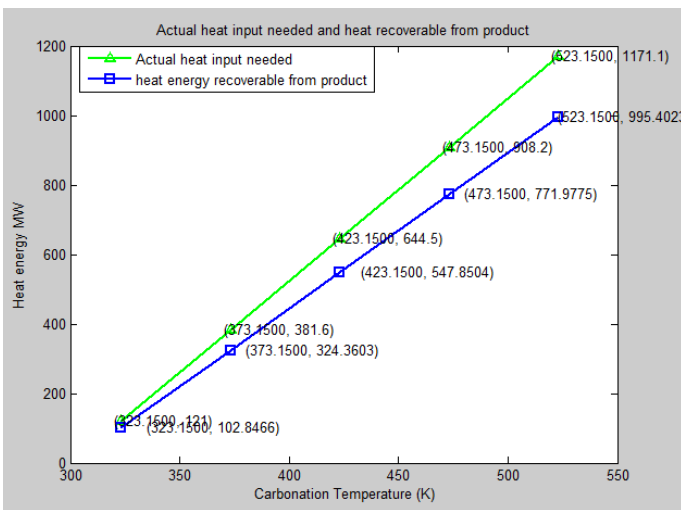


Figure 9 Actual heat input needed and heat recoverable from products

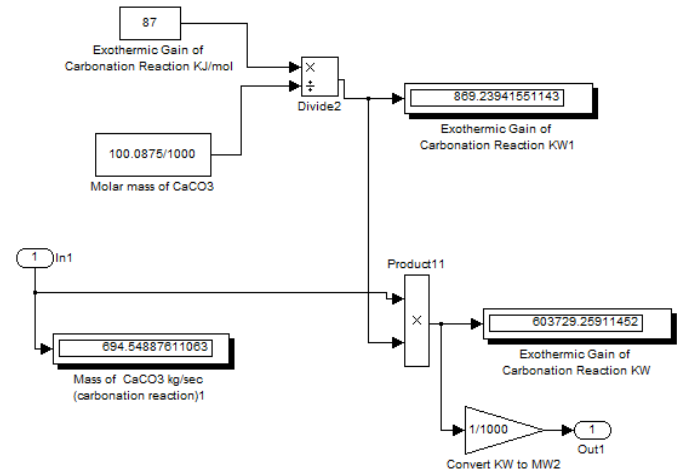


Figure 11: Exothermic gain

at carbonation temperatures above 373.15°K, energy needs to be recovered from the products to produce an energy self-sufficient carbonation system. At the maximum allowed carbonation temperature of 523.15 °K (250°C), 567.33 MW of heat energy needs to be recovered from product to maintain a self-sufficient carbonation system. Figure 12, shows the energy available in the product at various carbonation temperatures. Table 2 shows the summary of energy recovery and energy gain from carbonation reaction.

The model has calculated the desirable heat energy recovery needed from the carbonation system at different temperatures. The percentage recovery of the initial heat input has been found at the various carbonation temperatures to ensure that the respective systems are energy self-sufficient. This would ensure that the existing power plant would remain operating at its original efficiency. As the reactions are exothermic, there would be the potential to raise the operating efficiency of the existing power plant if sufficient energy capture methods are

employed. Power plant existing operating capacity 1,049.86 MW and operating capacity can be improved after using recoverable energy from the carbonation plant.

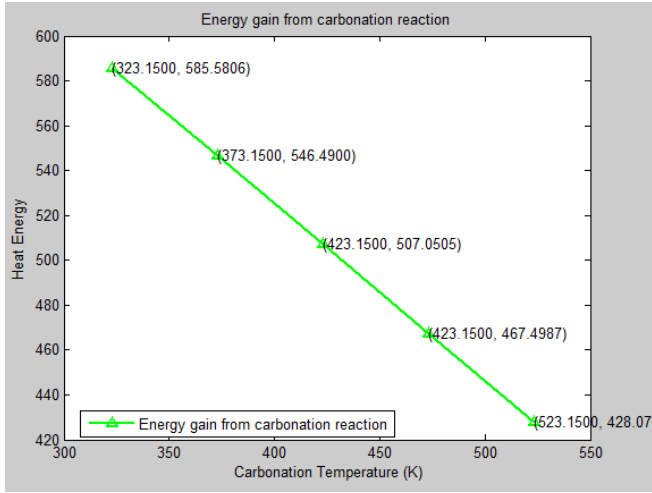


Figure 12 Energy available in the product

CONCLUSION

The reduction of CO₂ emissions, particularly from coal-fired power plants, is arguably a key issue in today's world. The main objective of this study was to evaluate the viability of carbonation technology. It is to be noted that the present analysis is based purely on the carbonation unit with compressed flue gas and grounded wollastonite. Other processes of the carbonation unit such as grinder, compressor, heater and heat-exchanger have not been considered in this present study. They will be studied later in this project. Energy balance of this study has been done based on the mass flow rate of 1,385.83kg/sec of wollastonite and 1506.88 kg/sec of flue gas. It has been observed from this study that substantial heat is produced in the carbonation reactions as a result of their exothermic nature. This heat will significantly reduce the operating costs of the process as it can be used to heat the new reactants up to the desirable carbonation temperature.

Heat energy can also be captured from the final product of the carbonation reaction. At temperature below 423.15° K carbonation system is energy self sufficient with exothermic heat and no heat recovery is needed from the product. At temperature above 423.15° K energy recovery is required to maintain the energy self sufficient carbonation system. It can be concluded that the power plant efficiency can be improved by incorporating the energy recovery system from the carbonation system into an existing power plant.

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Table 2 Energy recovery and energy available in the product

| Temperature (°K) | Heat input required (MW) | Energy recoverable from product (MW) | Energy recovery needed from product (MW) | Energy recovery needed from product (%) | Overall energy recovery needed from carbonation reaction (%) | Energy available in the product (MW) |
|------------------|--------------------------|--------------------------------------|--|---|--|--------------------------------------|
| 323.15 | 121 | 102.8466 | 482.7 (exothermic) | No energy recovery is needed | 17.12 | 585.58 |
| 373.15 | 381.6 | 324.3603 | 222.1 (exothermic) | No energy recovery is needed | 41.12 | 546.49 |
| 423.15 | 644.15 | 547.8504 | 40.8 | 7.4 | 55.97 | 507.05 |
| 473.15 | 908.2 | 777.9775 | 304.5 | 39.4 | 66.02 | 467.50 |
| 523.15 | 1171.1 | 995.4023 | 567.3 | 57.0 | 73.23 | 428.08 |

