Development of Highly Durable and Reactive Regenerable Magnesium-Based Sorbents for CO_2 Separation in Coal Gasification Process

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ABSTRACT

The specific objective of this project was to develop physically durable and chemically regenerable MgO-based sorbents that can remove carbon dioxide from raw coal gas at operating condition prevailing in IGCC processes.

A total of sixty two (62) different sorbents were prepared in this project. The sorbents were prepared either by various sol-gel techniques (22 formulations) or modification of dolomite (40 formulations). The sorbents were prepared in the form of pellets and in granular forms. The sol-gel based sorbents had very high physical strength, relatively high surface area, and very low average pore diameter. The magnesium content of the sorbents was estimated to be 4-6 % w/w. To improve the reactivity of the sorbents toward CO_2, The sorbents were impregnated with potassium salts. The potassium content of the sorbents was about 5%. The dolomite-based sorbents were prepared by calcination of dolomite at various temperature and calcination environment (CO_2 partial pressure and moisture). Potassium carbonate was added to the half-calcined dolomite through wet impregnation method. The estimated potassium content of the impregnated sorbents was in the range of 1-6% w/w. In general, the modified dolomite sorbents have significantly higher magnesium content, larger pore diameter and lower surface area, resulting in significantly higher reactivity compared to the sol-gel sorbents.

The reactivities of a number of sorbents toward CO_2 were determined in a Thermogravimetric Analyzer (TGA) unit. The results indicated that at the low CO_2 partial pressures (i.e., 1 atm), the reactivities of the sorbents toward CO_2 are very low. At elevated pressures (i.e., CO_2 partial pressure of 10 bar) the maximum conversion of MgO obtained with the sol-gel based sorbents was about 5%, which corresponds to a maximum CO_2 absorption capacity of less than 1%. The overall capacity of modified dolomite sorbents were at least one order of magnitude higher than those of the sol-gel based sorbents. The results of the tests conducted with various dolomite-based sorbent indicate that the reactivity of the modified dolomite sorbent increases with increasing potassium concentration, while higher calcination temperature adversely affects the sorbent reactivity. Furthermore, the results indicate that as long as the absorption temperature is well below the equilibrium temperature, the reactivity of the sorbent improves with increasing temperature (350-425°C). As the temperature approaches the equilibrium temperature, because of the significant increase in the rate of reverse (i.e., regeneration) reaction, the rate of CO_2 absorption decreases.

The results of cyclic tests show that the reactivity of the sorbent gradually decreases in the cyclic process. To improve long-term durability (i.e., reactivity and capacity) of the sorbent, the sorbent was periodically re-impregnated with potassium additive and calcined. The results indicate that, in general, re-treatment improves the performance of the sorbent, and that, the extent of improvement gradually decreases in the cyclic process. The presence of steam significantly enhances the sorbent reactivity and significantly decreases the rate of decline in sorbent deactivation in the cyclic process.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

INTRODUCTION

Coal gas cleaning at elevated temperatures and pressures has been recognized as crucial to efficient and economic coal utilization in advanced power processes such as Integrated Gasification-Combined Cycle (IGCC) processes, which are among the leading contenders for coal conversion in the 21st century. Separation of CO_2 from coal derived synthesis gas for capture and sequestration is a key technology in the reduction of greenhouse gas emissions to the environment. Although existing technologies can be applied to capture CO_2, such applications require expensive solvents and operate at low temperatures (i.e., <40°C,) imparting a severe energy penalty on the IGCC process. Therefore, advanced processes that are based on dry regenerable sorbents offer attractive advantages over the existing low temperature processes.

The use of alkali- or alkaline-earth metals for CO_2 capture has been previously reported in literature (1,2). Carbon dioxide can be removed from raw coal gas by magnesium-based sorbents in the temperature range of 350-550°C at 10 to 50 bar pressure. These temperature and pressure ranges closely match those expected in IGCC processes, including high temperature water-gas-shift operation, enhancing hydrogen production in IGCC processes. To improve sorbent reactivity, other chemical reagents such as potassium salts have been added to the sorbent (2).

The cyclic chemical reactions for CO_2 removal involving magnesium oxide are:

$MgO + CO_2 \rightarrow MgCO_3$ (CO_2 Absorption Reaction) (1)

$MgCO_3 \rightarrow MgO + CO_2$ (Sorbent Regeneration Reaction) (2)

While the CO_2 absorption reaction is accomplished at IGCC process condition, the regeneration reaction is carried out either by decreasing the pressure or increasing the temperature to produce concentrated stream of CO_2, to be utilized in another industrial application or is sequestered. However, to make such regenerative processes economically viable, highly durable, reactive, and attrition resistant sorbents are required to minimize attrition losses and the sorbent make-up rate. Reducing the concentration of CO_2 in IGCC process increases hydrogen production through the water-gas-shift (WGS) reaction:

$CO + H_2O \rightarrow CO_2 + H_2$ (3)

As the reaction is pushed toward the right, resulting in a significant decrease in carbon monoxide (CO) concentration and generates additional hydrogen in the process.

The equilibrium CO_2 partial pressure for Reactions (1) and (2) are presented in Figure 1. The results indicate that MgO-based cyclic process can easily be carried out within the ranges of the IGCC operating variables. Although other alkali- or alkaline-earth metals can also be used in a similar manner, the operating equilibrium temperatures are either too low resulting in a sever energy penalty, or too high resulting in sorbent agglomeration leading to sorbent deactivation.

To achieve high reactivity, the alkali- or alkaline-earth metals are either deposited on a high surface area substrate, which limits the sorbent capacity, or are mixed with a pore structure control agents which leads to high surface area with limited mechanical strength. Conventional sorbent preparation techniques require very high thermal treatment temperatures to impart physical strength, and as a result, they often produce sorbents with low reactivity. The desirable sorbent characteristics, such as surface area and porosity were found to diminish with increasing temperature, adversely affecting the reactivity of the sorbent.

The principal investigator of this project has developed a number of regenerable metal oxide-based sorbents which possess the challenging combination of high reactivity (desirable pore size distribution and high surface area) and high attrition resistance, (3) for removal of various pollutants from gas streams. A comparison of the attrition resistance and effective capacity of copper-based sorbents prepared by the PI, as well as those of a commercially produced sorbent and a FCC catalyst (for SO_2 removal from flue gases) is shown in Figure 2, indicating that the leading sol-gel based sorbents prepared by the PI's research team has about over four (4) times higher effective sulfur capacity and less than 1/4 attrition index, compared to the commercially available sorbent. One of the initial goals of this study was to use similar preparation technique to produce highly durable, reactive, and attrition resistant MgO-based sorbents for removal of CO_2 in IGCC process.

This work performed in this project was geared toward demonstration of the viability of a regenerative process for removal of CO_2 in IGCC process using MgO-based sorbents.

EXECUTIVE SUMMARY

The overall objective of this program is to develop a regenerative process for removal of CO_2 in Integrated Gasification Combined Cycle (IGCC) processes. The specific objective of this phase-I innovative concept project was to develop MgO-based sorbents than can remove carbon dioxide from raw coal gas at operating condition prevailing in IGCC processes. The sorbents were expected to have chemical and physical characteristics and long term durability that permit cyclic regeneration over many cycles with very low fresh sorbent make-up rate that is compatible with the fluidized bed or moving bed applications.

A total of sixty two (62) different sorbents were prepared in this project. The sorbents were prepared either by various sol-gel techniques (22 formulations) or modification of dolomite (40 formulations). The sorbents produced by sol gel technique included six (6) formulations by wet impregnation of alumina support prepared by sol-gel method, and sixteen (16) formulations in incorporation technique.

The sorbents prepared by wet impregnation technique consisted of four (4) sorbents in the form of pellets and two (2) in granular forms. The alumina support for all these sorbents was prepared from 2 Molar sol and wet impregnation was carried out with a 2 molar magnesium salt solution for 20 hours. These sorbents had very high physical strength, relatively high surface area (160-200 m^2/g), very low average pore diameter (5-8 nm). The magnesium content of the sorbents was estimated to be 4-6 % w/w.

In the sol-gel incorporation method, magnesium was incorporated into sorbent by adding a solution of magnesium salt (such as magnesium nitrate) to the Aluminum sol during gel production process. After drying process, sorbent calcined. The preparation parameters investigated in this method included sol molarity and magnesium oxide concentration. The sorbents prepared in pellet form exhibited very high BET surface area (i.e., 282 m^2/g), low average pore diameter (i.e., 5-8 nm), and low physical strength. On the other hand, granular sorbents showed a very high physical strength, acceptable BET surface area (120-140 m^2/g) and higher average pore diameter (up to 17 nm). To improve the reactivity of the sorbents toward CO_2, The sorbents were impregnated with potassium salts (i.e., potassium carbonate, potassium hydroxide). The potassium content of the sorbents was about 5%.

The parameters studies in preparation of dolomite-based sorbents included calcination temperature, duration of calcination, and calcination environment (CO_2 partial pressure and moisture), which have been reported to affect the characteristic of the products. Furthermore, potassium carbonate was added to the half-calcined dolomite through wet impregnation method. The estimated potassium content of the impregnated sorbents was in the range of 1-6% w/w. The attrition index of the half-calcined dolomite was in range of 1-2.5%.

In general, the modified dolomite sorbents have significantly higher magnesium content, larger pore diameter and lower surface area, resulting in significantly higher reactivity compared to the sol-gel sorbents.

The reactivities of a number of sorbents toward CO_2 at atmospheric and elevated pressures were determined in a Thermogravimetric Analyzer (TGA) unit. All the sorbents tested in TGA were in the form of granules with particle diameters in the range of 180 to 600 μm. These tests were conducted in different temperatures and CO_2 partial pressures.

A total of fifteen (15) ambient pressure runs at different absorption and regeneration temperatures were conducted with sol-gel and modified dolomite sorbents in the temperature range of 300-500°C. The results obtained indicated that without potassium impregnation, neither sol-gel nor calcined dolomite was reactive toward CO_2. Furthermore, highly pure and dispersed MgO (obtained from calcination of magnesium nitrate) also did not exhibit any reactivity toward CO_2. The results indicated that at the low CO_2 partial pressures (i.e., 1 atm), the reactivities of the sorbents toward CO_2 are very low.

To study the reactivities of the sorbents at elevated pressures, a large number of tests (i.e., 80) were conducted in a High Pressure TGA (HPTGA) unit with sol-gel-based and dolomite-based sorbents at 20 bar pressure where a CO_2 partial pressure of 10 bar was maintained in all absorption tests. The maximum conversion of MgO obtained with the sol-gel based sorbents was about 5%, which corresponds to a maximum CO_2 absorption capacity of less than 1%. Therefore, it was concluded than none of the sol-gel sorbents prepared in this project will be suitable for CO_2 removal in IGCC processes.

The results of HPTGA tests with modified dolomite indicated that the reactivity and the overall capacity of modified dolomite sorbents were at least one order of magnitude higher than those of the sol-gel based sorbents. The results of the tests conducted with various dolomite-based sorbent indicate that the reactivity of the modified dolomite sorbent increases with increasing potassium concentration, while higher calcination temperature adversely affects the sorbent reactivity, which should be attributed to higher extent of agglomeration at higher temperatures. Furthermore, the results indicate that as long as the absorption temperature is well below the equilibrium temperature, the reactivity of the sorbent improves with increasing temperature (350-425°C). As the temperature approaches the equilibrium temperature, because of the significant increase in the rate of reverse (i.e., regeneration) reaction, the rate of CO_2 absorption decreases.

The results of cyclic tests show that the reactivity of the sorbent gradually decreases in the cyclic process. To improve long-term durability (i.e., reactivity and capacity) of the sorbent, the sorbent was periodically re-impregnated with potassium additive and calcined. The results indicate that, in general, re-treatment improves the performance of the sorbent, and that, the extent of improvement gradually decreases in the cyclic process. The presence of steam significantly enhances the sorbent reactivity and significantly decreases the rate of decline in sorbent deactivation in the cyclic process.

PROGRAM OBJECTIVE

The overall objective of this program is to develop a regenerative process for removal of CO_2 in Integrated Gasification Combined Cycle (IGCC) processes.

The specific objective of this phase-I innovative concept project was to develop MgO-based sorbents than can remove carbon dioxide from raw coal gas at operating condition prevailing in IGCC processes. The sorbents were expected to have chemical and physical characteristics and long term durability that permit cyclic regeneration over many cycles with very low fresh sorbent make-up rate that is compatible with the fluidized bed or moving bed applications.

WORK PERFORMED

The work performed in this project is summarized below.

This project was divided into the following two tasks:

Task1. Sorbents Preparation and Characterization

Task 2. Sorbents Evaluation

EXPERIMENTAL

Task1. Sorbent Preparation and Characterization

A thorough review of the related literature was conducted early in this program to identify appropriate techniques for preparation of MgO-Based sorbent reported in the literature. Based on this review, and the results obtained in previous research conducted by the PI,(3) many of the conventional sorbent preparation techniques such as impregnation on substrate, co-precipitation, solid state (dry and/or wet) mixing were not included in this project. All the sorbent in this project were prepared either by various sol-gel techniques or modification of dolomite, as described below.

Sol-Gel Technique

Sol-gel processing is defined broadly as the preparation of ceramic materials by preparation of a sol, gelation of the sol, and removal of the solvent. Gels have huge interfacial area, typically 100-1000 m^2/g, and this enormous area serves as a driving force to bring about sintering at exceptionally low temperatures. Therefore, a considerable fraction of the extraordinary properties (high surface areas and small pore sizes) of unfired gels are retained following calcination, offering the possibility of using the gel as a substrate for chemical reactions.(4-10) Therefore, sol-gel technique was the first preparation method used to produce a number of MgO-based sorbents in this project. These sorbents were prepared by either wet impregnation of Alumina support prepared by sol-gel or incorporation of MgO into the sol. Furthermore, these sorbents were produced both in form of pellet as well as granules.

Wet-Impregnation Method

In this method, aluminum tri-*sec*-butoxide (ATSB) used to produce a “stable” sol, which was subjected to a gelation process, to produce the alumina gel. The gel was formed into either pellets or granules and dried. In the next step, the formed gel material was calcined at 550°C for 4-6 hrs to form the lattice structure of pure alumina (Al_2O_3). In the wet-impregnation the pellets (1-2.5 mm) or granules (180-600 μm) were submerged into solutions containing different concentration of magnesium salt (such as magnesium nitrate) for period range of 2 to 24 hrs. As the last step the impregnated alumina was calcined for a second time at the same condition to produce MgO-based material with alumina lattice structure as a support.

A total of six (6) sorbents formulations were prepared by this method, which included four (4) sorbents in the form of pellets and two (2) in granular forms. The alumina supports for all these sorbents were prepared from 2 Molar sol and wet impregnation was carried out with a 2 molar magnesium salt solution for 20 hours. The magnesium content of the sorbents was estimated to be 4-6 % w/w by weighting the pellets before and after impregnation and calcination. The physical strength of the sorbent was assessed by a simple crush test with a small hammer. The specific surface area and average pore diameter of the sorbents determined by BET. This estimate was further confirmed by performing chemical analyses of a selected number of the sorbent by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). To increase the magnesium content of the sorbent, one batch of wet-impregnated pellets was re-impregnated at the same condition.

Incorporation Method

In this method, magnesium is incorporated into sorbent by adding a solution of magnesium salt (such as magnesium nitrate) to the Aluminum tri-*sec*-butoxide (ATSB) sol during gel production process. After drying process, sorbent calcined at 550°C for 4 to 6 hrs. Similar to the wet-impregnation method both pellets (1-2.5 mm) and granules (180-600 μm) is produced with this method. A total of sixteen (16) different formulations were prepared by this method. The preparation parameters investigated in this method included sol molarity and magnesium oxide concentration. The chemical compositions of a number of selected sorbents prepared by this method were determined by ICP-MS and the physical properties of the sorbents were determined by BET tests.

As indicated earlier, addition of other chemical reagent, such as potassium salts has been reported to enhance the reactivity of the sorbents.(2) Therefore, to investigate the effect of additives, a number of sorbents were impregnated using different potassium salts solutions (i.e., potassium carbonate, potassium hydroxide) at various concentrations and calcined at 550°C. It should be noted that potassium carbonate is not expected to decompose at this temperature.(12)

Modification of Dolomite

One of the main sources of magnesium in the nature is dolomite with average concentration of 45% magnesium carbonate (magnesite) and 55% calcium carbonate (calcite). Dolomite with ideal formula $MgCa(CO_3)_2$ makes up 2% of the earth crust (13) and is specially abundant in the United States. This material also has very high physical strength (attrition index <1%).

Utilization of dolomite as sorbent material reported in the literature indicates that dolomite has mainly been used as a source of CaO for separation of SO_x, H_2S and CO_2 from industrial gases.(14-17) Half-calcined or partially-calcined dolomite (i.e., $MgO.CaCO_3$) theoretically contains 21%w/w MgO. However, because of especial lattice structure of dolomite (18),the measured concentration of MgO in the half-calcined dolomite may be significantly different than the theoretical value.

The dolomite used in this project (i.e., Dolomite-245) was obtained from a quarry located in Thornton, Illinois. The chemical composition of the dolomite is given in Table 1. A total of forty (40) formulations dolomite-based sorbent were prepared. The preparation parameters included calcination temperature, duration of calcination, and calcination environment (CO_2 partial pressure and moisture), which have been reported to affect the characteristic of the products.(19) Furthermore, potassium carbonate was added to the half-calcined dolomite through wet impregnation method. The estimated potassium content of the impregnated sorbents was in the range of 1-6% w/w. The attrition resistance of the half-calcined dolomite was determined by ASTM-5757.

Task 2. Sorbents Evaluation

In this task, the reactivities of a number of sorbents toward CO_2 at atmospheric and elevated pressures were determined. All the sorbents tested in this task were in the form of granules with particle diameters in the range of 180 to 600 μm. These tests were conducted in different temperatures and CO_2 partial pressures. The evaluation of the sorbents has been carried out in three separate units described below.

a) Atmospheric Pressure TGA Tests
b) High-Pressure TGA Tests
c) High-Pressure Packed-Bed Tests

a) Atmospheric pressure TGA Tests

A total of fifteen (15) runs at different absorption and regeneration temperatures were conducted with sol-gel and modified dolomite sorbents in the temperature range of 300-500°C. The schematic diagram of the ambient pressure TGA unit is shown in Figure 3. In a typical Atmospheric Pressure TGA test, the sample (i.e., sorbent) is placed in a wire mesh basket that is suspended from a recording microbalance and a simultaneous recording is made of the sample weight, the temperature in close proximity of the sample. The reactor is heated to the desired temperature, while an inert gas (usually nitrogen) is flowing into the reactor. After the desired reaction temperature is achieved, the inert gas is switched to a gas mixture containing the desired concentration of the reactive component. The sample weight changes as the result of reaction, which is proportional to the rate of reaction and the difference between the molecular weights of solid reactants and products. The experiment generally continued until the sample weight reaches a constant value (no weight loss or gain). Because gas flow rates in the reactor are sufficiently high to essentially eliminate changes in the gas composition, the reaction occurs under a constant and known environment. Under these conditions the weight loss-versus-time characteristics can be used to determine the reaction rates under constant conditions. The ranges of all operating variables used in the TGA tests are shown in Table 2.

b) High pressure TGA Tests

A shown in Figure 1, increasing pressure results in increasing equilibrium temperature, where due to significant dependency of the rate of the reaction on the reaction temperature, higher reactivity can be expected. Therefore, this series of tests were conducted in the High-Pressure TGA (HPTGA) unit at 20 bar pressure where a CO_2 partial pressure of 10 bar was maintained in all absorption tests. The schematic diagram of the High-Pressure TGA (HPTGA) unit is shown in Figure 4. The ranges of all operating variables used in the HPTGA tests are shown in Table 3. A total of 80 HPTGA tests were conducted with sol-gel-based and dolomite-based sorbents.

A total of fifteen (15) tests were conducted with sol-gel-based sorbents at 20 bar with a 50/50 mixture of CO_2/N_2 (CO_2 Partial Pressure =10 bar) in the temperature range of 300-500 °C. As will be shown later in this report, the maximum conversion of MgO obtained in these test was about 5%, which corresponds to a maximum CO_2 absorption capacity of less than 1%. Therefore, based on these results, the work performed in this task, mainly focused on the evaluation of modified dolomite sorbents.

A series of tests were conducted with the EP44 sorbent at the baseline temperature of 425°C to assess the reproducibility of the HPTGA results. The parameter studies included the effects of additive and sorption temperature as well as calcination temperature on the performance of the sorbent on the reactivity of the sorbent. Regenerability of the EP44 sorbent formulation was investigated over several cycles in the HPTGA. In this series of tests, the CO_2 absorption was carried out at 425°C and the regeneration was performed at 500°C. The reactor pressure was maintained at 20 bar during the entire absorption and regeneration cycles. The regeneration step was carried out by increasing the temperature to 500°C and switching the gas from a 50/50 mixture of CO_2/N_2 to pure nitrogen. The effect of regeneration temperature on the performance of the sorbent was also studies in this series of tests.

To improve long-term durability (i.e., reactivity and capacity) of the sorbent, the EP36 and EP44 formulations were was periodically re-impregnated with potassium additive and calcined at a predetermined temperature after the 5-8 cycles. The effect of steam (10%v/v) on reactivity and regenerability of the sorbent was also determined

c) High Pressure Packed Bed Tests

A high-pressure packed-bed reactor unit was designed and constructed during this project to evaluate the sorbents performance at elevated pressures. The schematic diagram of the packed-bed unit is shown in Figure 5.

The unit essentially consists of a stainless steel reactor, which is externally heated by an electric furnace, equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, and monitoring the reactor pressure. A coarse porous stainless steel frit near the middle reactor is used to support the sorbent bed. Temperature is recorded as a function of time using a computerized data acquisition system. The dry gases required for the absorption and regeneration of the sorbent are obtained from pressurized cylinders. The gases are passed through pre-calibrated electronic mass flow controllers, which are set to give the desired mixture composition prior to entering the reactor. A calibrated pump is used to introduce water through capillary tubing into the reactor. The absorption part of the cycle is carried out by feeding a simulated coal gas mixture containing the desired concentrations of CO_2, CO, H_2, H_2O, CH_4, and N_2 to the reactor until the CO_2 concentration in the reactor exit gas reaches the feed concentration. Following absorption part of the cycle, the reactor is switched to the regeneration mode by changing the reactor temperature, pressure, and/or gas composition. A slipstream of the gas from the reactor is diverted to a gas chromatograph for measurement of CO_2, CO, H_2, H_2O, CH_4, and N_2, concentrations using two dedicated gas chromatographs (GC) equipped with thermal conductivity, flame ionization, photo ionization, and flame photometric detectors. Shakedown of the unit was completed late in the project and a few preliminary tests were carried out in the high-pressure reactor at 425°C and 20 bar with a 50/50 mixture of CO_2/N_2. The ranges of all operating variables in the high pressure packed-bed are shown in Table 4.

RESULTS AND DISCUSSION

Task1. Sorbent Preparation and Characterization

All the sorbent in this project were prepared either by various sol-gel techniques or modification of dolomite, as described below. The sol-gel sorbents were prepared by either wet impregnation of Alumina support prepared by sol-gel or incorporation of MgO into the sol. Furthermore, these sorbents were produced both in form of pellet as well as granules.

Wet-Impregnation Sol-gel Method

A total of six (6) sorbents formulations were prepared by this method, which included four (4) sorbents in the form of pellets and two (2) in granular forms. The physical strength of the sorbent was assessed by a simple crush test with a small hammer, indicating that all the sorbents prepared by this method has very high physical strength. The specific surface area and average pore diameter of the sorbents determined by BET. The results of the BET tests indicate that all sorbents have relatively high surface area (160-200 m^2/g), very low average pore diameter (5-8 nm). The magnesium content of the sorbents was estimated to be 4-6 % w/w by weighting the pellets before and after impregnation and calcination. This estimate was further confirmed by performing chemical analyses of a selected number of the sorbent by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The results of physical and chemical characterization of the sorbent prepared by this method is summarized in Table 5.

To increase the magnesium content of the sorbent, one batch of wet-impregnated pellets was re-impregnated at the same condition. The weight gain of the pellets was around 5 %w/w, and a large fraction of MgO appeared to have been crystallized on the surface of the sorbent, resulting in a significant decrease in the surface area of the pellets as indicated by BET results (i.e., 75 m^2/g). Because of the low concentration of MgO in these sorbent (compared to those prepared by the incorporation method described below), further investigation of the sorbent produced by this method was not pursued.

Incorporation Sol-gel Method

A total of sixteen (16) sorbents formulations were prepared by this method. The physical properties of a selected number of the sorbents are shown in Table 6, which indicate that, in general, the sorbents prepared in pellet form exhibited very high BET surface area (i.e., 282 m^2/g), low average pore diameter (i.e., 6.81 nm), and low physical strength. On the other hand, granular sorbents showed a very high physical strength, acceptable BET surface area (120-140 m^2/g) and higher average pore diameter (up to17 nm) compare to wet-impregnation method. Sorbents designated as EC15 and EC19 were prepared using identical preparation technique and parameters resulted in similar physical properties which represent the extent of reproducibility of the sorbents (see Table 6). The results also indicate that increasing magnesium concentration in the sorbent leads to lower the BET surface area and average pore diameter (e.g., EC20). The attrition index measured under ASTM-5757(11) standard for sample EC19, was less than 1% that is significantly below the average index that is required for fluidization processes (4%). The chemical compositions of a number of selected sorbents prepared by this method were determined by ICP-MS and are presented in Table 6. The results indicate that the magnesium nitrate as well as aluminum tri-*sec*-butoxide (ATSB) completely calcined under calcination condition and sorbents just contain MgO and Al_2O_3.

To investigate the effect of additives, a number of sorbents were impregnated using different potassium salts solutions (i.e., potassium carbonate, potassium hydroxide) at various concentrations (see Table 7) and calcined at 550°C. The potassium content of one of these sorbents was determined by ICP-MS to be 5.81%.

The results of physical and chemical analyses given in Table 6, granular sorbents containing 10% and 20%w/w magnesium (i.e., EC19 and EC20) appeared to possess the best combination of physical strength, acceptable surface area (i.e., 120-130 m^2/g), higher average pore volume (i.e., 11.5-16.53 nm), and magnesium content (i.e., 8.4-14.3%). Therefore, these two sorbents and the sorbents produced by impregnation of these sorbents were subjected to further evaluation task 2. As will be shown later, the result of evaluation of the sorbents in the thermogravimetric analyzer (TGA), indicated that the sorbents produced by the sol-gel technique did not have sufficient capacity and consequently the project focused toward modification higher capacity sorbents such as dolomite which is described below.

Modification of Dolomite

A total of forty (40) formulations dolomite-based sorbent were prepared. The ranges of the preparation parameters are given in Table 8, while the preparation condition for the three (3) sorbent subjected to detailed evaluation are given in Table 9.

Some of the prepared samples have been impregnated twice and evaluated in the TGA to determine the effect of re-impregnation on reactivity and capacity of the sorbents. Furthermore, the sorbent EP-44 was re-impregnated "re-treated" several times after the sorbent was subject to series of 5 absorption/regeneration cycles. The attrition resistance of the half-calcined dolomite was determined by ASTM-5757 and the result indicated that attrition index in range of 1-2.5%. As stated earlier, attrition index less than 4% shows capability of the sorbent to be used in commercialized fluidization systems.

Table 10 shows the distribution of various types of sorbents prepared for this project, and the ranges of relevant sorbent properties are given in Table 11. All the sorbents used in task 2 met the requirement for the physical strength (attrition index <4% in ASTM 5757). In general, the modified dolomite sorbents have significantly higher magnesium content, larger pore diameter and lower surface area, resulting in significantly higher reactivity compared to the sol-gel sorbents.

Task 2. Sorbents Evaluation

a) Atmospheric pressure TGA Tests

A total of fifteen (15) runs at different absorption and regeneration temperatures were conducted with sol-gel and modified dolomite sorbents in the temperature range of 300-500°C. The results obtained indicated that without potassium impregnation, neither sol-gel nor calcined dolomite was reactive toward CO_2. Furthermore, highly pure and dispersed MgO (obtained from calcination of magnesium nitrate) also did not exhibit any reactivity toward CO_2.

As a next step, several potassium impregnated sol-gel sorbents, were tested in TGA unit and the weight gain of 2%w/w has been achieved. To further confirm the positive effect of potassium on the reactivity of the sorbent, a sample of pure MgO powder was impregnated with potassium and tested with the TGA unit at 300°C. The result of this run is presented in Figure 6, indicating that a weight gain of 8%w/w was achieved in 40 minutes. The reacted sorbent was regenerated (i.e., decomposed) by increasing the temperature to 400°C. This decomposition temperature at CO_2 partial pressure of one (1) atmosphere matches the equilibrium curve of the reaction (Figure 1).

In Summary, the results indicated that at the low CO_2 partial pressures (i.e., 1 atm) used in the experiments, the reactivities of the sorbents toward CO_2 are very low. Therefore, all the following tests were carried out in the High-Pressure TGA unit, where the sorbent could be exposed to high CO_2 partial pressure that is expected in the IGCC processes.

b) High pressure TGA Tests

A total of 80 HPTGA tests were conducted with sol-gel-based and dolomite-based sorbents. A breakdown of all the HPTGA tests is given in Table 12.

A total of fifteen (15) tests were conducted with sol-gel-based sorbents at 20 bar with a 50/50 mixture of CO_2/N_2 (CO_2 Partial Pressure =10 bar) in the temperature range of 300-500 °C. The maximum conversion of MgO obtained in these test was about 5%, which corresponds to a maximum CO_2 absorption capacity of less than 1%. Therefore, it was concluded than none of the sol-gel sorbents prepare in this project will be suitable for CO_2 removal in IGCC processes. The observed low reactivity and absorption capacity of the sol-gel sorbent may be attributed to the 1) very low average pore diameters (6-17 nm) that can prevent penetration and distribution of potassium salt on the active internal surface of the sorbents during wet-impregnation process, 2) plugging of the active sites by potassium carbonate during wet-impregnation, 3) formation of strong bonding MgO and Al_2O_3 during the gelation process that inhibits reaction toward CO_2.

The results of HPTGA tests with modified dolomite that followed indicated that the reactivity and the overall capacity of modified dolomite sorbents were at least one order of magnitude higher than those of the sol-gel based sorbents. A comparison of the typical results obtained with the two types of sorbents is presented in Figure 7. Based on these results, the work performed in this task, mainly focused on the evaluation of modified dolomite sorbents.

A series of tests were conducted with the EP44 sorbent at the baseline temperature of 425°C to assess the reproducibility of the HPTGA results. The results of this series of tests are presented in Figure 8, indicating that the HPTGA data can be reproduced with a high degree of accuracy. It should be noted that at high pressure, changes in the buoyancy force on the sample during switching of the gases (i.e., from N_2 to CO_2), is significant. Therefore, to account for these forces, a number of blank test were conducted in which the basket filled with an inert material (quartz granules) and the results were used to correct all the experimental data obtained with the sorbents.

The effects of additive on the performance of the sorbent are shown in Figure 9, indicating that the reactivity of the modified dolomite sorbent increases with increasing additive concentration. The effect of calcination temperature on the reactivity of the sorbent is presented in Figure 10. As expected, higher calcination temperature adversely affects the sorbent reactivity, which should be attributed to higher extent of agglomeration at higher temperatures.

The effect of temperature on reactivity of two sorbents (i.e., EP44 and EP 36) is shown in Figures 11 and 12. The results indicate that, as expected, as long as the absorption temperature is below the equilibrium temperature, the reactivity of the sorbent improves with increasing temperature (350-425°C). The decline in the sorbent reactivity at temperature above 450°C shown in Figure 12 is due to the significant increase in the rate of reverse (i.e., regeneration) reaction with increasing temperature, as shown in Figure 13.

Regenerability of the EP44 sorbent formulation was investigated over several cycles in the HPTGA. The results obtained in seven (7) consecutive cycles are shown in Figure 14, indicating that the reactivity of the sorbent gradually decreases in the cyclic process. In this series of tests, the CO_2 absorption was carried out at 425°C and the regeneration was performed at 500°C. The reactor pressure was maintained at 20 bar during the entire absorption and regeneration cycles. The regeneration step was carried out by increasing the temperature to 500°C and switching the gas from a 50/50 mixture of CO_2/N_2 to pure nitrogen. The effect of regeneration temperature on the performance of the sorbent is shown in Figures 15 and 16. The results indicate that sorbent exposure to higher regeneration temperature can adversely affect the sorbent reactivity toward CO_2 in the following absorption cycles.

To improve long-term durability (i.e., reactivity and capacity) of the sorbent, the EP36 sorbent was re-impregnated with potassium additive and calcined at a predetermined temperature after the 8th cycle. As shown in Figure 17, as the result of sorbent re-treatment, the sorbent capacity significantly increased after re-treatment. To further investigate the effect of re-treatment, similar re-treatment procedure was applied to EP 44 sorbent after 5th, 10th, 15th, and 20th cycles and the results are shown in Figure 18. The results indicate that, in general, re-treatment improves the performance of the sorbent, and that, the extent of improvement gradually decreases in the cyclic process. This decrease in the positive impact of re-treatment is probably due to pore plugging imparted by repeated re-impregnation, blocking the active MgO site, which leads to lower sorbent reactivity. Also, as shown in Figure 18, no improvement was observed after the first re-treatment that was applied after the 5th cycle. This suggests that the extent of improvement in sorbent performance is probably sensitive to the re-impregnation method, in that, over-impregnation can lead to pore plugging, resulting on lower performance. However comparison of sorbent performance shown in Figures 15 and 18 indicates that, although no immediate improvement was observed, overall sorbent performance in the following 5 cycles were significantly improved by re-treatment (15% conversion after the 10th cycle with re-treatment compared to 10% without re-treatment).

The effect of steam (10%v/v) on reactivity and regenerability of the sorbent was also determined and the results are presented in Figure 19, indicating that the presence of steam significantly enhances the sorbent reactivity and significantly decreases the rate of decline in sorbent deactivation in the cyclic process. Effect of steam in increasing the porosity and changing pore size distribution has been reported before for dolomite and limestone (20-22). The positive effect of steam is very significant because the coal gas in the IGCC process has significant amount of steam. Unfortunately, because of the difficulty in introduction of stream in the HPTGA unit, additional testing could not be performed in this project.

c) High Pressure Packed Bed Tests

Shakedown of the unit was completed late in the project and a few preliminary tests were carried out in the high-pressure reactor at 425°C and 20 bar with a 50/50 mixture of CO_2/N_2. A typical CO_2 breakthrough curve is showed in Figure 20, indicating that concentration of CO_2 initially decreases from 50% to 10%, which gradually increases to 50% as the sorbent is completely carbonated. It should be noted that, the 10% level achieved in these experiments corresponds to reaching the equilibrium value at 425°C as shown in Figure 1 (i.e., P_{CO2} = 2 bar). The preliminary results obtained in the packed-bed reactor indicate that the unit is suitable for evaluation of the sorbent.

CONCLUSION

This work performed in this phase-I innovative concept project demonstrated the viability of a regenerative process for removal of CO_2 in IGCC process using MgO-based sorbents. A number of regenerable MgO based sorbents were developed in this project that can remove carbon dioxide from raw coal gas at operating condition prevailing in IGCC processes. The lost-cost sorbents were shown to have acceptable long term durability that permit cyclic regeneration over many cycles with very low attrition rate that is compatible with the fluidized bed or moving bed applications. The sorbent capacity appeared to be gradually decreases in the cyclic process. Although, because of the low-cost nature of the sorbent, the requirement for sorbent durability is achievable, further improvement can be made to further decrease sorbent deterioration rate and/or improve sorbent re-treatment technique to lower fresh sorbent make-up rate, to make the process economically more attractive. The following specific conclusions can be made from the results obtained in this project:

1. Sorbents prepared by sol-gel technique have very high attrition resistance but low reactivity and capacity.

2. Sorbents prepared by modification of half-calcined dolomite showed good absorption rate (reactivity) in the temperature range of 350- 450°C and CO_2 partial pressure of 10 bar as well as good decomposition rate in the temperature range of 500- 550°C and CO_2 partial pressure of less than 1 bar. Furthermore, these sorbents exhibited high attrition resistance (Attrition index << 4%)

3. To maintain high sorbent reactivity, the calcination/or regeneration temperature should not exceed 500°C.

4. Sorbent reactivity increases with increasing temperature up to 450°C. At higher temperature the rate of CO_2 absorption reaction decreases. This is mainly due to the significant increase in the rate of decomposition reaction.

5. Sorbent reactivity and capacity decreases with cycling but appear to be approaching a stable level. The reactivity and capacity can be periodically enhanced through sorbent re-treatment.

6. The presence of steam significantly enhances the reactivity of the sorbent and improves long-term durability of the sorbent.

Based on the results obtained in this project, a proposal was submitted to continue the work in a Phase-II innovative concept project that contains detailed recommendation to further improve the process economics and move the process toward commercialization. A brief summary of the proposed recommendations is given below.

1. Comprehensive study of absorption kinetics over the entire range of IGCC conditions generate the data required for designing the commercial absorption reactor.

2. Comprehensive study of regeneration kinetics including the effects of of regeneration

temperature, pressure, and CO2 concentration to generate the data required for designing the commercial regeneration reactor.

3. Development of kinetics models for the absorption and regeneration reactions. The model should incorporate the effect of physical properties of the sorbent such as BET surface area, porosity, and pore size distribution to account for changes in the physical properties of the sorbent in the cyclic process.

4. Determination of sorbent performance in packed-bed and development of a non-isothermal packed-bed reactor which includes effect of the catalytic activity of the sorbent in the water-gas-shift reaction.

5. Determination of sorbent durability and optimum re-treatment technique

6. Preliminary economical assessment of the regenerative CO_2 removal process using a commercially available process simulator.

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Table 1. Chemical Composition of Dolomite-245

Components /Elements	Amount, %w/w
$CaCO_3$	55
$MgCO_3$	44
SiO_2	0.6
Carbon Dioxide	46.5
Calcium	22.1
Magnesium	13.5
Potassium	0.7
Iron	0.13
Aluminum	0.12
Silicon	0.36
Sulfur	0.01
Strontium	0.006

Table 2. Ranges of Operating Variables in Ambient-Pressure TGA tests

Operating Variable	Range
Absorption Temperature, °C	300-500
Regeneration Temperature, °C	300-500
Total Pressure, atm	1
CO_2 Concentration, %v/v	100
Carrier Gases	He, N_2

Table 3. Ranges of Operating Variables in High-Pressure TGA tests

Operating Variable	Range
Absorption Temperature, °C	350-500
Regeneration Temperature, °C	425-600
Total Pressure, bar	20
CO_2 Concentration, mole %	50
N2 Concentration, mole%	50, 40
H_2O, mole %	0, 10

Table 4. Ranges of Operating Variables in the Packed-Bed

Pressure, bar	1-50
Temperature, °C	25-800
Flow Rate, cc/min	10-500
Bed Capacity, cc	Up to 50
Gas Analyzing Units	GC and IC

Table 5. Characterization of Sol-Gel Based Wet-Impregnated Sorbents

Sample Name	Type Granule Vs Pellet	Impregnation/ Calcination Temperatures	BET surface Area, m^2/g	Average Pore diameter (nm)	Al, %w/w	Mg, %w/w
EP4	P	20 C / 550 C	181.97	7.43		
EP6	G	20 C / 550 C	161.33	5.66	39.51	6.88
EP10	P	20 C / 550 C	189.01	7.67		
EP14	G	50 C / 550 C	195.64	7.56	42.58	4.19

Table 6. Characterization of Sol-Gel Based Incorporated Sorbents

Sample Name	Sol Molarity	Nominal Mg Content % w/w	Type Granule vs. Pellet	Physical Strength	BET Surface Area, m^2/g	Average Pore Diameter (nm)	Al, %w/w	Mg, %w/w
EC12	2	10	P	Very soft				
EC16	1	10	P	Medium	282.12	6.81		
E17	1	0	P	Very hard				
EC15	1	10	G	Very hard	133.03	17.08	39.51	8.31
EC19	1	10	G	Very hard	129.09	16.53	39.23	8.42
EC20	1	20	G	Hard	119.97	11.50	34.51	14.32
EC21	1	20	G	Hard and more transparent	141.81	6.81		
E23	1	0	G	Very Hard	235.41		45.96	0.04

Table 7. Wet-Impregnated Sorbents with Potassium Solution

Sample Name	Original Sample Name	Impregnation solution /Molarity
ECP24	EC19	K_2CO_3 / 1 M
EP25	EC19	K_2CO_3 / 1 M
EP27	pure MgO	K_2CO_3 / 1 M
EP30	EC19	KOH / 1 M
EP33	EC19	K_2CO_3 / 0.5 M
EP34	EC19	K_2CO_3 / 0.25 M
EP35	EC20	K_2CO_3 / 0.25 M
EP38	pure MgO	KOH / 1 M
EP37	Pure Al_2O_3 sorbent	Mixture of K_2CO_3 and $Mg(NO_3)_2$ (Molar ratio Mg:K=7:1)

Table 8. Ranges of Preparation Parameters for Dolomite-Based Sorbents

Parameter	Range
Potassium Salt	K_2CO_3
Solution Molarity	0.5-2M
Calcination Temperature	550-700°C
Duration of Calcination	3-6 hours
Calcination Environment	N_2, CO_2

Table 9. Modified Dolomite Preparation Conditions

Sample Name	Impregnation Solution /Molarity	Calcination Temperature, °C	Calcination Duration, hr	BET Surface Area m^2/g	Average Pore Diameter, nm	K, % w/w
EP36	K_2CO_3 / 1 M	550	4			
EP39	K_2CO_3 / 0.5 M	550	4			
EP44	K_2CO_3 / 2 M	550	4	5.74	70	4.22

Table 10. Distribution of Types of Sorbents

Sorbent Type	No.
Total No. of Sorbents	62
-- Sol-Gel Sorbents	22
-- Modified Dolomite	40
-- Impregnated Sorbents	43
-- Incorporated Sorbents	16
-- Granular Sorbents	50
-- Pellet Sorbents	12
-- Modified Sorbent with additive	51
-- No. of additives	5

Table 11. Sorbents Characteristics

Sorbent Characteristics	
Magnesium Content, % w/w	10-20
Specific Surface Area, m^2/g	5-280
Additive Content, % w/w	1-6
Attrition Index, %	0.04-2.5

Table 12. Summary of High-Pressure TGA Tests

TGA Test	**No.**
-- Runs	**80**
-- Individual TGA Cycle	**160**
-- Maximum # of Cycles (without re-treatment)	**14**
-- Maximum # of Cycles (with re-treatment)	**25**

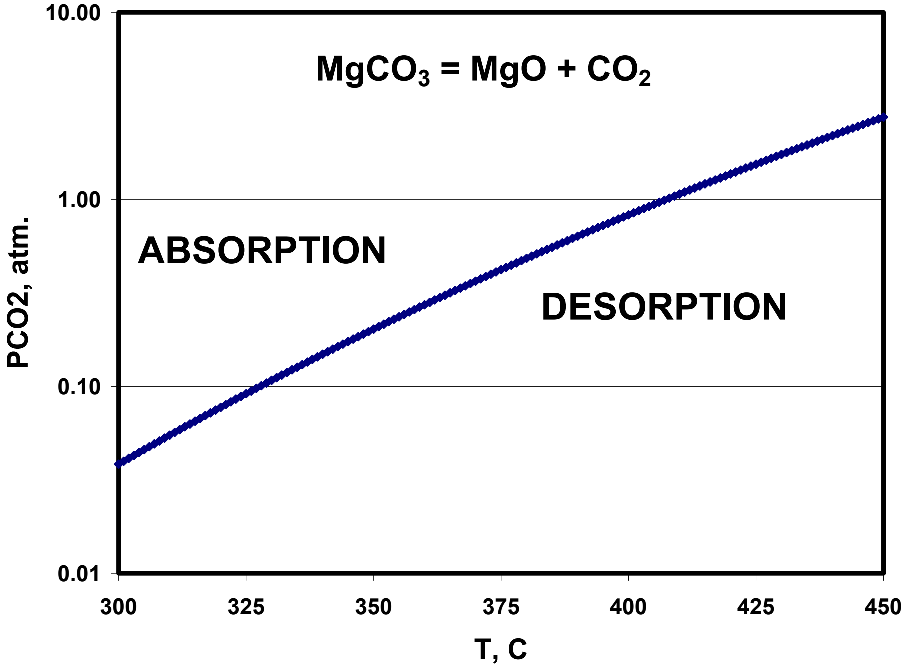

Figure 1. MgO Absorption/Desorption Equilibria with CO_2

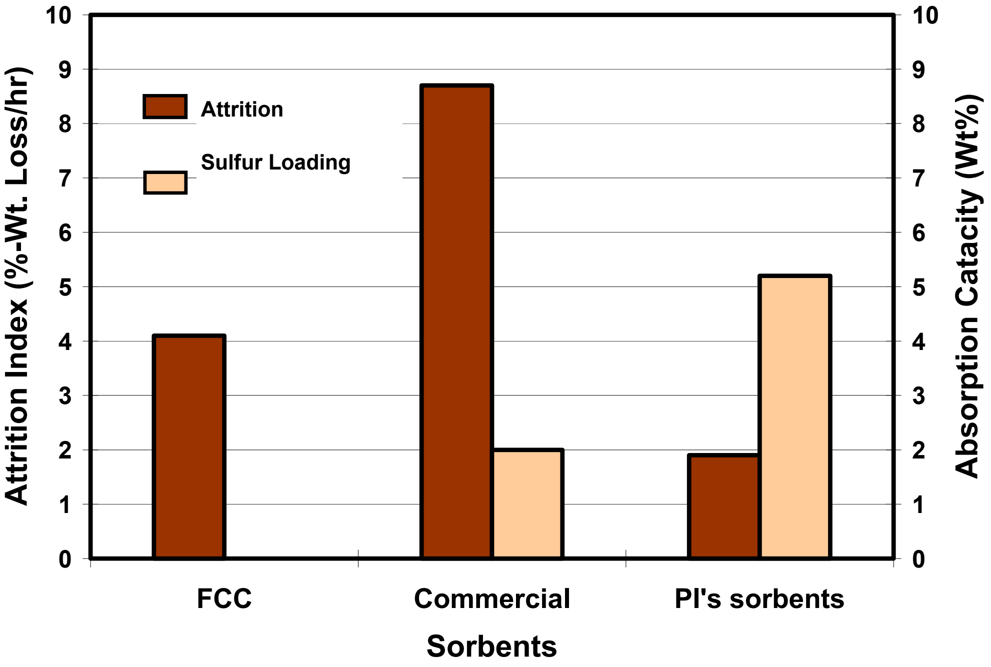

Figure 2. Comparison of Attrition Resistance and Absorption Capacity

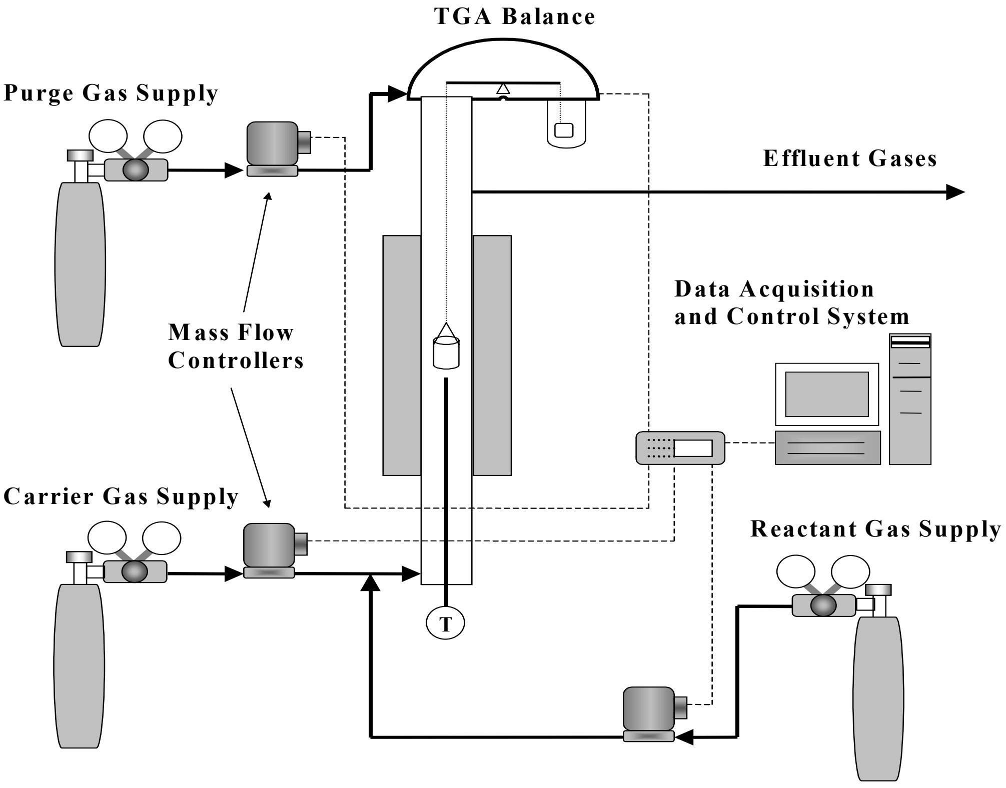

Figure 3. Schematic Diagram of the Ambient-Pressure TGA Unit

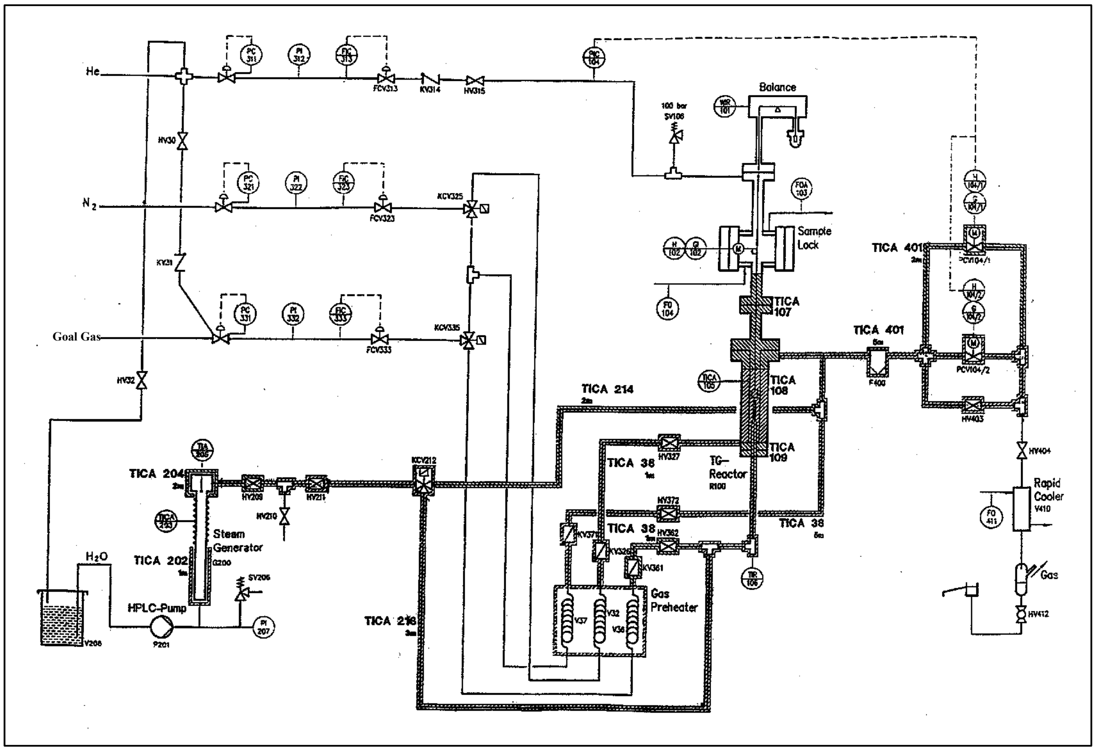

Figure 4. Schematic Diagram of the High-Pressure TGA Unit

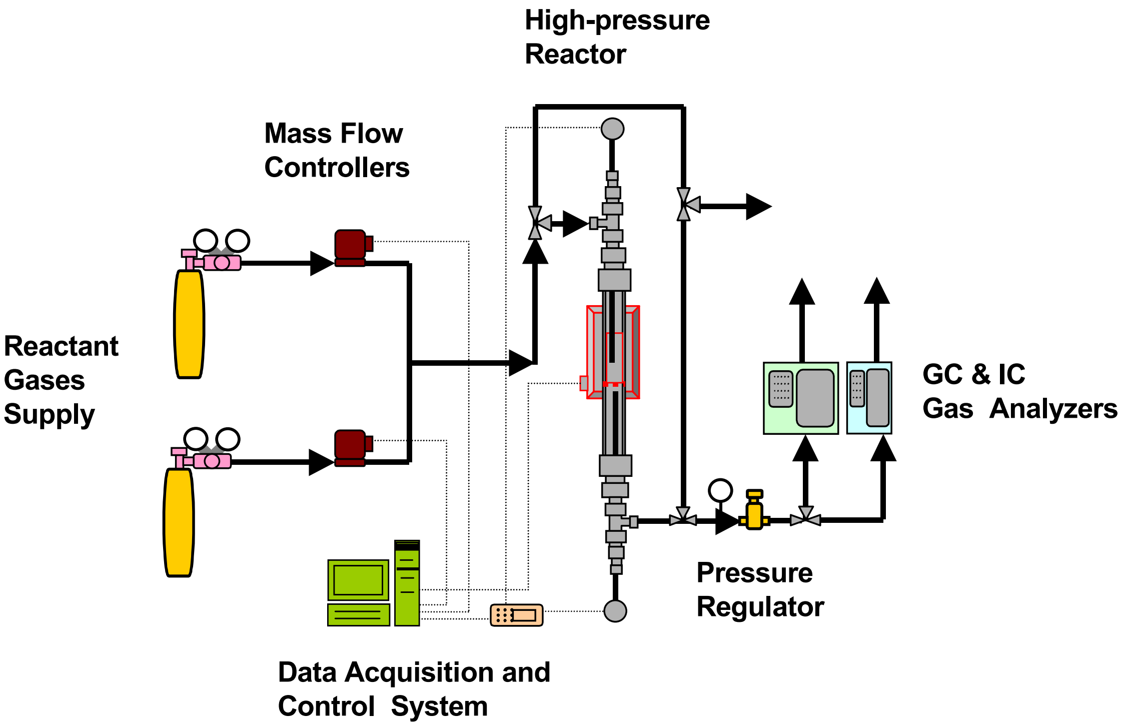

Figure 5. Schematic Diagram of High-Pressure Packed-Bed Unit

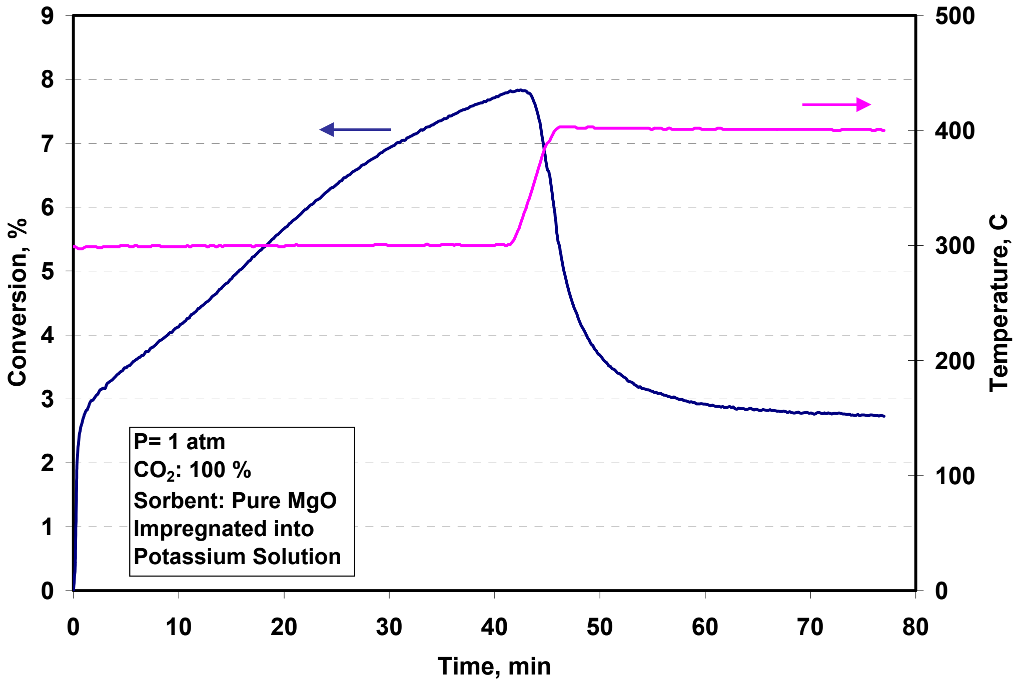

Figure 6 Absorption/Decomposition of Potassium Impregnated Pure MgO

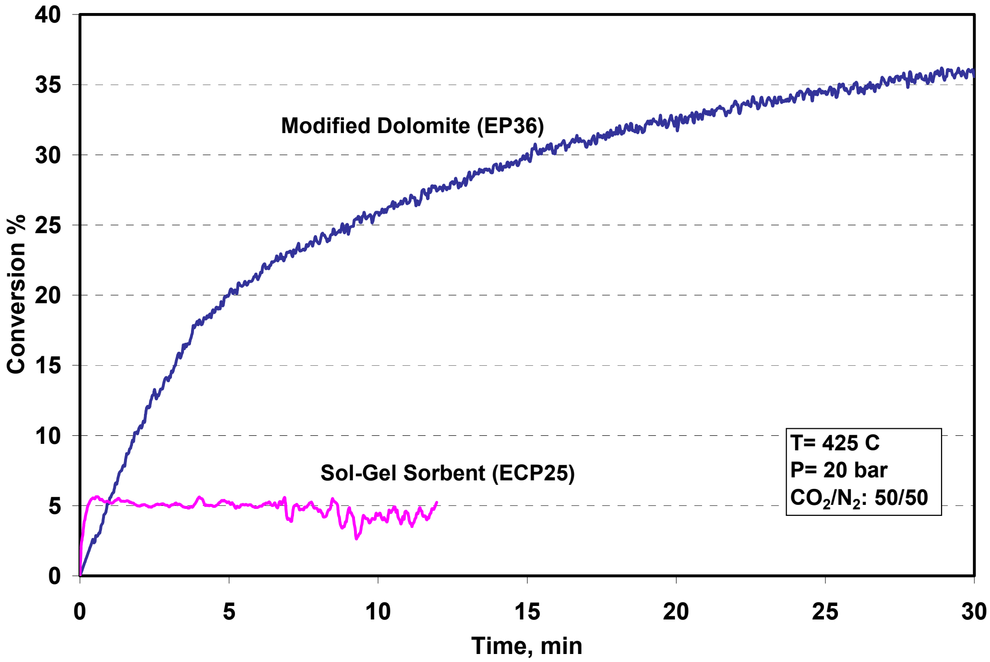

Figure 7. Comparison of Sol-gel and Modified Dolomite Sorbents

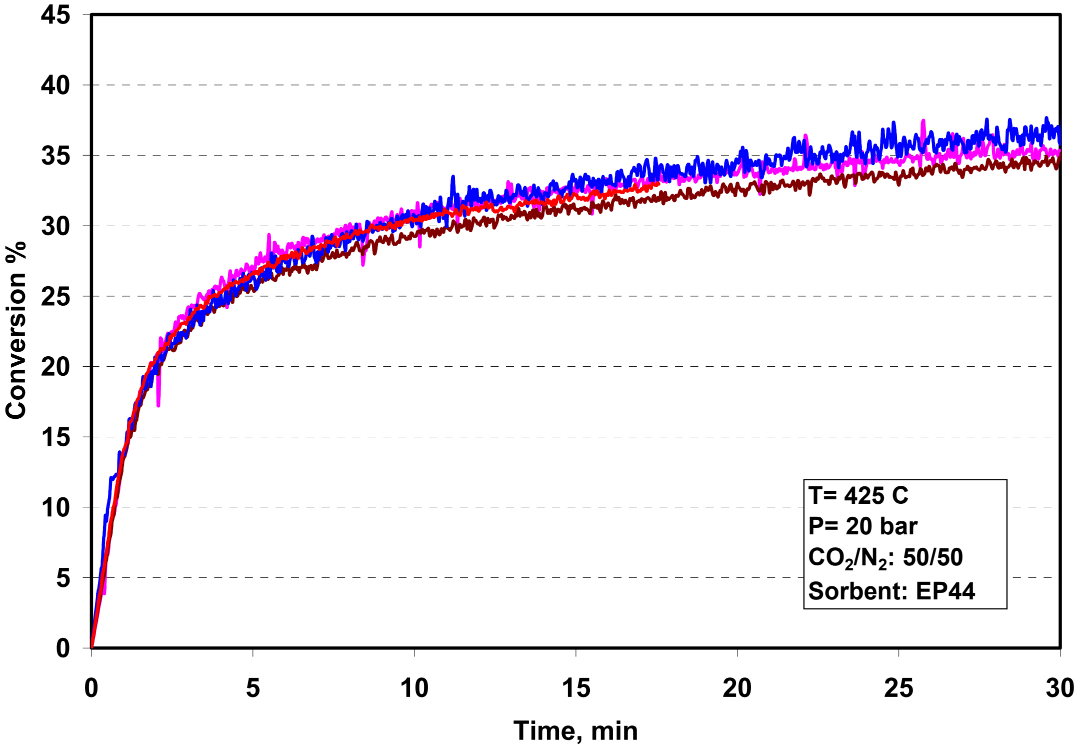

Figure 8. Reproducibility of the TGA Runs

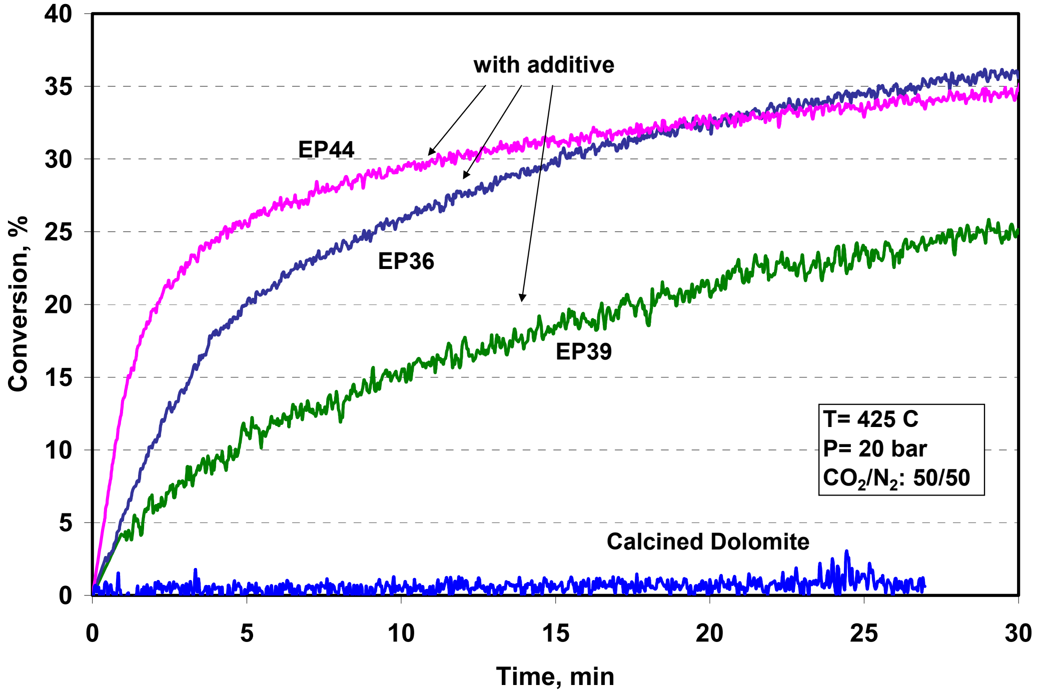

Figure 9. Effect of Additive Concentration on Sorbents Performance

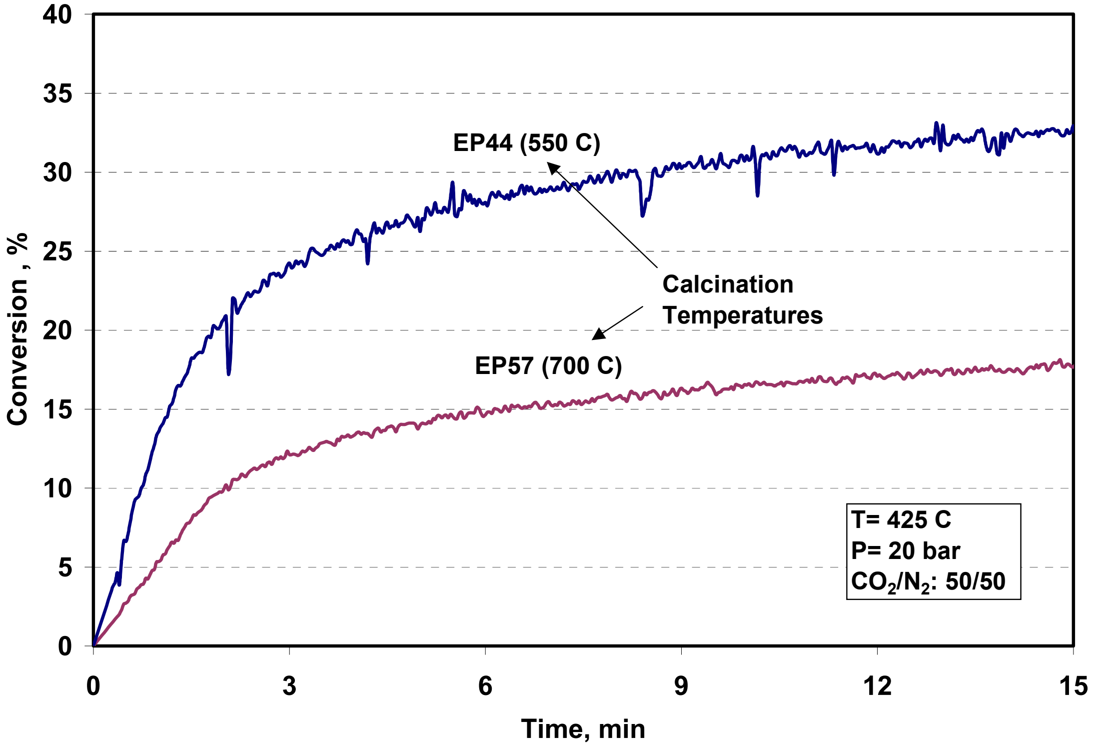

Figure 10 . Effect of Calcination Temperature on Sorbent Reactivity

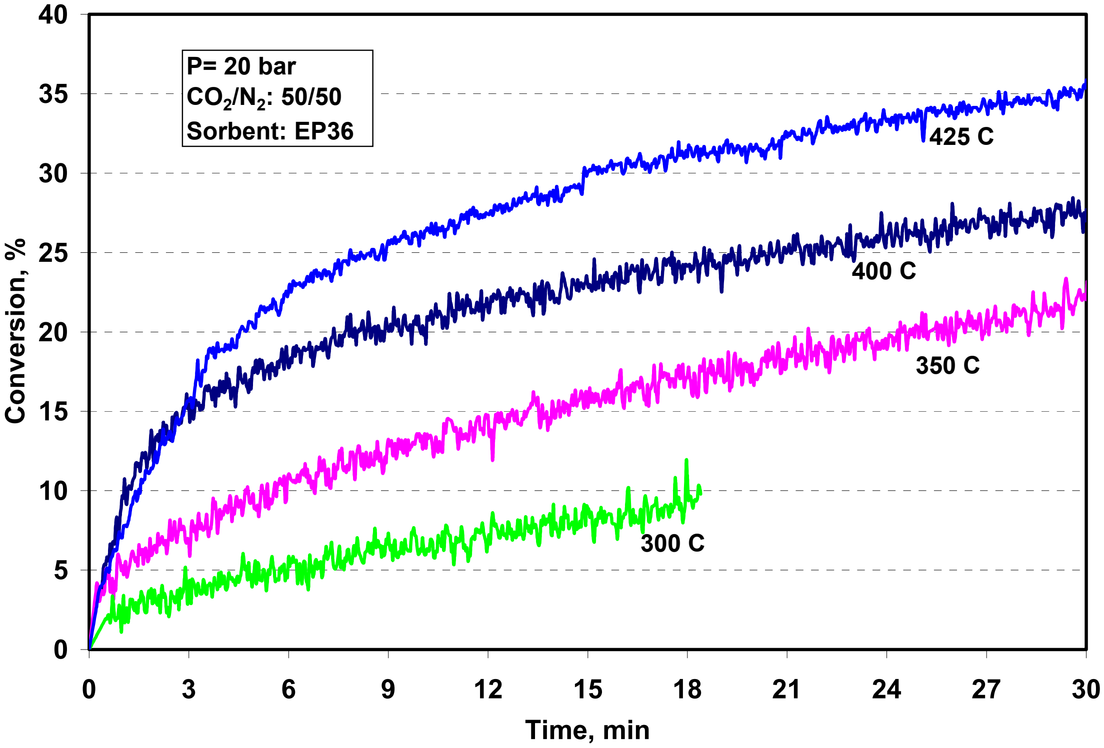

Figure 11. Effect of Temperature the Reactivity of the EP36 Sorbent

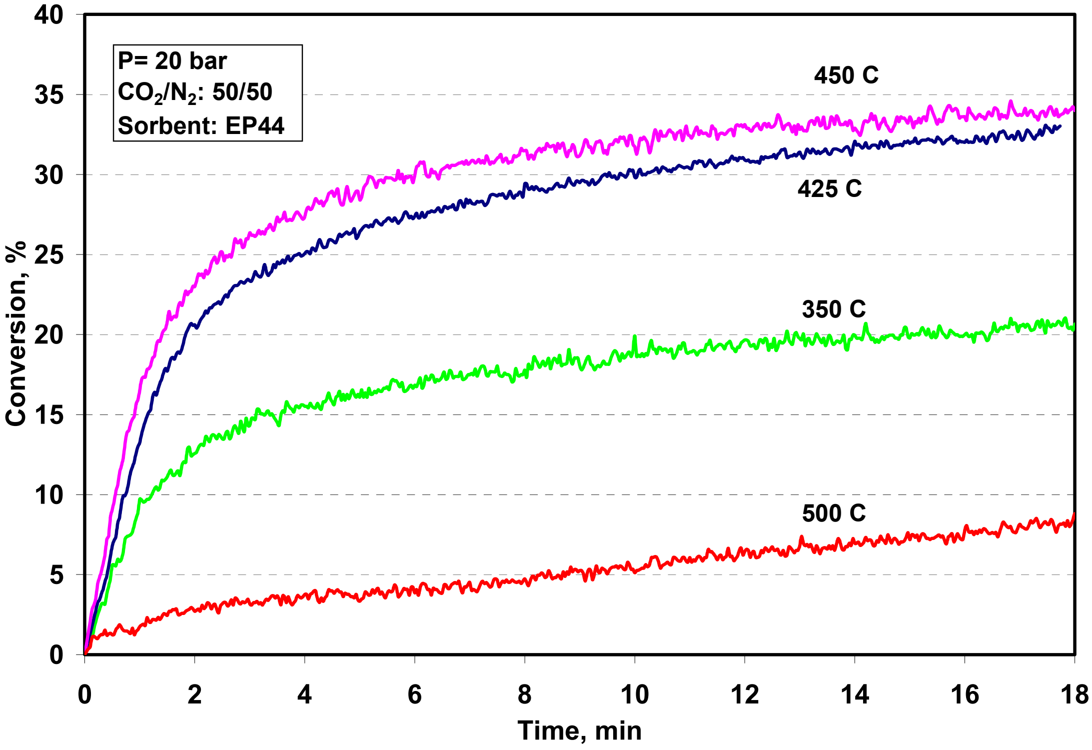

Figure 12. Effect of Temperature the Reactivity of the EP44 Sorbent

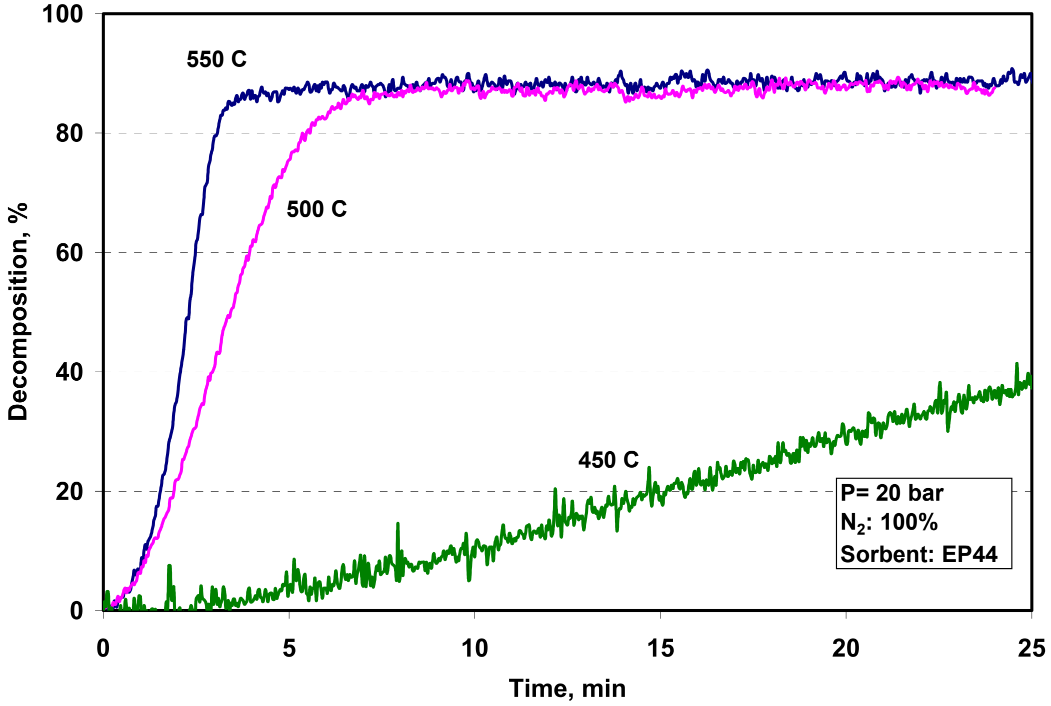

Figure 13. Effect of Temperature on Sorbent Decomposition

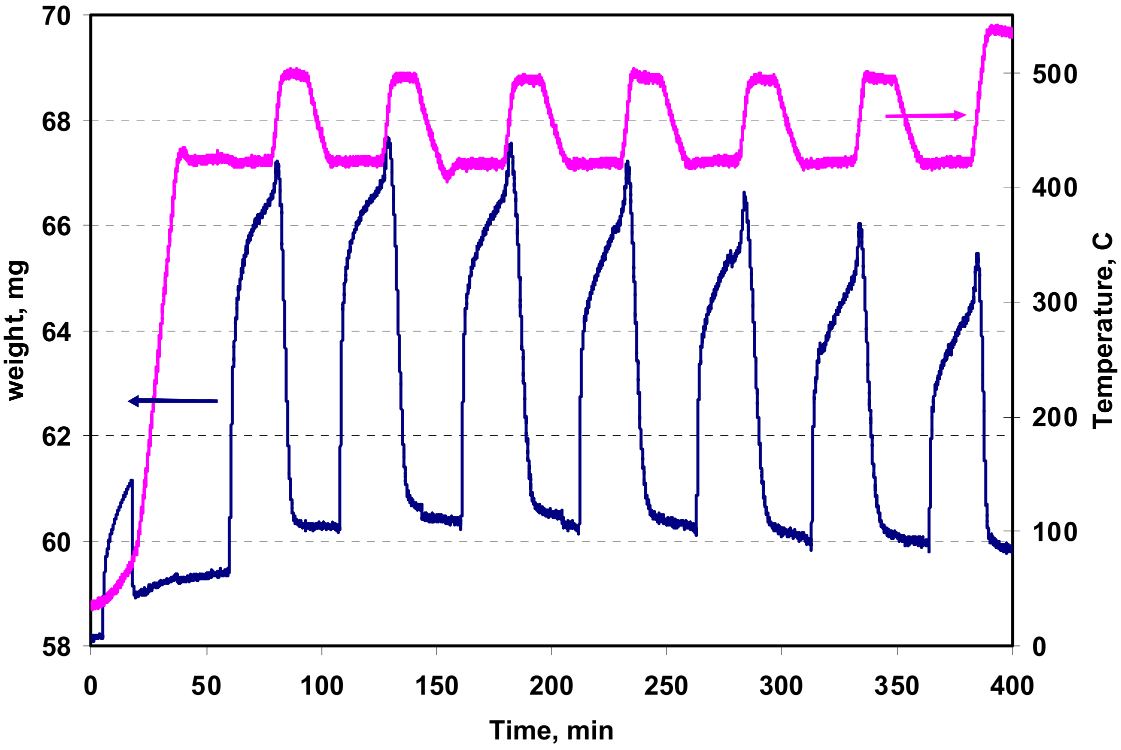

Figure 14. Regenerability of (EP44) Half-Calcined Dolomite with Additive

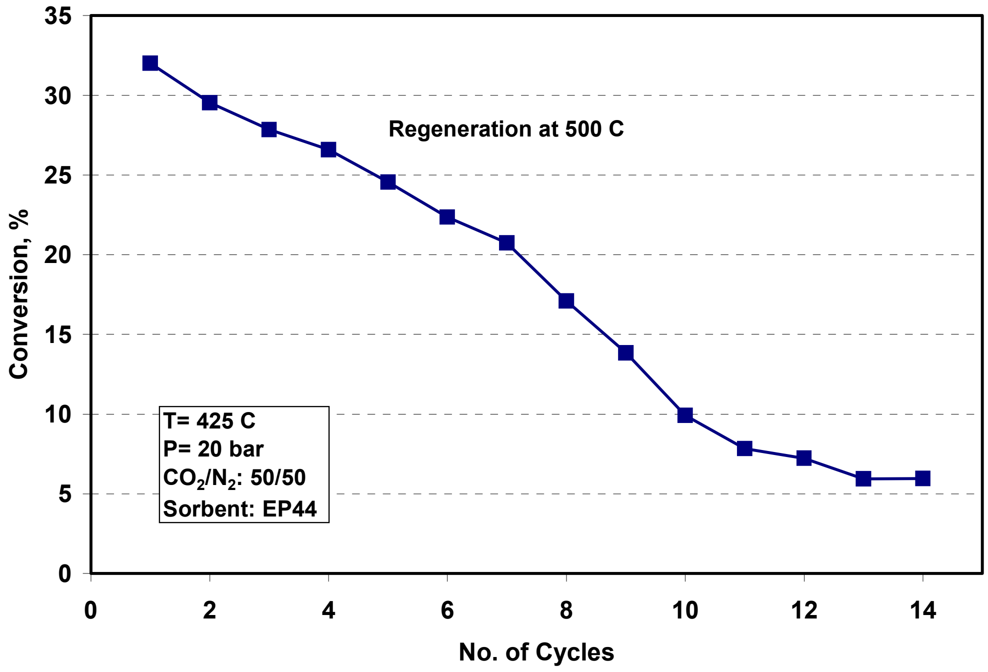

Figure 15. Effect of Cycling on Reactivity and Capacity of the Sorbent (Conversion after 15 mins)

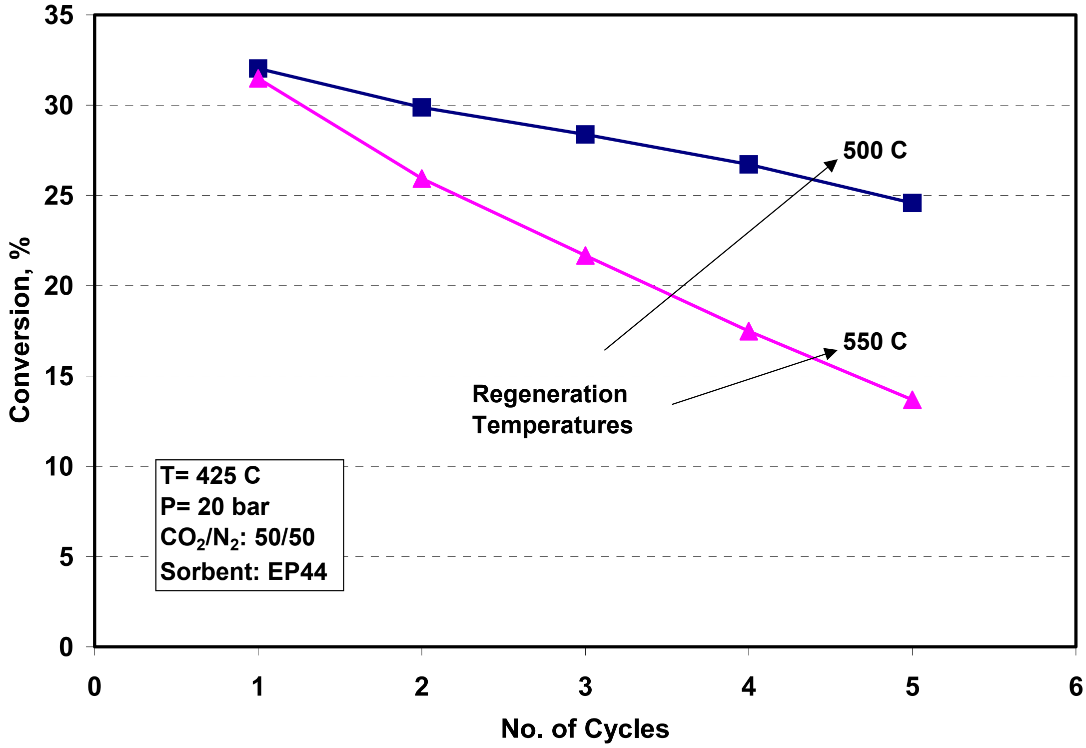

Figure 16. Effect of Regeneration Temperature on Sorbent Performance

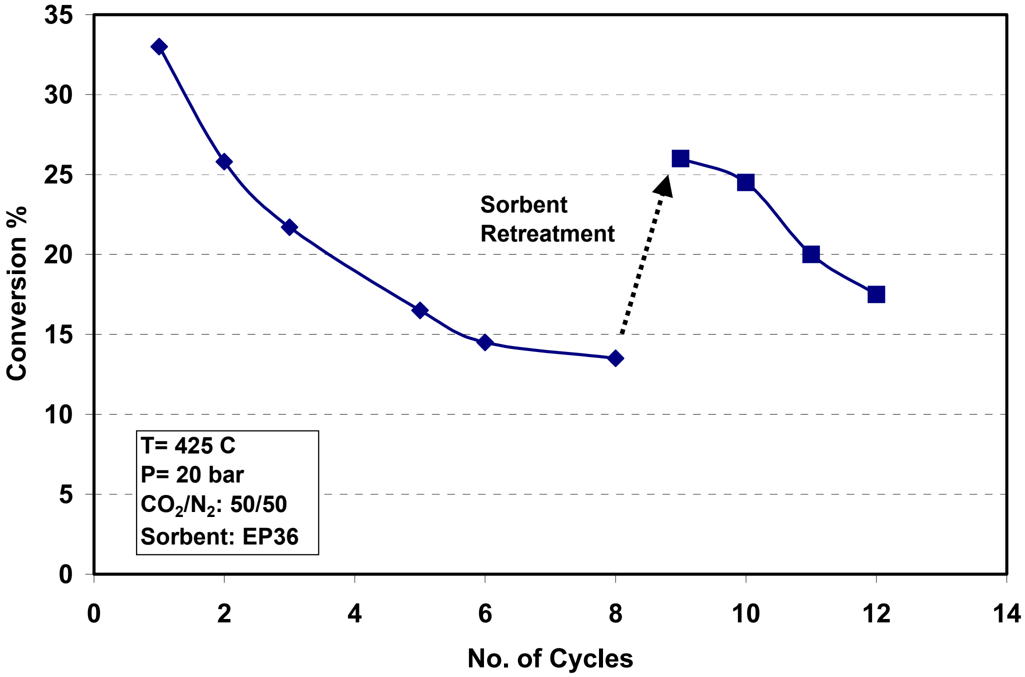

Figure 17. Effect of Re-treatment on Reactivity and Capacity of EP36 Sorbent (Conversion after 15 mins)

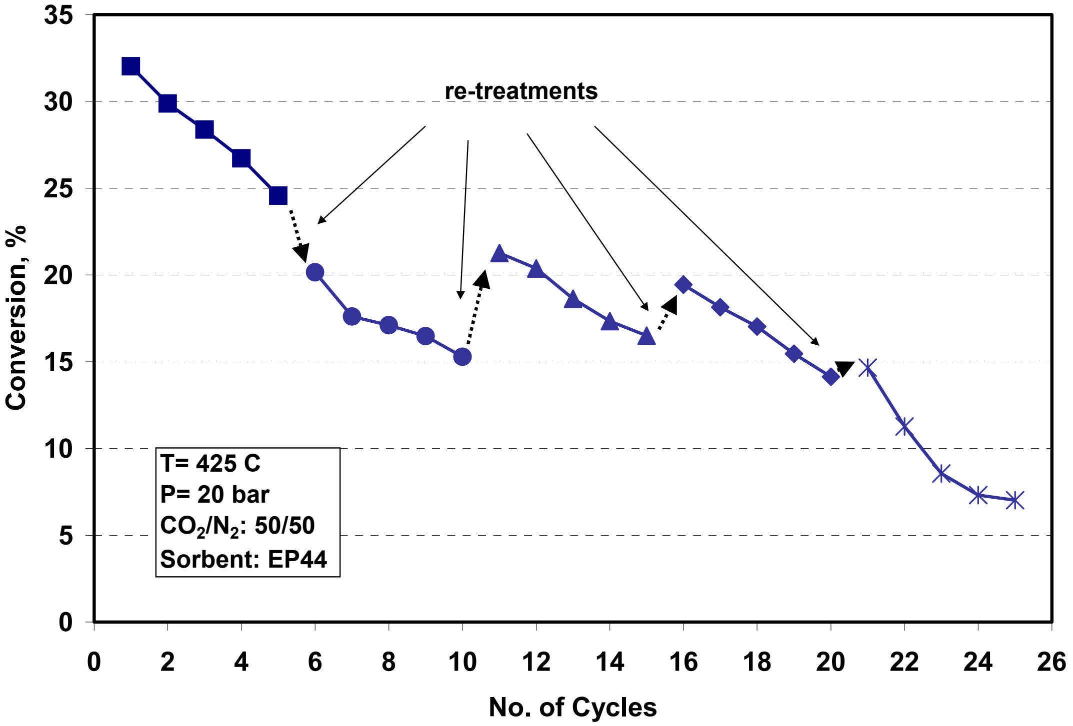

Figure 18. Effect of Re-treatment on Reactivity and Capacity of EP44 Sorbent (Conversion after 15 mins)

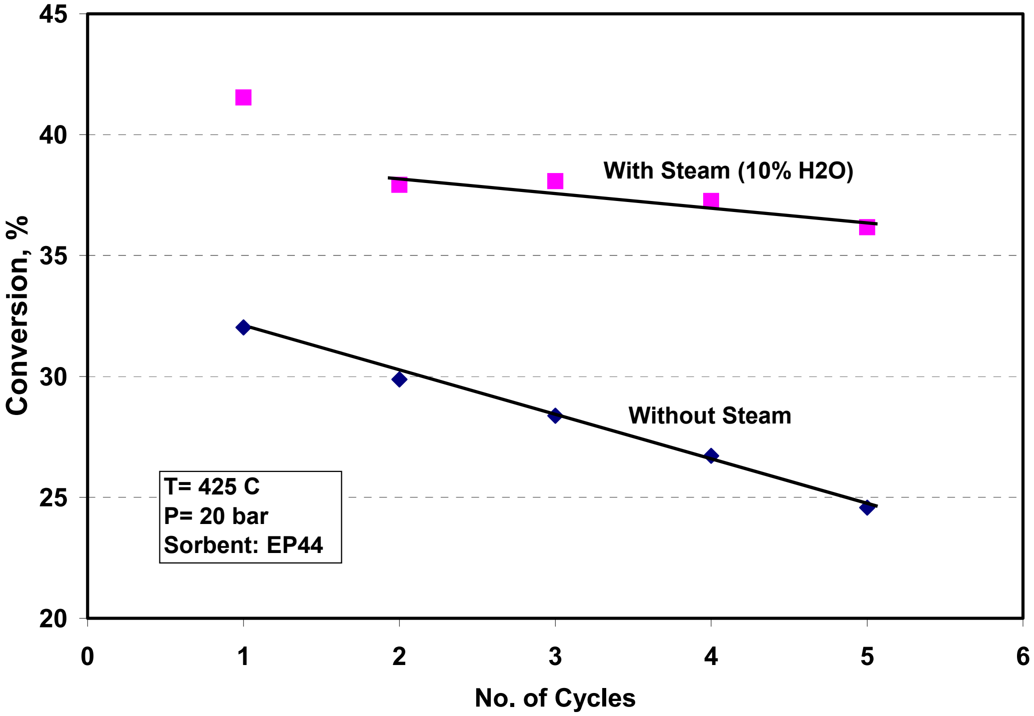

Figure 19. Effect of Steam on Sorbent Reactivity and Regenerability (Conversion after 15 mins)

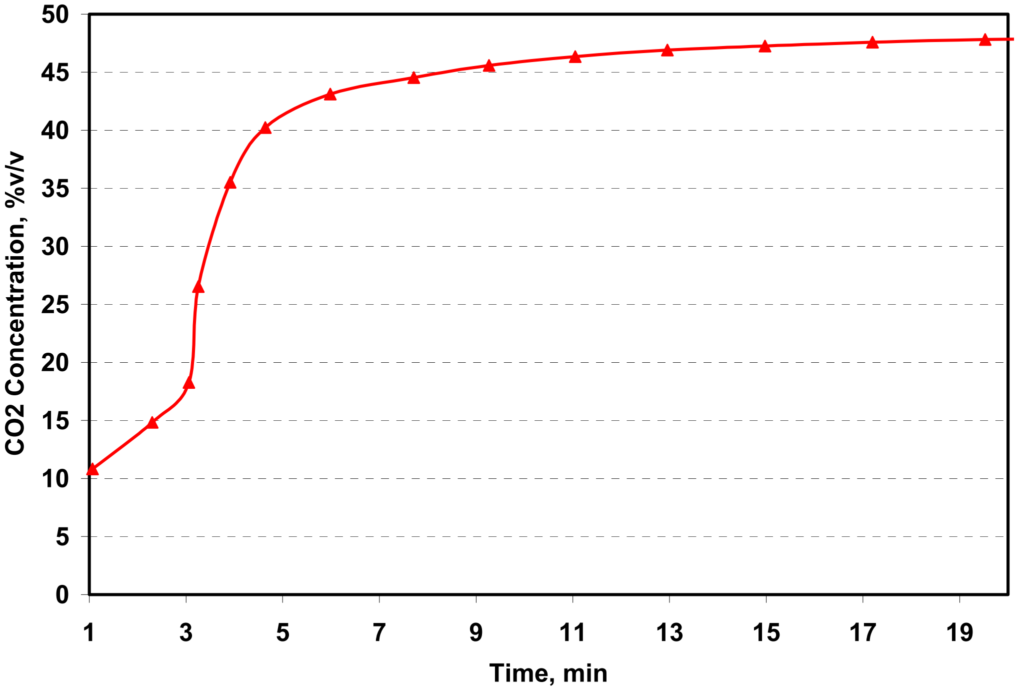

Figure 20. A typical Packed-Bed Breakthrough Curve on Dolomite Sorbent (EP39)