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Project Title: ZERO EMMISSION COAL GASIFICATION PROCESS FOR ILLINOIS COAL – MINI-BENCH SCALE TEST

ICCI Project Number:	02-1/2.3A-2
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ABSTRACT

The objective of this project is to determine the gas cleaning requirements of the raw gas produced via the hydrogasification of an Illinois coal, within the context of the Zero Emission Coal (ZEC) process. GTI has demonstrated the feasibility of the ZEC concept for an Illinois coal in last year's project (ICCI Project No. 01-1/2.3C-2). In the current project, we conducted a combination of theoretical and experimental studies for high sulfur Illinois coal on the desulfurization and carbonation steps of the ZEC process.

Thermodynamic simulation predicts that the H_2S content of the syngas is about 0.4% after the hydrogasification. If calcium oxide is used as a desulfurization sorbent, the H_2S level can be reduced to about 20 ppm at 1500°F (816°C) and 60 bar. This very low level of H_2S enters the downstream reformer/carbonator and potentially competes with CO_2 for the carbonation sorbent, which is also a calcium-based sorbent. The main focus of this project is to assess the effect of H_2S on CO_2 capture in the carbonation bed.

The experimental work was conducted in a High Pressure Thermogravimetric Analyzer (HPTGA) unit. Single component H_2S or CO_2 (in helium) was first measured on a calcined dolomite and a calcined limestone at various pressures and temperatures, up to 62 bar (900 psig) and 1800°F (982°C). Both sorption capacity and rate for sulfidation increased with increasing partial pressure of H_2S and no anomalies were observed at elevated pressures. Addition of steam was found to have no significant effect on the sulfidation reaction. The carbonation reaction rate appeared to be independent of the partial pressure of $CO_{2.}$

When both H_2S and CO_2 were reacted with the sorbent simultaneously at 1500°F and 60 bar, H_2S was preferentially reacted with the sorbent over CO_2. Chemical analysis of the reacted sorbents also showed no reaction of CO_2. This would imply that traces of H_2S could impede the carbonation reaction. The desulfurization unit needs to remove the sulfur down to its equilibrium level for the CaO sorbent to be carbonated with CO_2.

Future work is recommended for developing remedial solutions to resolve the issue of sulfur contamination and the decay of the CaO sorbent under carbonation-calcination cycle conditions in the carbonator of the ZEC process.

EXECUTIVE SUMMARY

The overall objective of the project is to determine the gas cleaning requirements of the raw gas produced via the hydrogasification of an Illinois coal, within the context of the Zero Emission Coal (ZEC) process. In 2002, GTI demonstrated the feasibility of using the Illinois #6 coal for the ZEC process (ICCI Project No. 01-1/2.3C-2). The coal reactivity data were obtained under hydrogasification conditions. In this project, we turned our attention to the gas clean-up section of the ZEC process. This effort included a combination of theoretical and experimental studies on the desulfurization and carbonation steps of the ZEC process for high sulfur Illinois coal.

Because the ZEC process operates at high temperature and high pressure conditions, 1500 to 1800^{o}F (816 to 982^{o}C) and 60 bar, one viable sorbent for sulfur removal at these high temperatures is a calcium-based sorbent. However, calcium-based sorbents are also used in the reformer/carbonator section of the ZEC process to remove CO_2 generated from the reforming reaction. Furthermore, both CO_2 (about 10%) and H_2S (about 0.4%) are produced from the hydrogasifier. Potentially, sulfidation with H_2S and carbonation with CO_2 will compete using the CaO sorbent in both the downstream desulfurizer and reformer/carbonator of the ZEC process. Evaluation of the mutual interference effect of sulfidation and carbonation reactions is the main focus of this project.

The effort was conducted in a series of steps to determine the relationship between sulfur and carbon capture mechanisms within the process:

- Perform thermodynamic analysis for the cleanup section of the ZEC process.
- Measure the sorption parameters for capture of hydrogen sulfide and carbon dioxide independently.
- Measure the competing reaction rates for simultaneous sulfidation and carbonation reactions as they would occur in the process.

Thermodynamic analysis was performed for the gas clean-up section of the ZEC process to provide an initial estimate for the range of the compositions expected in the process. The compositions of H_2S range from 0.4% in the gasifier to 0.02% (200 ppm) in the desulfurization unit, whereas those of CO_2 vary from 2.2% in the gasifier to 0.6% in the reformer/carbonator unit. These are the theoretical limits for the gas compositions. If kinetics information is taken into consideration, final concentrations of both H_2S and CO_2 can be expected to be much higher.

Kinetics information or reactivity data were obtained in a High Pressure Thermogravimetric Analyzer (HPTGA) unit, where the sample weight gain from the reaction was recorded as a function of time. Two calcium-based sorbents were selected for this study. One is a dolomite and the other is a limestone. Single component's H_2S or CO_2 (in helium) was first measured on the calcined dolomite and the calcined limestone for various compositions, at pressures and temperatures up to 60 bar and 1800^{o}F. Both sorption capacity and rate for sulfidation increased with increasing partial pressure of H_2S and no anomalies were observed at elevated pressures. The reactivity of the calcined dolomite increased with increasing temperature, as expected. The reaction rate was reasonably fast, reaching 80% conversion in about 10 minutes for 0.2% H_2S at 1500^oF and 60 bar, a typical condition in the desulfurizer of the ZEC process. The effect of steam on the sulfidation reaction was also studied and was found to have no significant effect. Dolomite showed slightly higher reactivity for sulfidation than limestone.

The carbonation reaction rate generally increased with increasing temperature, up to the equilibrium temperature, above which no carbonation reaction could be observed. However, the carbonation reaction rate appeared to be independent of the partial pressure of CO_2 provided that the CO_2 partial pressure was above its equilibrium pressure. The overall conversion rates for these two sorbents tested were generally comparable. The limestone showed a slightly higher initial rate, whereas the diffusion rate for the dolomite was faster at the later stage of the reaction.

When both H_2S and CO_2 were reacted with the sorbent simultaneously at 1500^oF and 60 bar, H_2S was preferentially reacted with the sorbent over CO_2. Chemical analysis of the reacted sorbents also confirmed no reaction of CO_2 with the sorbent. The carbonation reaction could not proceed even at a H_2S level as low as 0.02% at 60 bar and 1500^oF. This would imply that traces of H_2S could impede the carbonation reaction. The calcium-based sorbent has very low tolerance of sulfur level for the carbonation reaction. This finding is very important for the desulfurization and reforming/carbonation sections of the ZEC process. In order for the ZEC process to work properly, the desulfurization unit needs to remove the sulfur content down to a level that the CaO sorbent can be carbonated with CO_2. Theoretically, this level is the equilibrium H_2S concentration at the given operation condition.

Fundamentally, the same reaction mechanism has been postulated for both sulfidation and carbonation, i.e. an initial chemical reaction control regime followed by a product layer diffusion control regime. The experimental uptake curves obtained in this work all clearly showed two distinct slopes, confirming the classical shrinking core model for this type of gas-solid reaction system. The preferential reaction of CaO with H_2S can also be explained based on the above picture of two rate-controlling steps. Formation of a CaS product layer blocks the entry of CO_2 to the interior of the sorbent particle while the $CaCO_3$ product layer can still be converted to CaS by reaction with H_2S.

Further work employing a fixed bed reactor is recommended for determining the realistic H_2S level exiting the desulfurization step, as well as the maximum H_2S level that the sorbent can tolerate for the carbonation reaction. Solutions need to be developed for the desulfurization unit to ensure removal of sulfur down to its equilibrium level for the CaO sorbent to be carbonated with CO_2. Sufficient amounts of sorbent may have to be used in the desulfurization unit to ensure that the concentration of H_2S reaches its equilibrium. Lowering the desulfurization temperature and/or using other sorbents such as ZnO or CuO can achieve a lower H_2S concentration according to the thermodynamics of the sulfidation reaction. The drawback is additional cooling and heating steps required in the ZEC process. For the carbonator, the decay of the CaO-based sorbent under carbonation-calcination cycle conditions also needs to be addressed in the future.

OBJECTIVES

The overall objective of the project is to determine the gas cleaning requirements of the raw gas produced via the hydrogasification of an Illinois coal, within the context of the Zero Emission Coal (ZEC) process. The main goal of the project is to conduct a combination of theoretical and experimental studies into the desulfurization, carbonation, and calcination characteristics of potential candidate sorbent materials under the preferred hydrogasification conditions. The competitive effect of sulfidation and carbonation on calcium-based sorbents is the particular focus of this project.

INTRODUCTION AND BACKGROUND

ZEC process is currently being developed by ZECA (Zero Emission Coal Alliance)[1], which consists of eighteen member companies representing the energy industry and government. The process uses hydrogen to gasify coal to produce a methane rich gas. The methane is subsequently reformed using steam and a CaO-based sorbent. The sorbent can remove the CO_2 generated from the reforming reaction by producing $CaCO_3$ and simultaneously supplying the energy needed for the reforming reaction. The resulting hydrogen, with approximately half of it recycled to the gasifier, is used to generate electricity in a Solid Oxide Fuel Cell (SOFC). The $CaCO_3$ product from the reforming stage is calcined using the waste heat from SOFC to generate a pure stream of CO_2, which can be readily sequestered. Overall the process is effectively a closed loop with zero gaseous emissions to the atmosphere. A simplified diagram for the ZEC process is shown in Figure 1.

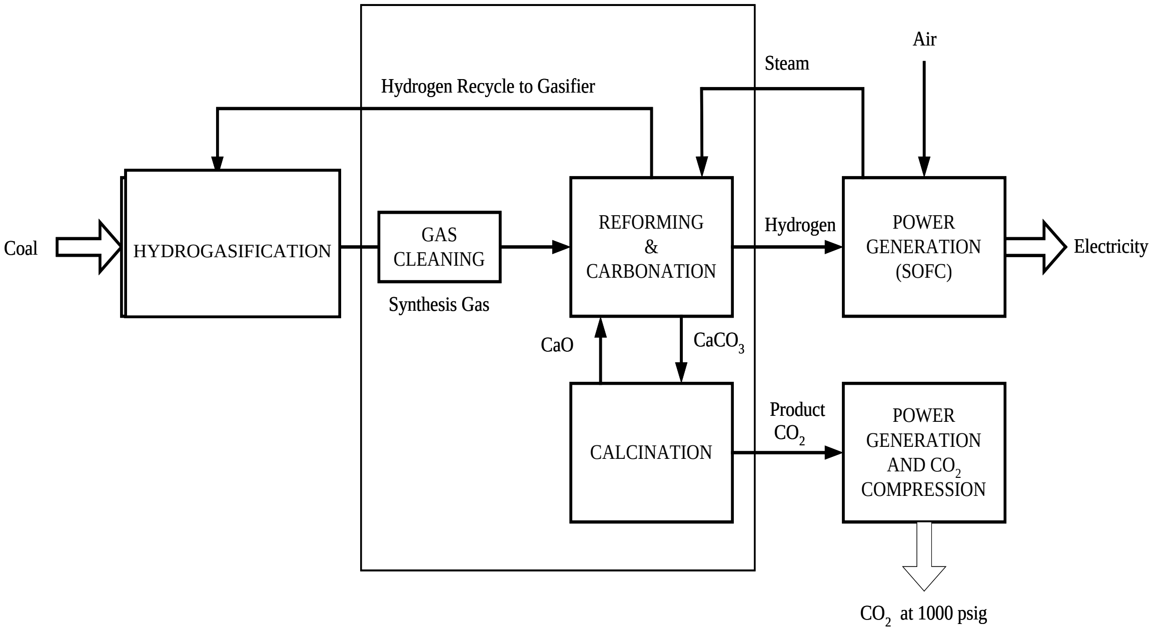

Figure 1. A simplified diagram for the ZEC process.

GTI's HYGAS system was chosen as the gasification unit in the ZEC process because it yields high concentrations of methane directly from the gasification reactor. HYGAS was originally developed for Synthetic Natural Gas (SNG) production. It is a good fit to the overall ZEC process scheme because methane is expected to be produced from the gasification section of the ZEC process. With its long history of coal gasification technology development, GTI is in a good position to contribute to the overall ZEC process development.

In last year's project funded by ICCI (project No. 01-1/2.3C-2), data for hydrogasification of Illinois No. 6 coal was encouraging, and suggested that further work was warranted.[2] The tests were done in GTI's high-pressure thermogravimetric analyzer (HPTGA) at temperatures and pressures exceeding 1800^{o}F (982^{o}C) and 60 bar. An important finding from the study was that hydrogasification temperatures in the order of 1800^{o}F are required to achieve 95+% carbon conversion in 20 to 30 minutes for Illinois No. 6 coal.

As shown in Figure 1, following the gasification unit is a gas-cleaning step, which is of paramount importance for any coal, especially for high-sulfur Illinois coal. The raw gasifier gas has to be desulfurized to a very high degree to meet the stringent requirements of the downstream reformer. Furthermore, any sulfur escaping from the reformer/carbonator can contaminate either the hydrogen stream or the CaO sorbent, which may eventually influence regeneration or calcination of the sorbent.

As the gasifier needs to operate at 1800^{o}F for the Illinois coal and the methane reformer typically operates at 1500^{o}F, the desulfurization unit preferably will be operating in this temperature range. At such high temperatures, one of the very few viable sorbents is CaO. Desulfurization using a CaO sorbent can be subjected to the influence of small amounts of CO_2 generated from the hydrogasifier. On the other hand, calcium-based sorbents are also used in the reformer/carbonator for CO_2 removal in the ZEC process. As mentioned earlier, any sulfur not captured in the desulfurization unit can affect the downstream reformer/carbonator. Consequently, it is important to investigate the mutual interference from CO_2 and H_2S on the reactivity of the CaO sorbent. This part of the ZEC process that is relevant to this study is shown in Figure 1 within the enclosed rectangle.

In last year's project, Nexant developed the mass and energy balances for the ZEC process. The reduced sulfur compounds (i.e. H_2S) were predicted to be completely removed by reaction with CaO in the desulfurization unit. This may have been oversimplified, warranting further investigation. Based on the calculation of the thermodynamic equilibrium, the minimum contents of H_2S in the gas coming out of the desulfurization unit can range from 20 to 200 ppm depending on the temperature and the water contents in the syngas. Furthermore, there has not been any data reported for the CaO sulfidation reactions for pressures higher than 20 bar. The effectiveness of using CaO to remove sulfur under ZEC process conditions needed careful research and examination for further design work to proceed.

The reformer/carbonator in the ZEC process contains reforming catalysts, typically nickel, and lime. Depending on the effectiveness of the desulfurization unit, the catalyst can be poisoned by sulfur compounds. If H_2S content from the desulfurization unit is above its equilibrium, reaction of H_2S with CaO will continue into the reformer/carbonator.

If CaO is preferentially reacted with CO_2 in carbonation over sulfidation, H_2S may stay in the syngas or hydrogen stream. On the other hand, if sulfidation is dominant, CaS will be formed and mixed with $CaCO_3$ entering into the calcination unit. In an extreme case, where carbonation is completely suppressed by sulfidation, only CaS and no $CaCO_3$ will be formed. Regeneration of CaS requires the use of oxygen to form the stable sulfate. Once sulfate is formed, it cannot be regenerated into CaO for reuse. Heat alone will not regenerate CaS as in the case of $CaCO_3$, which is calcined during regeneration to CaO. The presence of CaS in the solid stream is equivalent to poisoning the CaO sorbent for the ZEC process. The fate of the sulfur needs to be addressed.

Uses of calcium-based sorbents as sulfur-capturing agents in an in-situ coal gasification/desulfurization process have been extensively studied under a variety of condtions[3]. Yrjas et. al. investigated the H_2S uptake by a set of physically and chemically different limestones and dolomites under typical pressurized gasification conditions (20 bar, 950C)[4]. In the second part of their paper[5], a generalized model was developed to describe the reaction and diffusion mechanism for sulfidation of calcium oxide. It is generally believed that the initial rate of sulfidation reaction is determined by the gas-solid reaction at the surface. At later stages of the reaction, diffusion through the product layer becomes the rate-limiting step. However, it is still controversial and not clear whether the CaS product layer is porous or not[6,7].

Lin et. al.[8] studied sulfidation of limestone and calcined limestone and found that the former had a much lower initial reaction rate and final conversion. They attributed this to the poor porosity of the product layer produced by the uncalcined limestone. The effects of CO_2 partial pressure, steam and H_2 on sulfidation reaction were also reported. However, their data for the calcined limestone were obtained under CO_2 partial pressures below the equilibrium, therefore, no conclusion can be drawn regarding the competitive reaction between sulfidation and carbonation.

Carbonation of carbon dioxide with calcium oxide is also a very important reaction-based separation process in the area of CO_2-capture for both fuel gas from gasification and flue gas from combustion. The reaction mechanism is very similar to sulfidation, proceeding through two rate-controlling regimes. The first is rapid heterogeneous chemical reaction. This is followed by a second regime, where CO_2 diffuses through a product layer formed by $CaCO_3$.[9] Regeneration of the sorbent by calcination of $CaCO_3$ produces a CO_2-rich stream ready for sequestration. One of the critical issues for this process is the decay of CO_2 capacity when cycling between carbonation and calcinations. This has received much attention recently.[10,11] What has not been studied in the literature is the effect of contaminants, especially sulfur compounds, on carbonation reaction.

The current project was undertaken with the main objective to elucidate the competitive effect of sulfidation and carbonation on calcium-based sorbents and its implication on the design of gas clean-up section of the ZEC process.

EXPERIMENTAL PROCEDURES

Task 1. Background Studies and Exploration of Specific Needs

Before the experimental program began, thermodynamic analysis for sulfurization and carbonation reactions of CaO were conducted to determine the theoretical limits for the gas stream compositions under equilibrium conditions. This was done using HSC Chemistry 5 program from Qutokumpu Research, Finland. Literature review on the state-of-the-art using CaO sorbent for sulfidation and carbonation reactions was also performed, mainly to understand the basic reaction mechanisms. GTI has conducted extensive studies into the sulfurization characteristics of calcium oxide under low to medium gasifier pressure conditions (0-25 bar). This experience in running the experimental tests and selection of sorbents was also utilized in this project. Some of the previous data were also used for comparison with the current measurements in the low pressure range.

Task 2. Material Procurement, Preparation, and Characterization

Two sorbents were selected for this study. One is a dolomite, designated as D-245 and the other is a limestone, designated as L-246. These two sorbents were acquired by IGT in a previous project.[12] The sorbents were ground and screened to a size between 180 and 300 microns or –60 to +80 mesh. Their chemical compositions, surface area and porosity are shown in Table 1.

Table 1 Chemical analysis, surface area and porosity of sorbents.

Analysis, wt %	Dolomite 245	Limestone 246
Calcium	22.1	40.6
Magnesium	13.5	0.58
Potassium	0.7	0.032
Iron	0.13	0.054
Aluminum	0.12	0.051
Silicon	0.36	0.22
Sulfur	0.01	0.01
Strontium	0.006	0.016
Carbon dioxide	46.5	43.5
Oxygen (by diff.)	17.204	14.937
BET/ CO_2 adsorption, m^2/g	0.6	0.65
Porosity, ml/g	0.014	.023

Prior to each test, the samples were baked out or calcined at 1500°F under helium flow for at least 2 hours until there was no weight change. Chemical analysis on two representative samples after calcination showed virtually no CO_2 contents in the samples, thus confirming the completeness of sorbent calcination.

Task 3. HPTGA Validation and Parametric Testing

Experimental Unit

All the tests in this project were conducted in GTI's HPTGA unit. A schematic diagram of the high-pressure/high-temperature HPTGA unit used in this project is presented in Figure 2. Reaction chamber details are shown in Figure 3. This state-of-the-art HPTGA unit is capable of operation at 1850°F at 70 bar. All the hot wetted parts of the unit are made of quartz to eliminate reaction with corrosive and reactive gases, which would result in the loss of the reactant species in the gas phase.

The HPTGA unit is capable of continuously weighing a sample that is undergoing reaction in a gaseous environment of desired composition at constant pressure. The temperature can be kept constant or varied at a desired rate. The gas flow rates used with this system are sufficiently large, relative to the reaction rate such that the gas composition is essentially constant.

In a typical HPTGA test, about 20 mg of sorbent is placed inside a wire mesh basket, which is then lowered to the heated zone of the reactor tube. The desired temperature and pressure conditions are then established in the lower, heated section of the reactor in the presence of flowing inert gas. The reactant gas mixtures with the desired composition are also prepared and initially bypassed to the reactor. When the reactor temperature and pressure have reached the desired values, the test is initiated by switching from the inert gas to the reactant gas mixture. The sample weight is continually monitored and recorded as the solid sample reacts with the gas. The test is terminated when the sample weight reaches a constant value (no weight loss or gain).

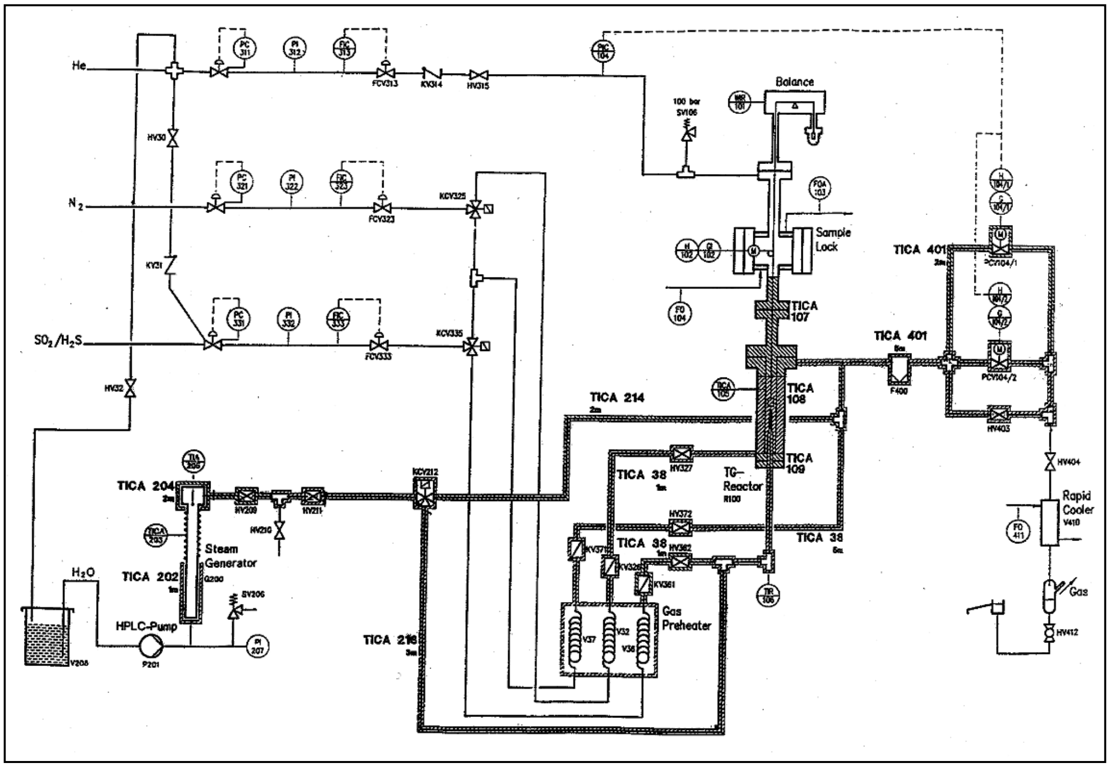

Figure 2. Schematic Diagram of GTI's High Pressure Thermogravimetric Analyzer (HPTGA)

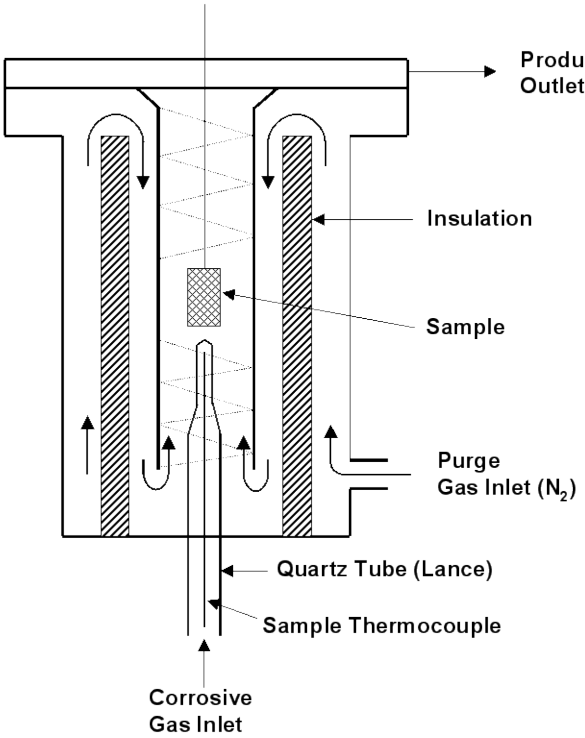

Figure 3. HPTGA Reaction Chamber Details

The gas mixture is prepared by measuring and controlling the flow rates of each gas in several streams using mass flow controllers. A backpressure control valve maintains the pressure. The temperature in the vicinity of the basket is measured by a thermocouple. The experimental data including sample weight, pressure, temperature, and flow rates in different streams are collected by a computerized data acquisition system and stored on diskettes for further analysis.

Conversion Calculations

Magnesium oxide in the dolomite is believed to be unreactive to H_2S. Therefore the sulfidation of calcined dolomite can be expressed by the following reaction for CaO:

$$CaO + H_2S = CaS + H_2O \qquad (1)$$

As the atomic weight of sulfur is 32 while that of oxygen is 16, for each mole of CaO reacted there are 16 grams of weight gain. The CaO conversion to CaS can be calculated by

$$\text{CaO conversion} = \frac{w/16}{w_{Ca}/40} \qquad (2)$$

w : weight gain from reaction
w_{Ca} : calcium weight in sample

For completely calcined dolomite 245, the calcium fraction in the sample is 22.1/(100-46.5) = 0.413 according to Table 1. The CaO conversion to CaS can then be related to the weight gain by

$$\text{CaO conversion} = 6.05\frac{w}{w_o} \qquad (3)$$

w_o : original sample weight

Although magnesium oxide in the dolomite can react with CO_2 at low temperatures, around 500^{o}F, MgO is not expected to react with CO_2 in the temperature range of the ZEC process, 1500-1800^{o}F. The carbonation reaction for CaO can be expressed as

$$CaO + CO_2 = CaCO_3 \qquad (4)$$

The conversion of dolomite for the carbonation can be related to the weight gain by

$$\text{Carbonation conversion} = \frac{(w/44)}{(w_{Ca}/40)} \qquad (5)$$

The final expression for the carbonation conversion for D245 is

$$\text{Carbonation conversion} = 2.2\frac{w}{w_o} \tag{6}$$

Similar relationships can be derived for the calcined limestone 246. They are

$$\text{sulfidation conversion} = 3.5\frac{w}{w_o} \tag{7}$$

$$\text{carbonation conversion} = 1.24\frac{w}{w_o} \tag{8}$$

Validation and Parametric Testing

The validation tests were conducted at ambient pressure for the sulfidation reaction with an aim to ensure the accuracy of the experimental unit and the procedures used in this work. The parametric testing was carried out to study the effect of temperature, pressure, and concentration on both the sulfidation and carbonation reactions. The pressure ranged from 1 to 60 bar and the temperature from 1500 to 1800^oF. Finally, tests with simultaneous sulfidation and carbonation were performed to determine if there was any interaction for these two competing reactions.

Previous GTI tests indicated that the reaction of CaO with H_2S did not depend on the gas composition provided that H_2S concentration remained constant.[3] Therefore, it was not necessary to use a syngas mixture for the sulfidation study. For the carbonation reaction, because CO_2 may be generated from the water gas shift reaction in the syngas mixture, the measurement for the CO_2 carbonation reaction in HPTGA would not have been reliable with syngas mixture. The gas mixture used throughout this project is H_2/He mixture with appropriate amounts of H_2S or/and CO_2. The presence of hydrogen in the mixture also ensured there was no decomposition of H_2S during the sulfidation tests.

For the sulfidation tests, gas cylinders with 7.74% of H_2S in H_2 were used. This gas mixture was mixed and diluted with He to obtain the desired H_2S concentrations. For carbonation tests, pure CO_2 was mixed with He to reach the required compositions. Another gas mixtures with 6.14% CO_2 in H_2 was also used during the tests of simultaneous sulfidation and carbonation reactions. All gas cylinders were supplied by Matheson.

Selected reacted samples were analyzed by GTI's Chemical Analysis Group for their chemical compositions.

RESULTS AND DISCUSSION

Task 1. Background Studies and Exploration of Specific Needs

Equilibrium Pressures for Sulfidation and Carbonation

The equilibrium pressures of H_2S for the sulfidation reaction, Reaction (1), at different temperatures are plotted in Figure 4 under three different steam partial pressures. Assuming the gas product from the gasification contains about 20% steam, the equilibrium pressure of H_2S will be about 0.012 bar, or approximately 0.02% if the total pressure is 60 bar and the temperature is 1500^{o}F. Equilibrium H_2S concentration increases with increasing temperature.

The equilibrium pressures of CO_2 for the carbonation reaction (Reaction (4)) at different temperatures are shown in Figure 5. For temperatures in the range of 1300 - 1800^{o}F, the CO_2 equilibrium pressure can vary by more than two orders of magnitude. Carbonation can only occur if the partial pressure of CO_2 is greater than its equilibrium pressure. If about 10% of CO_2 is generated from the gasifier at 60 bar and 1800^{o}F, the carbonation reaction in the desulfurization unit is expected to take place based on the thermodynamic reasoning, especially if the temperature is decreased to 1500^{o}F. However, whether the carbonation reaction will take place in the desulfurization unit will depend on the reaction kinetics, which is determined by the HPTGA tests experimentally.

Thermodynamic Analysis for the Gas Clean up of ZEC Process

The mass balance for the ZEC process was performed for the gas clean up section of the ZEC process based on the thermodynamic calculation. Figure 6 shows the mass flows for the major process streams in the ZEC process for the Illinois #6 coal. Gas compositions from the hydrogasifier were calculated based on the gasifier conditions at 1800^{o}F, 62 bar and a 50/50 molar mixture of hydrogen/steam.[2] The concentrations of CO_2 and H_2S are estimated to be 2.2% and 0.4% respectively. Both CO_2 and H_2S concentrations are reduced after the desulfurization unit because both carbonation and sulfidation are assumed to take place. There is no sulfidation reaction in the reformer/carbonator because the H_2S concentration is already at equilibrium. Although CO_2 is formed in the reformer/carbonator, it is immediately carbonated by CaO to form $CaCO_3$. Therefore the final CO_2 concentration at the outlet of the reformer/carbonator is the same as the inlet due to the equilibrium condition. One of the objectives of this study is to verify the validity of these thermodynamic assumptions. As will be shown later, some of the assumptions proved to be incorrect and the importance of the reaction kinetics needs to be taken into consideration for the clean up section of the ZEC process. The thermodynamic analysis only provides an initial estimate for the range of compositions expected in the process.

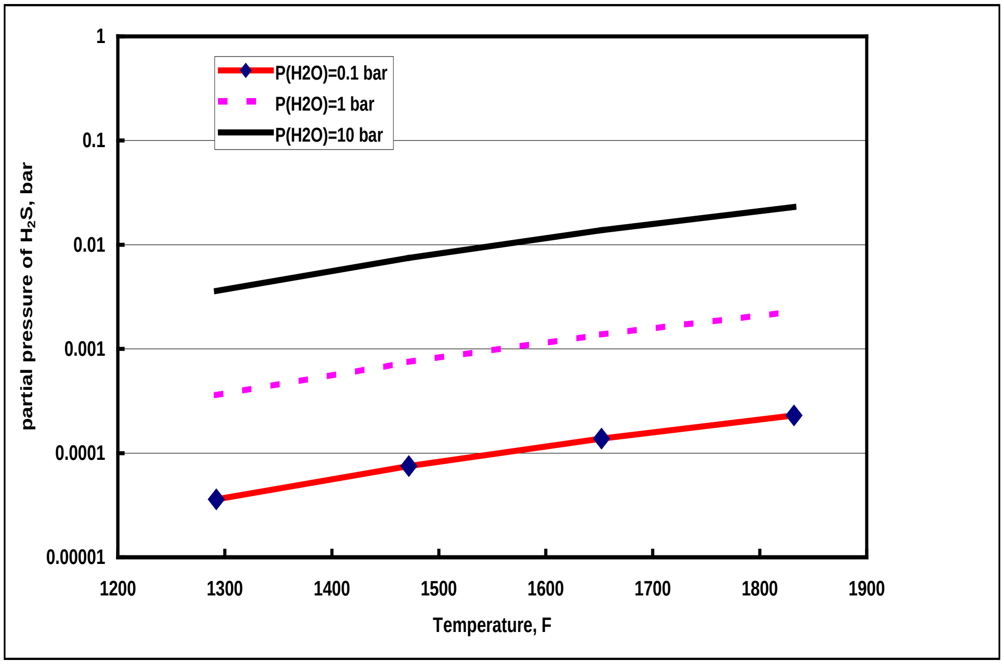

Figure 4. Equilibrium partial pressure of H_2S for sulfidation reaction with CaO.

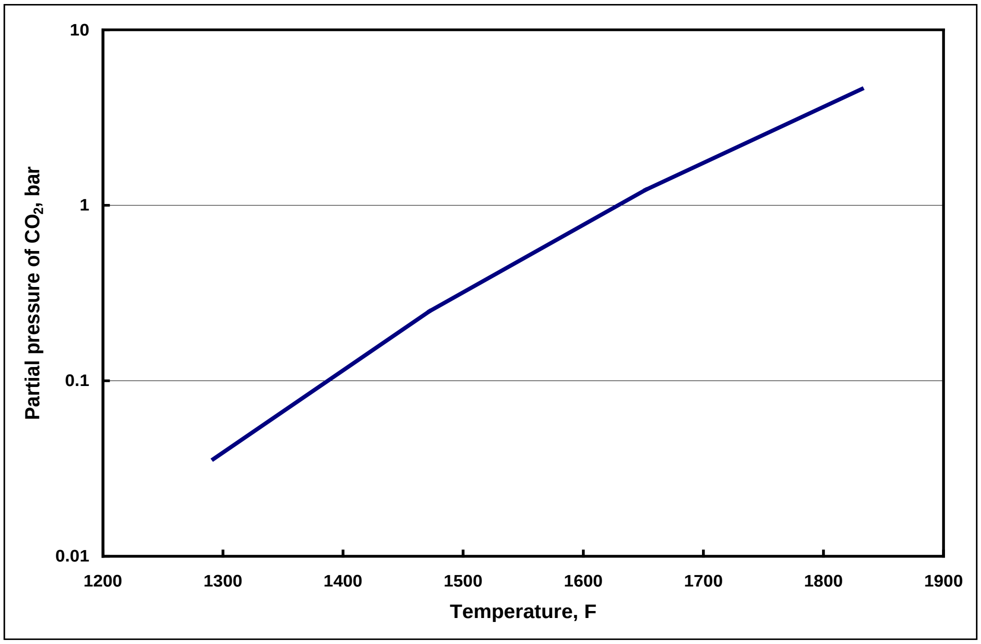

Figure 5. Equilibrium partial pressure of CO_2 for carbonation reaction with CaO.

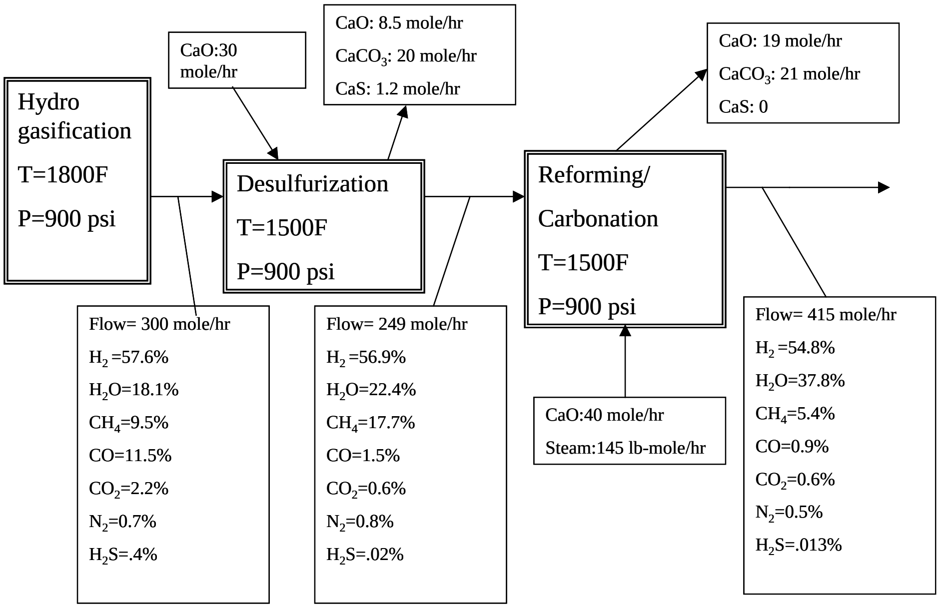

Figure 6. Mass balance for the clean-up section of the ZEC process based on thermodynamic equilibrium calculations

Task 2. Material Procurement, Preparation, and Characterization

The chemical analysis results for dolomite 245 and limestone 246 are shown in Table 1, in the Experimental Procedures section.

Task 3. HPTGA Validation and Parametric Testing

Validation Test

To verify the accuracy of our experimental equipments and procedures, sulfidation results for dolomite 245 obtained at ambient pressure and 1800°F were compared with previous data reported by IGT.[12] Figure 7 shows this comparison for CaO conversions at different H_2S concentrations. As expected, the dolomite reactivity increases with increasing H_2S concentration. Although the current data were not obtained at the identical conditions as previous data, they show the right trend and appear to be reasonable in terms of absolute values. The accuracy of HPTGA test data is also supported by the chemical analysis results on other tested samples, as will be shown later.

Sulfidation Testing

Sulfidation tests were conducted on the calcined dolomite at different temperatures, pressures, and steam compositions. Limited numbers of tests were also conducted on the calcined limestone.

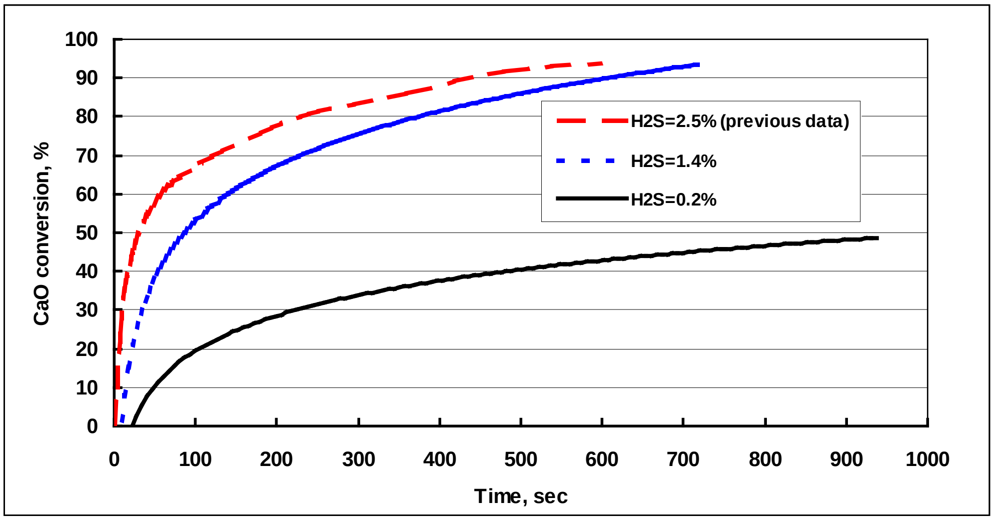

Figure 7. Dolomite reactivity increases with increasing H_2S concentration, T=1800°F, P=1 bar

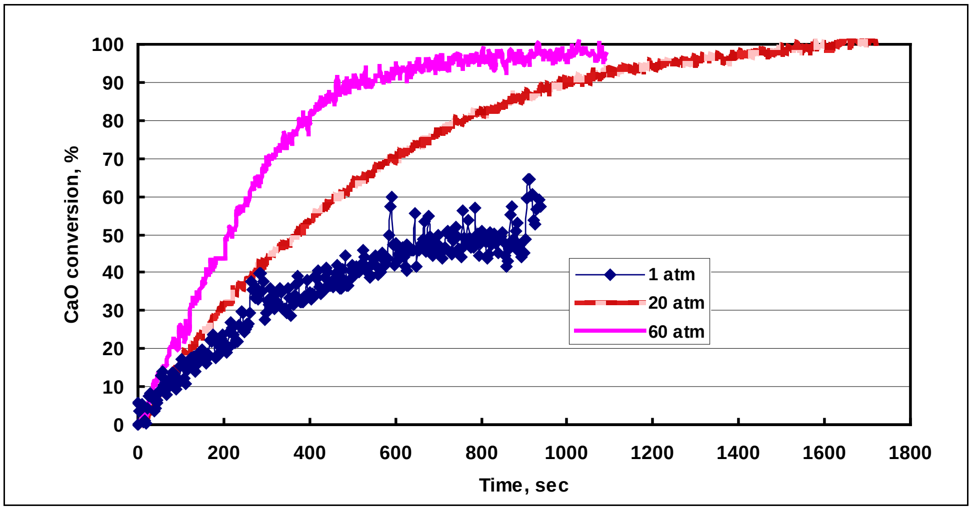

Figure 8. Dolomite reactivity increases with pressure, H_2S =0.2%, 1800°F

Effect of Pressure on Sulfidation

The effect of total pressure on the reactivity of dolomite at 1800°F and 0.2% H_2S concentration is shown in Figure 8. As the total pressure increases, the partial pressure of H_2S also increases, which then increases the dolomite reactivity similar to the effect of H_2S concentration above. An experiment was also conducted at 40 bar and the obtained conversion data generally were between those of 20 and 60 bar, but due to significant noise of the data, they are not shown here.

As mentioned earlier, the sulfidation reaction is controlled by the kinetics of the gas-solid reaction at the initial stage and by the diffusion of the reactants through the product layer at the later stage. To illustrate the sulfidation reaction mechanism, the classical shrinking core model for spherical particles of unchanging size[13] can be applied to the data in Figure 8. For the reaction-controlled regime, the reaction rate is expressed by

$$1-(1-x)^{1/3}=\frac{t}{\tau} \tag{9}$$

where x is the sulfidation extent of CaO and τ is the time required for complete conversion, which is inversely proportional to the kinetic rate constant and H_2S concentration.

For the diffusion-controlled regime, the reaction rate is expressed by

$$1-3(1-x)^{2/3}+2(1-x)=\frac{t}{\tau} \tag{10}$$

where τ is inversely proportional to the diffusivity of the reactants. Data correlated with Eq. (9) and (10) are shown in Figure 9 for the pressure of 60 bar. The obtained values for τ are 952 and 2390 sec for kinetics-controlled and diffusion-controlled regimes respectively. This example demonstrates that the sulfidation reaction follows the 2-stage reaction mechanism, as described by the shrinking core model.

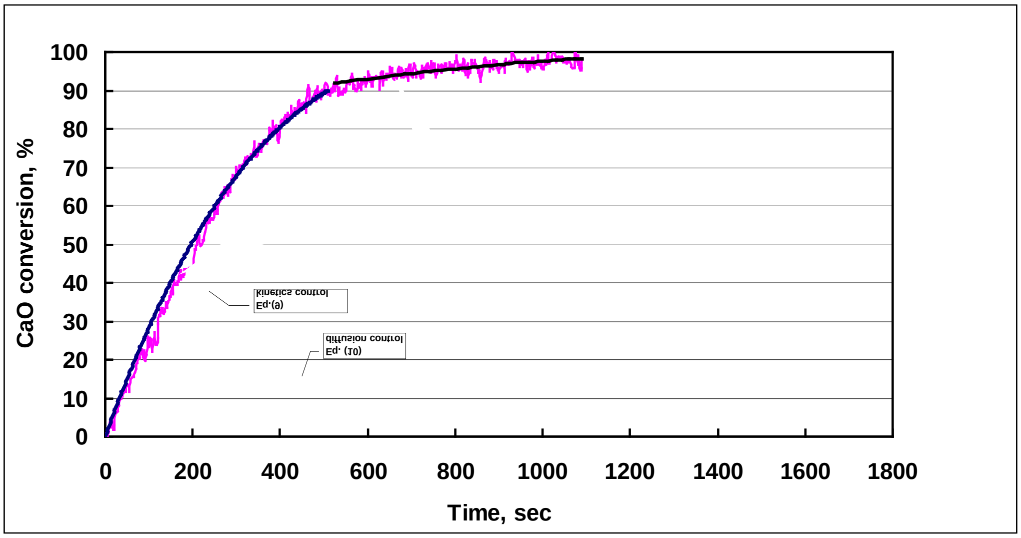

Figure 9. Shrinking core model for sulfidation reaction of dolomite, H_2S =0.2%, 1800°F, 60 bar

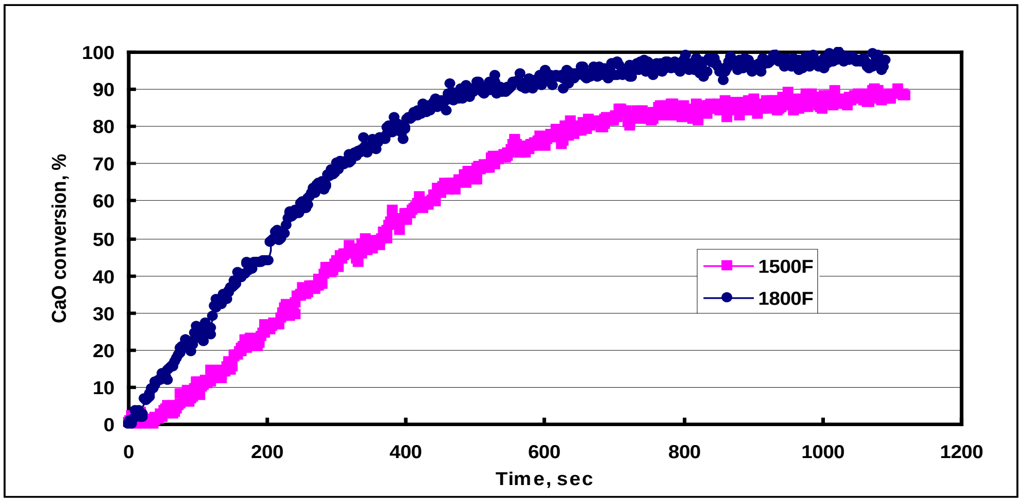

Figure 10. Effect of temperature on sulfidation reaction for dolomite, H_2S =0.2%, 60 bar

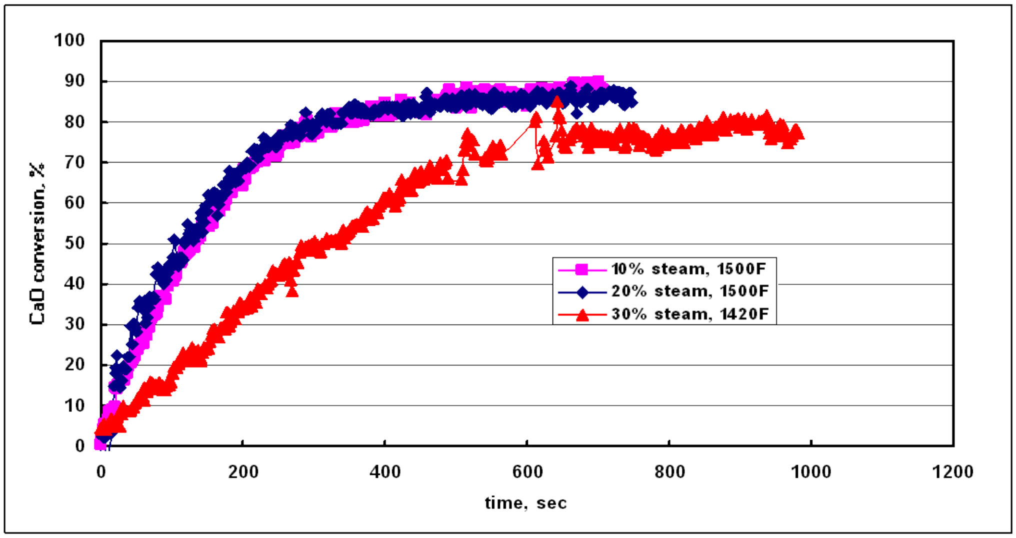

Figure 11. Effect of steam on sulfidation reaction for dolomite, H_2S =0.4%, 1500°F, 40 bar

Effect of Temperature on Sulfidation

Effect of temperature on sulfidation is shown in Figure 10 for 0.2% H_2S at 60 bar. The reactivity increases with increasing temperature. Because of the strong temperature dependence of the reaction kinetics, this difference is mainly at the initial stage of the reaction curve, where the reaction kinetics dominates. The reaction rate is still reasonably fast for 1500°F, reaching 80% conversion in about 10 minutes.

Effect of Steam on Sulfidation

Because water is one of the reaction products for the sulfidation reaction of CaO, it is important to examine the effect of steam on sulfidation. Figure 11 shows this effect for 10, 20 and 30% steam at 1500°F, 40 bar and 0.4% H_2S. No difference in the reaction rate and final conversion was observed between 10 and 20% steam. This is reasonable because the sulfidation reaction rate depends on the concentrations of the reactants, i.e. H_2S and unreacted CaO, but not the gaseous product H_2O. The much slower conversion-time curve for the case of 30% steam is attributed to the temperature drop in the HPTGA unit by the presence of large amount of steam. The recorded temperature for the 30% steam run was only about 1420°F.

Sulfidation for Limestone

The sulfidation reaction for limestone 246 is shown in Figure 12 for different H_2S concentrations at 1500°F and 60 bar. Similar to dolomite, the reactivity increases with increasing H_2S concentration. Chemical analysis of the reacted sample for the case of 0.4% H_2S showed 89% conversion, confirming the accuracy of the HPTGA test data. The reaction rate became very slow at 0.02% H_2S concentration, which is the equilibrium H_2S concentration at the outlet of the desulfurization unit calculated from thermodynamic analysis in Figure 4.

Comparison of limestone and dolomite for the sulfidation reaction under the same conditions, 0.4% H_2S, 20% steam, 1500°F and 60 bar is shown in Figure 13. Dolomite shows higher reactivity than limestone, as was concluded in a previous study.[3] This may be attributed to the presence of MgO in the dolomite. Because MgO does not react with H_2S, it helps the material maintain its porous structure instead of forming a completely impervious product layer.

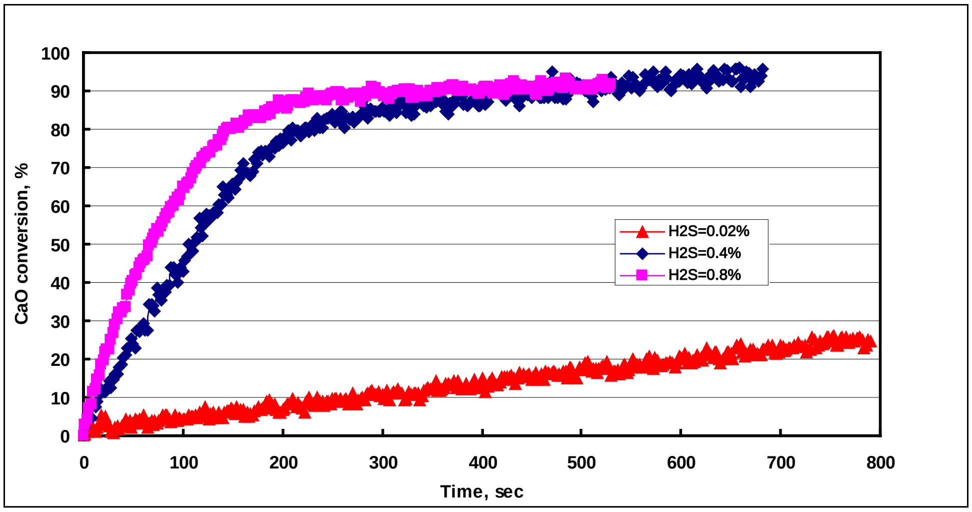

Figure 12. Sulfidation reaction on limestone steam=20%, 1500°F, 60 bar

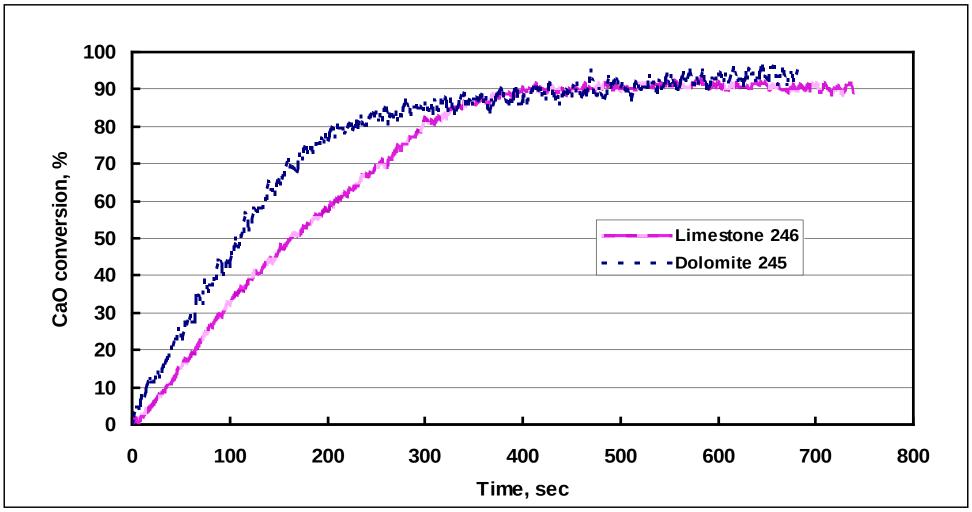

Figure 13. Comparison of dolomite and limestone for sulfidation H_2S =0.4%, steam=20%, 1500°F, 60 bar

Carbonation Test

Effect of Temperature

The effect of temperature on the carbonation reaction for the dolomite is shown in Figure 14 for a CO_2 partial pressure of 1 bar or 5% of CO_2 in He at 20 bar. The carbonation reaction rate generally increases with increasing temperature, up to the equilibrium temperature, above which no carbonation reaction is observed. The equilibrium temperature for CO_2 at a partial pressure of 1 bar is 1620°F according to the thermodynamic calculation from Figure 5. In contrast to Figure 8 and 10 for the sulfidation reaction, the initial rate is quite independent of the temperature, indicating that the carbonation reaction may be dominated by diffusion. Furthermore, the reaction rate at the later stage of carbonation is faster at 1500°F than at 1300°F. This conclusion is also in line with the literature data.[10]

Effect of CO_2 Partial Pressure

At 1500°F, the equilibrium partial pressure of CO_2 is approximately 0.5 bar as calculated in Figure 5. There is very little carbonation reaction when CO_2 partial pressure is 0.1 bar, as shown in Figure 15. Above the equilibrium pressure, the conversion of CaO to carbonate generally is independent of the CO_2 pressure. The conversion-time curve clearly shows that the carbonation proceeds through two rate-controlling regimes. The first is rapid heterogeneous chemical reaction. This is followed by a second regime, where CO_2 diffuses through a product layer formed by $CaCO_3$. The rate of the second regime appears to be independent of CO_2 pressure, as the slopes for the later parts of the curves are almost the same.

For CO_2 partial pressure at 1 bar (5% CO_2 at 20 bar), the carbonated sample after the HPTGA test was submitted for chemical analysis and showed about 82.4% carbonation conversion, which is close to the final conversion number shown in Figure 15.

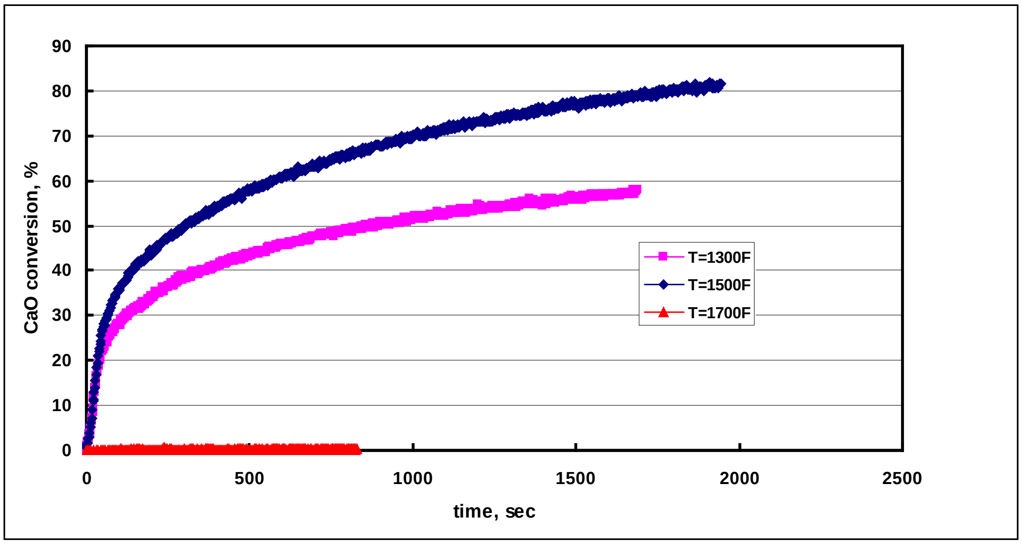

Figure 14. Temperature dependence of carbonation reaction for dolomite at 1 bar of CO_2 pressure

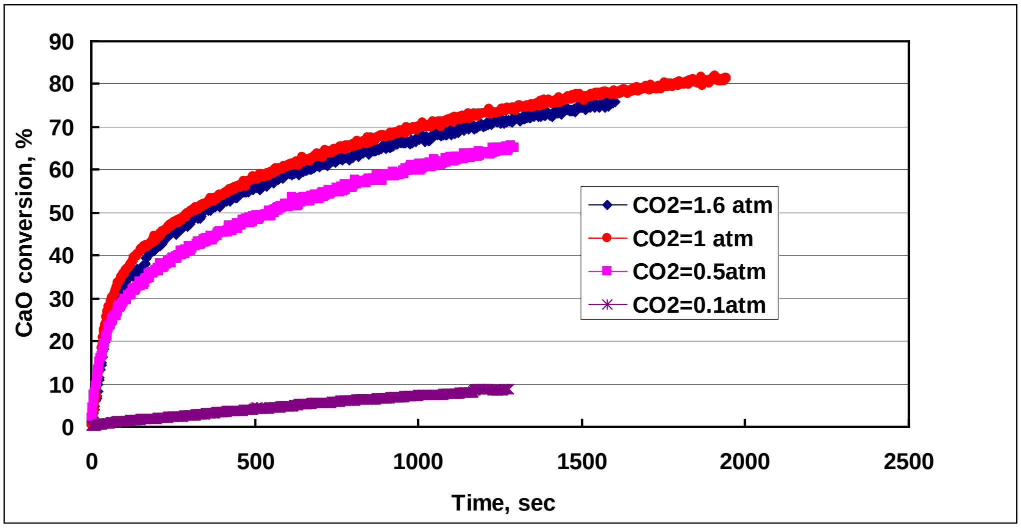

Figure 15. Carbonation reaction for dolomite at 1500°F

To further confirm the pressure independence of CO_2 carbonation, additional tests were conducted at 1650°F for CO_2 partial pressure at 1.1 bar and 1.6 bar, as shown in Figure 16. No significant difference can be seen in the reaction curves for these two pressures.

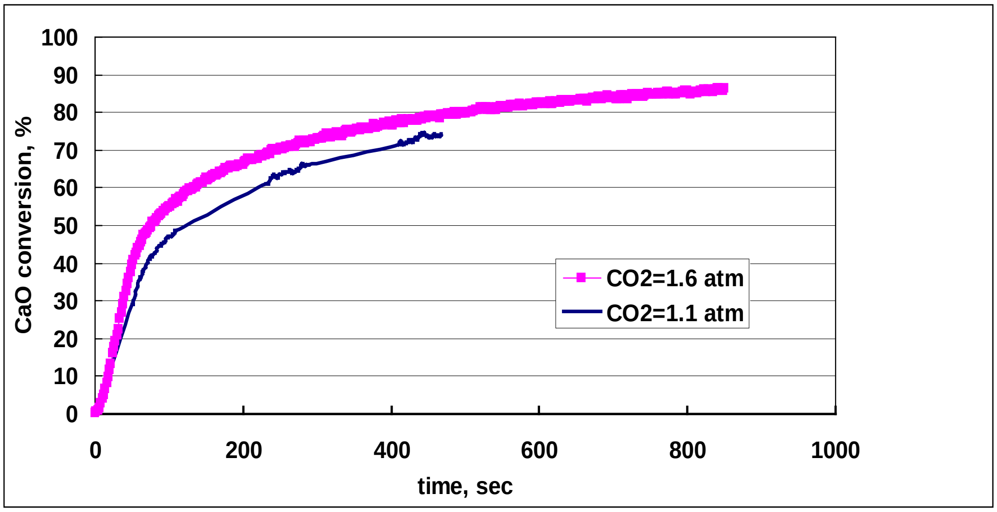

Figure 16. Effect of CO_2 partial pressure on carbonation of dolomite at 1650°F

Comparison of Dolomite and Limestone for Carbonation

The comparison of dolomite and limestone for the carbonation reaction is shown in Figure 17 at two temperatures. The CO_2 partial pressure is kept constant at 1 bar, (5% CO_2 at 20 bar). The overall conversion rates for these two sorbents are generally comparable. The limestone seems to have slightly higher initial rate, whereas the diffusions rate at the later stage of the reaction appears to be faster for the dolomite. Again, the presence of MgO may have opened up the pore structure of the dolomite and helped the diffusion process of the reactants.

Simultaneous Sulfidation and Carbonation Reactions

Dolomite

Simultaneous sulfidation and carbonation reactions were tested on dolomite 245 at 1500°F, 60 bar, 0.4% H_2S concentration and different CO_2 concentrations. This simulates H_2S and CO_2 compositions from the gasifier outlet. Steam with 20% concentration was also added, although it was not expected to have any significant effect on reactions. The results are shown in Figure 18 in terms of weight gain for CO_2 compositions at 0, 1 and 2.2%. The presence of carbon dioxide does not seem to affect the curves of weight gain vs. time. The corresponding CaO conversions from the sulfidation reaction are also shown on the axis of the right hand side. It may be inferred that the weight gain is almost entirely due to the sulfidation reaction, but not the carbonation reaction. This conclusion is confirmed by the chemical analysis of the reacted samples after the HPTGA tests. The chemical analysis for the above three samples show 83.3, 79.5, and 85.6% sulfur conversion respectively. No carbon dioxide was detected for any of the reacted samples.

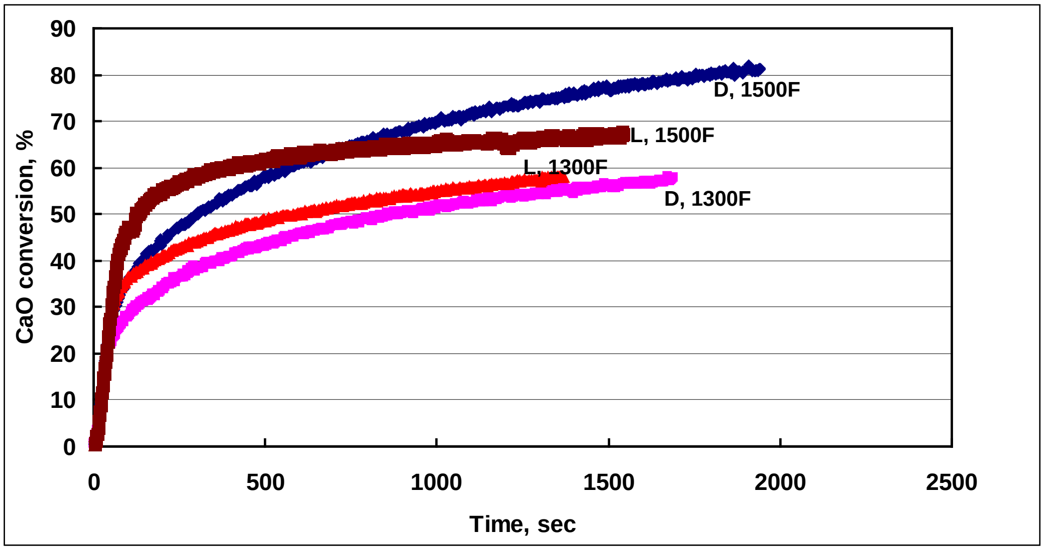

Figure 17. Carbonation reaction for dolomite 245 and limestone 246 at CO_2 partial pressure of 1 bar

Fundamentally, the preferential reaction of sulfidation over calcination can be explained from the postulated reaction mechanism, where both reactions proceed first with solid-gas reaction and then diffusion in the product layer. At the initial stage of the reaction, both sulfidation and carbonation probably take place at the surface of the sorbent particle. However, the formed CaS layer may prevent carbonation reaction by blocking carbon dioxide reactants from entering the interior of the particle. If the CaS product layer is non-porous, solid-state diffusion would be the major mechanism for the diffusion process, i.e. migration of S^{2-} ions and counter-migration of O^{2-} ions.[6] Consequently, CO_2 can not diffuse through the CaS layer. On the other hand, the formed $CaCO_3$ product layer can still react with H_2S, albeit with much slower rate,[8] according to the following reaction:

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O \qquad (11)$$

Once the particle surface is covered entirely by CaS, the carbonation reaction of CO_2 with CaO will be completely stopped. Obviously, the above picture to explain the competitive reaction mechanism for sulfidation and carbonation needs further verification.

The results from Figure 18 have very significant implication for the clean up section of the ZEC process. In the presence of H_2S, the carbonation is completely suppressed for the calcium-based sorbent. For the reformer/carbonator in the ZEC process, in addition to the potential poisoning of reforming catalysts by sulfur, the CaO sorbent has low sulfur tolerance in terms of the carbonation reaction.

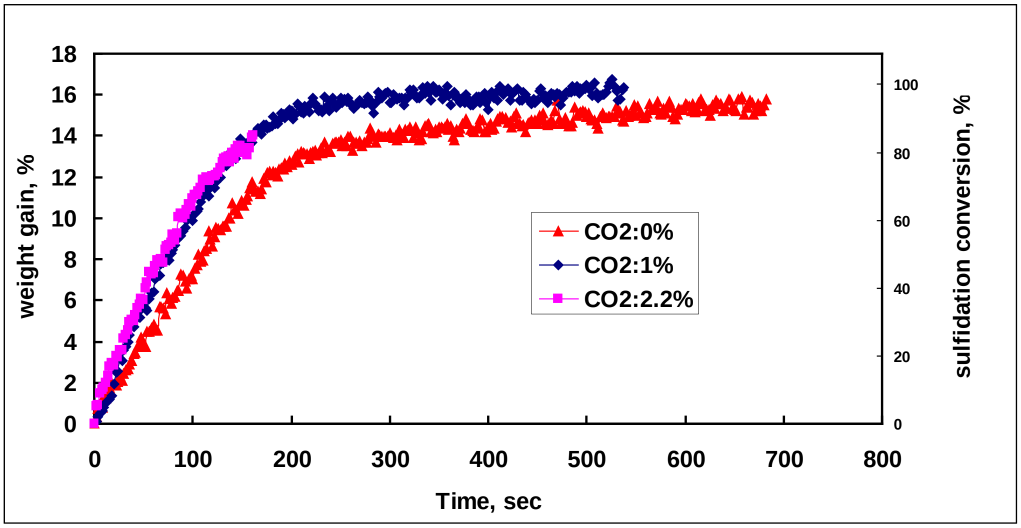

Figure 18. Sulfidation Dominates Over Carbonation Reaction for Dolomite, 1500°F, 60bar, H_2S: 0.4%, steam: 20%

Limestone

Similar tests were also conducted for the limestone at 1500°F, 60 bar, 20% steam, 0.02% H_2S and various CO_2 concentrations. The concentration of H_2S entering the reformer/carbonator after the desulfurization unit can be as low as 0.02% according to the equilibrium calculation in Figure 4. Very low H_2S concentration at 0.02% was also chosen to test if the carbonation reaction could occur at such a low level of H_2S. Figure 19 shows the curves of weight gain for limestone 246 in the presence of both CO_2 and H_2S. Again, similar to the results for the dolomite, no carbonation reaction could be observed for CO_2 concentration up to 2%. Actually, no partial carbonation reaction could be observed either, which indicates that simultaneous sulfidation and carbonation reactions can not take place as originally assumed in the thermodynamic analysis. If there were carbonation reaction from CO_2, the expected weight gain would have been much higher as shown by the carbonation curve at CO_2 pressure of 1 bar and without the presence of H_2S. The sulfidation reaction obviously dominates over the carbonation reaction.

If the sulfidation reaction dominates, CO_2 probably will not affect the desulfurization step of the ZEC process and H_2S can be removed down to its equilibrium concentration with very little or no CO_2 being removed. For the carbonation unit, if H_2S is above the equilibrium concentration, the carbonation reaction will not proceed at all, as demonstrated from the experimental results in this project. The gas clean up unit in the ZEC process needs to remove the sulfur down to a level that the CaO sorbent can be carbonated with CO_2. As no carbonation reaction of limestone was observed for 0.02% of

H_2S concentration at 1500°F and 60 bar, the level of H_2S may have to be at or below the equilibrium H_2S concentration.

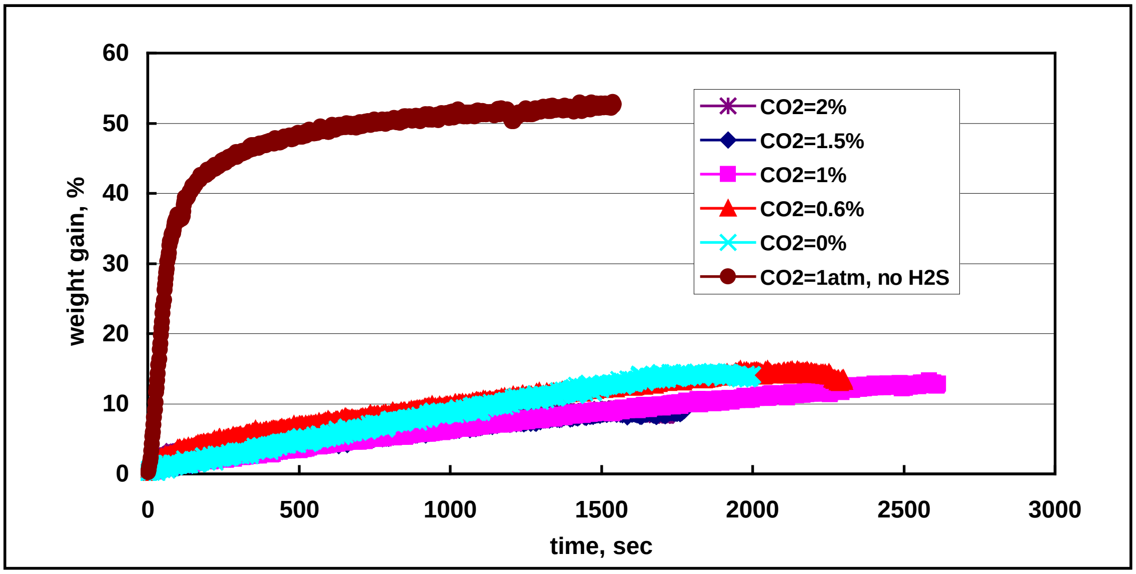

Figure 19. Sulfidation dominates over carbonation reaction for limestone, H_2S =0.02%, steam=20%, 1500°F, 60 bar

The maximum H_2S level that the calcium-based sorbent can tolerate for the carbonation reaction can be assumed to be its equilibrium pressure of H_2S. However, this is also the minimum level of H_2S that can be achieved for the desulfurization bed if the same calcium-based sorbent is used for the carbonator and both units are also operating at the same temperature and pressure. The realistic H_2S level that the sorbent can tolerate for the carbonation reaction may need to be determined experimentally by running the desulfurization reaction and the carbonation reaction in series, not simultaneously. More comprehensive tests will be needed to determine the sulfur tolerance levels for the calcium-based sorbents to be used for the carbonation reaction.

CONCLUSIONS AND RECOMMENDATIONS

In this project, the sulfidation reaction for two calcium-based sorbents, a dolomite and a limestone, was studied using HPTGA under ZEC process conditions, i.e. temperature in the range of 1500-1800°F and pressure to 60 bar. The sorbent reactivity increased with increasing H_2S partial pressure and showed no anomalies at elevated pressures. The effect of steam on the sulfidation reaction was found to be insignificant. The carbonation reaction was also investigated using the same sorbents under different CO_2 partial pressures at temperatures between 1300-1700°F. The carbonation reaction rate was independent of the partial pressure of CO_2.

When both CO_2 and H_2S were in contact with the calcium-based sorbent, only the sulfidation reaction occurred with the carbonation reaction completely suppressed under the conditions of this investigation, i.e. H_2S down to 0.02%, CO_2 up to 2% at 60 bar and 1500°F. The calcium-based sorbent has a very low tolerance of sulfur which interferes with the carbonation reaction. This finding is very important for the desulfurization and reforming/carbonation sections of the ZEC process. In order for the ZEC process to work properly, the desulfurization unit needs to remove the sulfur down to a level that the subsequent carbonation sorbent, CaO, can be carbonated with CO_2. Theoretically, this level is the equilibrium H_2S concentration at the given operation condition.

Further work employing a fixed bed reactor is recommended for determining the realistic H_2S level exiting the desulfurization step as well as the maximum H_2S level that the sorbent can tolerate for the carbonation reaction. A technical solution needs to be developed for the desulfurization unit to remove the sulfur down to its equilibrium level so that the downstream CaO sorbent can be carbonated with CO_2 without experiencing sulfur poisoning. Sufficient amounts of sorbent may have to be used in the desulfurization unit to ensure that the concentration of H_2S reaches its equilibrium. Lowering the desulfurization temperature can achieve lower H_2S concentration according to the thermodynamics of the sulfidation reaction. The drawbacks are a lower reactivity of the sorbent and additional cooling and heating steps in the process. Other metal oxide sorbents such as ZnO, CuO can remove H_2S well below 20 ppm, but require much lower operation temperatures, typically below 900°F (482°C).

For the carbonator, the decay of the CaO-based sorbent under carbonation-calcination cycle conditions also needs to be addressed.

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