Reduction of Carbon Dioxide Emissions by Mineral Carbonation

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Abstract: - The study investigates the technologies that have the potential to provide feasible reduction of carbon dioxide (CO_2) from a reference power plant. Particular focus has been given to mineral carbonation (at 1 bar) in which magnesium (Mg) and/or calcium (Ca) bearing materials fixate themselves to CO_2 molecules to produce Mg and/or Ca carbonates in a solid stable form. The study also involved energy and mass balances of various mineral carbonation systems for simulation in Simulink. Furthermore, the various carbonation systems were incorporated into a model of a reference plant's operating efficiency. This allowed for analysis of the impact that the carbonation systems would have on the existing plant's performance.

Key-Words: - Mineral carbonation, Emissions, Carbon dioxide.

1 Introduction

The consumption of fossil fuels by the energy infrastructure is one of the greatest sources of greenhouse gases which is responsible for recent global warming and climate change concern [1]. In 2005, the global atmospheric concentration of CO_2 has been reported as 379 parts per million (ppm) which is increased from its pre-industrial value of 280 ppm [2]. CO_2 is currently responsible for 60 percent of the enhanced greenhouse effect [3]. Global energy consumption is expected to increase by 52 percent from 2006 to 2030 [4]. Quadrelli and Peterson [5] reported that CO_2 emissions from fossil fuel usages are increasing to 26.6 Gt of CO_2 per year.

The global demand to reduce CO_2 emissions is receiving great concern now a days. Emerging technologies that are being developed to reduce or eliminate these greenhouse emissions are of the utmost importance and will continue to be in the foreseeable future. In order for coal and other fossil fuelled power generation techniques to remain large components of energy generation, harmful emission reduction systems must continue to make technological advancements. If desired changes are not sought after, energy sources such as renewable and nuclear may be the only viable options available. As the coal industry is a major factor in driving Australia's economy, it is essential that industry's which utilise it, such as coal-fired power stations, remain operational. Hence the need to investigate the feasibility of reduction of harmful gas emissions (such as CO_2) from such plants. In today's world it is becoming increasingly important to reduce harmful emissions from the production of power, to lessen their environmental impacts. Electricity generation from coal-fired power plants is accountable for a large percentage of (CO_2) emissions throughout the world. As increased amounts of carbon dioxide in the atmosphere are considered to contribute to global warming, it is imperative that such emissions are reduced.

This study offers an investigation and analysis into the thermodynamics of mineral carbonation methods to reduce CO_2 emissions from a reference power plant. These methods involve using calcium (Ca) or magnesium (Mg) based reagents to fixate themselves to the CO_2 molecules forming stable carbonate materials. The reactions (for instance, CaO, MgO + CO_2 → $CaCO_3$, $MgCO_3$ etc.) that are used in the fixation of CO_2 all produce significant amounts heat energy (exothermic reactions). If captured and utilised effectively this energy can increase the efficiency of the carbonation process and possibly the power plant's performance (operating efficiency). Also, if the marketable by-products of the carbonation reactions can be suitably utilised, the costs of the operation can be significantly reduced, making it much more feasible. The initial scope of the study is to focus on the aqueous method of carbonation and produce conceptual designs for implementation into a typical coal-fired power station. Due to the large scale of the scope and the need to produce accurate thermodynamic results prior to any conceptual designs, the final objectives of the of the study are to model the mass of flue gas emissions, to model the mass and energy balances of CO_2 fixation using various calcium and magnesium bearing oxides, to model the effect the carbonation system has on the existing power plant in regards to operating efficiency, to analyse and compare the Simulink models.

2   Power Plant Emissions and Mineral Carbonation

The emissions scenarios of the Intergovernmental Panel on Climate Change (IPCC) always referred to climate change to estimate the impacts of climate change, and analysis of greenhouse gas (GHG) emission reduction policies [6]. The greenhouse effect is being enhanced by the increasing greenhouse gas emissions from human activities [7, 8]. In particular, the burning of fossil fuels is significantly adding to the CO_2 levels in the atmosphere. Scientific models predict that the Earth's average temperature could rise between 1.5^oC to 5^oC by 2100 [7]. Therefore, it is necessary to investigate a possible technology to reduce carbon dioxide emissions. The burning of fossil fuel plays a major role in adding to the greenhouse effect. However, fossil fuels are also critical in satisfying increasing global energy demands. The conversion of fossil fuels accounts for 80% of the primary energy consumption and that large energy consumption per capita is the defining characteristic of modern society [9].

In regards to Australia's economy, on the surface, it would be in our best interests to continue the utilisation of coal. The Industry Commission [8] states that 'coal in Australia is abundant, conveniently located near major population centres and of relatively high quality'. They have also indicated that nearly all of Australia's electricity is produced by fossil fuel-fired power stations [8]. Current clean coal technologies (CCTs) are mainly concerned with the reduction of harmful emissions including, sulphur oxides (SO_X), nitrogen oxides (NO_X) and other particulates. While these technologies are 'proven and effective and are contributing substantially to the reduction of pollutants from existing fossil fuel units', limited developments have occurred in regards to reducing CO_2 emissions [10].

Coal power plants represent one of the largest sources of CO_2 emissions worldwide. A possible approach is to retrofit the power station fleet by adding a separation process to the flue gas known as post-combustion capture. Amine-based absorption, post-combustion capture is most excellent to be adapted immediately for power station flue gas with minimal technical risk. The Australian Government has authorised the Kyoto Protocol in 2008 and has committed funding for the R&D of GHG reducing systems with very strong partnerships with coal industries [11]. In Australia, development of CO_2 technologies directly related for post-combustion capture are mostly managed by the Cooperative Research Centre for Greenhouse Gas Technologies (CO_2CRC), a collaboration of government, industry, and academic institutions. Viebahn et al. [12] described that the life cycle assessment of carbon capture and storage

technology showed substantially lower reductions of green house gas emissions in total. It was reported that cleanest power plant without carbon capture and storage (natural gas combined cycle) caused only 45% more emissions (400 g CO_2 equ./kWh) than the worst power plant with CCS (pulverized hard coal with 274 g CO_2 equ./kWh) [12]. Balat et al. [13] commented that a significant reduction in global CO_2 emissions can be achieved only through the broad and deep application of a portfolio of measures that includes major technological breakthroughs, increasing the share of non-fossil forms of energy production, and carbon capture and storage technology.

Direct mineral carbonation has been investigated as a process to convert gaseous CO_2 into a geologically stable, solid final form. The mineral dissolution rate is primarily surface controlled, while the carbonate precipitation rate is primarily dependent on the bicarbonate concentration. Lackner, et al. [14, 15] discussed CO_2 storage as mineral carbonates. The direct mineral carbonation tests have focused thus far on ultra mafic minerals as the primary reactants. Geologic studies by Goff et al. [16, 17] indicate that reserves of these ultramafic minerals are sufficient to provide raw materials for the mineral carbonation of all annual CO2 emissions for many years. Recent research has been directed towards investigating the viability of using dry or aqueous carbonation methods to reduce CO_2 emissions from power plant flue gases. Particular focus has been on the chemistry underlying the carbonation process. The aqueous method of carbonation may become a more feasible option than that of the dry carbonation method due to its more desirable fast reaction rates [18].

Significant amounts of the technology required for the aqueous method are also already in use throughout many industries today. The extraction methods to separate pure Mg- or Ca- hydroxide from that of naturally occurring Mg- and Ca- bearing minerals is typically used in magnesium manufacturing plants. It is from these existing technologies that a carbonation system could be based. The carbonation process essentially consists of CO_2 binding with Ca- and/or Mg-based minerals to form stable carbonates. There are currently limited technologies that have been successfully developed for the carbonation of CO_2 emissions.

This study aims to investigate the feasibility of implementing a carbonation process into an existing power plant's emissions exhaust system. With the successful utilisation of by-products of the carbonation process it is hoped that such a system would become a part of CO_2 emission reduction schemes.

3 Methodology

In this study, Simulink modelling was performed for the mass and energy balances of the fixation of CO_2 from the reference power plant.

3.1 Description of the reference plant

For the modelling purposes, general operating characteristics were sourced from the reference power station. They are indicated table 1 along with the calculated operating capacity and capacity factor. The overall efficiency of the plant was assumed to be 45%. This is a typical operating efficiency for generators of a supercritical plant [10].

Table 1: Operating Characteristics Stanwell Power Station [19]

Characteristic	Value
Total Capacity (MW)[a]	1,400
Greenhouse Intensity (t.CO$_2$/MWh)[a]	0.900
CO$_2$ Emissions (t.CO$_2$/yr)[a]	10,000,000
Operating Capacity (MW)[b]	1268.39
Capacity Factor[b]	0.906
Efficiency (%)[c]	45

[a] Values sourced from Stanwell Power Station 2009
[b] Calculated from sourced values
[c] Assumed value for supercritical plant[5]

The total CO_2 emissions from the reference power station of 10 million tonnes per year was taken as a worst case scenario, as they indicated that less than this amount is actually emitted each year.

3.2 Characteristics of the flue gas

The flue gas characteristics are essential for the carbonation modelling, as the flue gas enters the carbonation system to react with the fixation agent (Ca- or Mg- bearing mineral). As flue gas characteristics for the reference power plant were obtained from a similar coal-fired power station [20]. To simplify the modelling equations it is assumed that the flue gas only contained CO_2 and N_2 components. Therefore the volume percentages used are shown in table 3. With the above data, solutions to the mass balance equations for each of the carbonation models were found. Once the mass balances were solved, solutions to the energy balance equations could be calculated.

Table 2: Flue Gas Characteristics [20]

Component	% Volume
CO$_2$	12.0
N$_2$	73.7
H$_2$O	8.3
O$_2$	5.5
SO$_2$	0.5

Table 3: Simplified Flue Gas Characteristics

| Component	% Volume
CO$_2$	14.0
N$_2$	86.0

3.3 Simulink modelling

Simulink is chosen to model the mass and energy balances of the carbonation system as it is ideal for graphical presentation of the models. Also the ability of Simulink to model over a time range is modified to allow simulation over a desired maximum carbonation temperature range. This is made possible by using the time input as a temperature input. A lookup table is able to convert the time scale into a temperature scale. By modelling the carbonation systems over a temperature range, analysis and comparison between models is made much easier with the creation of graphs. Following completion of the models, it is aimed to analyse and compare the simulations, with the main focus on the energy requirements for CO_2 fixation of each material used. Also, the effect of the carbonation systems on the existing power plant is analysed in regards to maximum carbonation temperature.

The materials, CaO (Calcium Oxide), MgO (Magnesium Oxide), Ca(OH)$_2$ (Calcium Hydroxide), Mg(OH)$_2$ (Magnesium Hydroxide), CaSiO$_3$ (Calcium Silicate, Wollastonite), MgSiO$_3$ (Magnesium Silicate, Clinoenstatite or Pyroxene) were used throughout the carbonation models. Pure CaO and MgO are modelled as they present the 'ideal' minerals with which to perform carbonation reactions. In practice it would be unlikely that pure compounds such as CaO and MgO can be used, therefore Ca- and Mg- hydroxides and silicates are also modelled. The use of raw materials such as Wollastonite and Pyroxene would most likely produce slower than needed reaction rates and as a result broken down compounds such as the pure oxides and hydroxides are desirable [18]. It is for this reason that the aqueous method of breaking down the raw material prior to carbonation may present a more feasible option. The higher maximum allowable carbonation temperatures of the oxides and hydroxides, along with their molecular structures also aid in the kinetics of the reaction process [18].

The mass models are completed first, as these are needed for the completion of the energy balance models. The mass models are found the masses of materials needed to balance each carbonation chemical reaction. The fundamental law, 'mass of reactants = mass of products' is followed for the mass balance calculations. Following the completion of the mass balance models, the energy balance models are created. They are found

the energy input required to heat the reactants to the desired maximum carbonation temperature. As the energy of reactants equals the energy of products, the energy input is assumed to equal the total amount of energy recoverable from the products. The models are created to allow desirable energy recovery (% of energy input) from the carbonation system. It is to be noted that 'free bond energies' of the components contributed to the overall energy balance of the reactions. In the case of the carbonation reactions, the reactants have less free bond energies than their respective reactants, the reactions are exothermic (i.e. they produce heat energy). The exothermic nature of the carbonation reactions increases the feasibility of introducing such a system into existing power plants.

Fig. 1 displays the method used to calculate the energy required to heat the flue gas from ambient temperature (25°C or 298.15K) to the desired maximum temperature of the carbonation reaction. The initial heat capacity and temperature of the flue gas are displayed in the orange and blue blocks respectively. The clock is connected to the lookup table (temperature range) so that a temperature range of 350K to 1161K (for CaO model) is fed through the model. This enables analysis of the carbonation system operating over the desired temperature range. A polynomial block is used to calculate the specific heat capacity of the flue gas at the operating carbonation temperature. An average specific heat capacity value is then found between the specific heat capacity of the flue gas at ambient and the operating carbonation system temperature. A similar model is used to calculate the heat energy required for heating of the carbonation mineral.
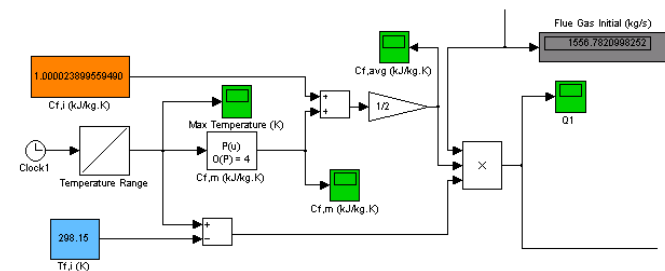

**Fig. 1:** Energy balance model - heat energy required to heat flue gas

4   Results

It is found that the carbonation of dry CaO and MgO has produced energy self-sufficient systems at or below carbonation temperatures of 843.18K (570.03°C) and 676K (402.85°C) respectively (Fig. 2 and Fig. 3). At their maximum allowed carbonation temperatures, CaO and MgO required input energy recoveries of 39.43% and 1.10% respectively. This difference is seen due to

CaO's maximum allowable carbonation temperature of 1161K (887.85°C), compared to MgO's maximum allowable carbonation temperature of 680K (406.85°C). Therefore, it can be proved that CaO is a feasible option in regards to mineral carbonation. If suitable energy recovery systems are put in place, it is possible to theoretically raise the operating efficiency of the reference power plant from the assumed value of 45% up to approximately 90% and 75% for CaO and MgO carbonation respectively. Please note that these are purely hypothetical efficiencies, assuming 100% recovery of heat input (Practically impossible). However, even with limited heat recovery systems in place, it is still possible for a carbonation system to improve the existing plant's overall performance due to the favourable thermodynamical reactions.
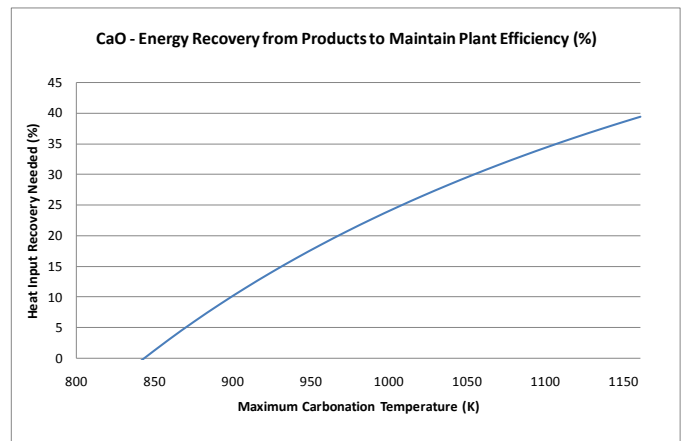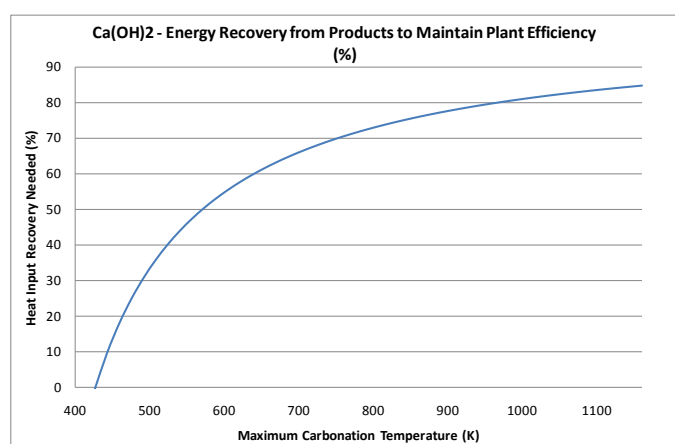

Fig. 2: Energy recovery needed from products to maintain plant efficiency CaO
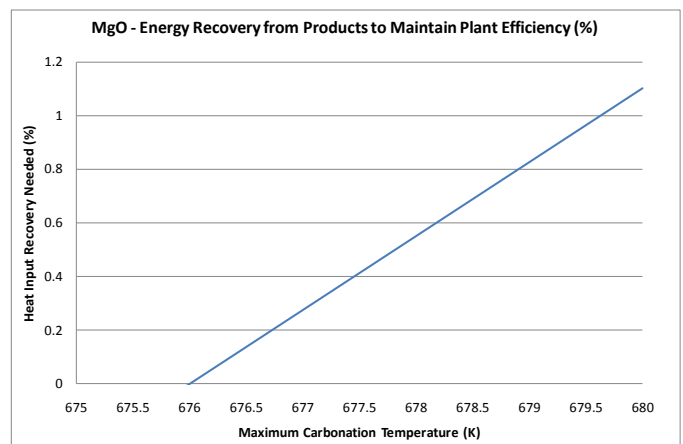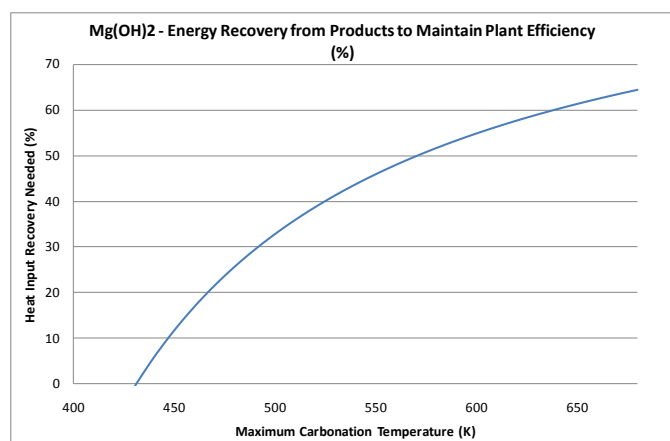

Fig. 3: Energy recovery needed from products to maintain plant efficiency – MgO

In regards to the Ca- and Mg- hydroxides, the carbonation systems become dependent on energy recovery to remain energy self-sufficient at 427.59K (154.44°C) and 430.99K (157.84°C) respectively (Fig. 4 and Fig. 5). At their maximum allowable carbonation temperatures, energy recoveries of approximately 84.71% and 64.36% of the initial heat input are required.

Therefore, it is evident that the hydroxides present significantly unfavourable reaction thermodynamics when compared to dry CaO and MgO. However, as discussed in the paper, it is the increased reaction rates of dehydrated minerals that may make them feasible options for carbonation methods. The raw materials, $CaSiO_3$ and $MgSiO_3$, were also modelled to provide further comparison particularly of the pure dry oxides. These materials have significantly lower maximum allowable carbonation temperatures of 554K (280.85°C) and 474K (200.85°C) respectively. As a result, the thermodynamics of these particular materials 'appear' to be quite favourable; however suitably fast reaction rates are generally not possible with the use of raw carbonation materials [18].

Fig. 1: Energy Recovery Needed from Products to Maintain Plant Efficiency – $Ca(OH)_2$

Fig. 2: Energy Recovery Needed from Products to Maintain Plant Efficiency – $Mg(OH)_2$

5 Conclusion

The reduction of CO_2 emissions, particularly from coal-fired power plants, is arguably a key issue in today's world. The main impetus for this study was to work towards a solution to this problem. Appropriate simplifications of the Simulink models were necessary due to the limited flue gas and power plant data

obtained. Future thermodynamical analysis would benefit from the reduction of simplifications to more closely resemble the real-world operation of a carbonation system. Following the necessarily simplified models, it was found that carbonation of the dry oxide's have particularly good thermodynamics compared to that of the hydroxides and raw silicates. However, the results has indicated that dehydrated Ca- and Mg-bearing minerals have higher chemical reactivity (due to metastable non-crystalline amorphous materials left behind), future comparative work would be required between the feasibility of using dry carbonation (better thermodynamics) or aqueous carbonation (better reaction rates).

It is found that the broken down Ca- and Mg- bearing minerals (i.e. CaO, MgO, $Ca(OH)_2$ and $Mg(OH)_2$) have higher allowable carbonation temperatures than that of the more compound raw materials. The dry oxides have been found to produce quite favourable thermodynamics, with the possibility of improving the performance (operating efficiency) of the associated power plant. While the thermodynamics of the hydroxide carbonation systems are not as favourable, their increased reaction rates improve their feasibility. Therefore, an aqueous acid method of breaking down the initial raw material may prove vital in the overall feasibility of the carbonation methods to be employed.

Future work could be directed towards analysing and developing suitable extraction methods for implementation prior to a carbonation system. Also, conceptual design work could follow on from the thermodynamic results presented in this paper. The conceptual designs would cover the following components such as carbonation combustion chamber (Continuous fluidised bed), feed system into carbonation combustion chamber, separation device for products from the carbonation combustion, water recycling device, fitting of gas flue line to carbonation chamber, requirements for acid extraction process.

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