Studies of In-Situ Calcium Based Sorbents in Advanced Pressurized Coal Conversion Systems

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ABSTRACT

The overall objective of this project titled "Studies of In-Situ Calcium-Based Sorbents in Advanced Pressurized Coal Conversion Systems" was to obtain experimental data on the reactions of calcium-based sorbents in both air-blown coal gasification systems and second generation fluid bed coal combustion systems (partial gasification) as well as stabilization of the spent sorbent produced. The project consisted of six tasks: Tasks 1 and 2 dealt mostly with project-related activities and preparation of test equipment, Task 3 - study on sulfidation of calcium-based sorbents, Task 4 - kinetic studies on calcium-catalyzed carbon gasification reactions, and Task 5 - oxidation of CaS present in LASHs and DASHs (mixtures of coal ash and limestone or dolomite respectively) to CaSO_4 and absorption of SO_2 on various solids, and Task 6 - economic evaluation of the most promising CaS oxidation method developed under this program. Experimental studies were conducted primarily to address Task 5 issues.

Spent sulfide-containing solids from KRW Energy Systems (KRW) and Tampella Power Corporation (TP) gasifiers, the Foster Wheeler Development Corporation (FW) carbonizer and Kellogg's Transport Reactor Test Unit (TRTU) were oxidized in a 2 inch-diameter fluidized bed. SO_2 absorption on these solids and fresh sorbents was studied in a fixed bed unit. For lightly-sulfided KRW and FW LASHs, an increase in oxidation was obtained with an increase in temperature over the range of 1500 to 1700°F at atmospheric pressure in air for an hour and all subsequent tests were, therefore, performed at 1700°F. Higher oxidation levels were obtained with the KRW LASH compared to the FW and TRTU LASHs. This may be attributed to the dolomitic limestone used in producing the KRW LASH. For LASHs, the oxidation levels ranged from about 22% to 80%, and with an alkali impregnation, they increased up to 90 to 95%. With TP and FW DASHs, 100% and 93% oxidation levels were achieved showing the advantage of using a dolomite over a limestone in a gasifier. Weathering of LASHs does not appear to be a viable technique to complete oxidation based on the results from the exposure of KRW and FW LASHs.

SO_2 absorption on fresh sorbents, LASHs, and DASHs was studied in a fixed bed reactor and a pressurized thermogravimetric analyzer (PTGA). The absorption of SO_2 by lightly-sulfided as well as heavily-sulfided sorbents is very good after exposing the sorbents for a period of time to supply enough O_2 for the conversion of any CaS to CaSO_4 . The absorption of SO_2 by KRW LASH, and KRW and TP DASHs after oxidation was very poor. This may be attributed to the relatively high temperatures at which these solids were processed. This was confirmed by a fundamental study on the effect of heat treatment temperature on SO_2 absorption and by physical characterization of the solids. The absorption of SO_2 by FW DASH after oxidation was very good, reflecting an advantage of using a dolomite over a limestone in the FW carbonizer. Characterization of various solids by mercury porosimetry shows good correlation between SO_2 absorption and pore size distribution.

Several samples of LASHs and DASHs were tested as per the EPA interim test to evaluate potentially reactive sulfide-containing solids in terms of the amount of H_2S

released upon acidulation. The DASHs, in general, appear to be more reactive than the LASHs in releasing H_2S just as they are towards sulfide oxidation and SO_2 absorption. Based on the results of this study, it can be stated that the inherent reactivity of solids, temperature at which they were processed and the residual CaS content are major contributing factors to the behavior of these solids in the EPA test.

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SECTION 1.0 - EXECUTIVE SUMMARY

1.1 LASH Oxidation Studies in Bench-scale Reactor Unit

Oxidation studies were performed in a 2-inch diameter fluidized bed by injecting about 25 to 30 grams of CaS-containing LASH or DASH into a 200-gram inert bed. LASH and DASH refer to mixtures of limestone or dolomite, respectively, with coal ash. The solids were oxidized for a desired time period while SO_2 concentration in the offgas and bed temperatures were monitored. All the experiments were done at atmospheric pressure in air. A summary of the oxidation studies is presented below. All abbreviations or acronyms are listed at the end of the report.

The effect of temperature on the oxidation of as-received, lightly-sulfided, and carbon-free KRW Energy Systems (KRW) LASH was studied over the temperature range of 1500 to 1700°F in air for a period of an hour. The temperature of 1700°F appears to be the most preferred giving the highest level of oxidation. The effect of temperature on the oxidation of as-received, lightly-sulfided, and carbon-free Foster Wheeler Development Corporation (FW) LASH was also studied over the temperature range of 1500 to 1700°F in air over a period of an hour. The highest level of oxidation for the FW LASH was also obtained at the temperature of 1700°F. The reason for appreciably lower conversions for FW LASH compared to KRW LASH may be attributed to the differences in the characteristics of the limestones used and/or the process conditions at which the LASHs were formed. No appreciable SO_2 evolution was observed in any of these tests based on continuous monitoring of SO_2 in the offgas during the experiments. All the subsequent tests were performed at 1700°F in order to investigate the effect of sulfidation level, grinding and doping with an alkali. The alkali selected in this study was a 2% Na_2CO_3 aqueous solution.

The results from the study of LASH/DASH oxidation, at a temperature of 1700°F and atmospheric pressure in air for an hour in a fluidized bed, can be summarized as follows:

- For LASHs, the oxidation levels ranged from about 22% to 80%. With alkali impregnation, the oxidation levels increased to 90 to 95%. Higher oxidation levels were obtained with KRW LASH compared to FW and TRTU LASHs. This may be attributed to the dolomitic limestone used in producing the KRW LASH.
- With Tampella Power Corporation (TP) and FW DASHs, 100% and 93% oxidation levels were achieved respectively showing the advantage of using a dolomite over a limestone in the gasifier.
- Fundamental kinetic studies conducted with a LASH on a thermogravimetric analyzer showed that after about 20 to 50% oxidation level was achieved, the rate slowed down substantially, possibly due to diffusional resistance in the CaSO_4 layer.

Table 1.1 shows a summary of the data on conversion of CaS to CaSO₄ achieved in the Bench-scale Reactor Unit (BRU) for various untreated, ground, doped and ground and doped LASHs and DASHs at 1700°F and atmospheric pressure in air for an hour. The oxidation level obtained during carbon burn-off in a muffle furnace is also given. Carbon-containing solids could not be directly processed in the BRU due to the inability to control the large exotherm which would result from carbon combustion and competition for the limited oxygen supply. Oxidation level was calculated based on CaS content in the feed and the solids oxidized in the BRU.

Table 1.1 - Oxidation Levels of LASHs and DASHs in the BRU

LASH/DASH	Muffle*	UT	G	D	GD
CFHS KRW LASH	20	72	79	90	85
CFHS FW LASH	0	22	75	86	94
LSCF KRW LASH	20	58	65	94	-
LSCF FW LASH	0	33	-	-	-
HSCF KRW LASH	78	80	80	-	96
HSCF TRTU LASH	12	40	-	79	-
Tampella DASH	100	100	-	-	-
FW DASH	92	93	-	-	-

* Oxidation level during carbon burn-off in a muffle furnace.

UT-untreated

G-ground to -140 mesh

D-doped with Na₂CO₃

GD-ground and doped with Na₂CO₃

Table 1.2 - Data on LASHs and DASHs

Material	Calcium Utilization %	Sulfide level, %
HSAR KRW LASH	61	60
LSAR KRW LASH	35	33
HSAR FW LASH	43	42
LSAR FW LASH	23	21
LSCF Tampella DASH	14	0
LSAR FW DASH	56	55
HSAR TRTU LASH	58	55

Calcium utilization (mole% of calcium present as sulfide and sulfate of total moles of calcium) and the level of CaS (mole% of calcium present as CaS) in lightly-sulfided and heavily-sulfided materials are given in Table 1.2. The temperature and the feedstock used in the various tests performed in the BRU are given in Table 3.1.

1.2 SO₂ Absorption Studies (SO₂ + ½O₂ + CaO → CaSO₄)

The experimental apparatus consisted of a quartz reactor (1.65-inch I.D. and 15-inch long) in a horizontal fixed bed configuration, with a quartz fritted disc for gas distribution, that is heated by an electrical furnace. The reactor was packed with the desired solids and quartz wool is placed on both ends such that the solids are held firmly in position. The length of the bed generally ranged from 10 to 12 inches. The wall temperature is monitored near the inlet, the middle, and the outlet locations of the bed by means of thermocouples strapped to the outside of the reactor. The gas leaving the packed bed is passed through bubblers to scrub the gas of any sulfur compounds present before venting it to the atmosphere. The concentration of H₂S or SO₂ was measured by means of Draeger tubes before the gas enters the bubblers. All the experiments were done at atmospheric pressure. A summary of the SO₂ absorption studies is given below.

- The absorption of SO₂ in the presence of O₂ by fresh sorbents was very good with breakthrough periods (corresponding to SO₂ concentration of 100 ppm in the exit gas) up to 12 hours at the experimental conditions employed in the studies. The absorption of SO₂ by fresh limestones in the absence of O₂ was poor, possibly due to the absence of a stable product.
- The absorption of SO₂ by lightly-sulfided as well as heavily-sulfided Sierra Pacific Power Corporation (SP)-supplied and Greer limestones, and PR dolomite was very good after exposing the sorbents to 10-21 % O₂ for a period of time sufficient for the conversion of most CaS to CaSO₄ or after they were oxidized in a separate step.
- The absorption of SO₂ by KRW LASH, and KRW and TP DASHs was very poor. This may be attributed to the relatively high temperatures at which these solids were processed in the gasifiers. The absorption of SO₂ by FW DASH was very good, after converting most CaS to CaSO₄, reflecting the advantage of using a dolomite over a limestone in the FW carbonizer.
- The absorption of SO₂ by mixtures of LASHs and limestones was synergistic compared to the performance of individual solids. The absorption of SO₂ by a mixture of FW DASH and PR dolomite was about the same as that expected from individual solids.
- The absorption of H₂S by KRW LASH was as good as that observed for the SP and Greer limestones with a breakthrough period (corresponding to a H₂S concentration of 100 ppm) of 7 hours at the experimental conditions employed in the study.

The discharge product from a KRW gasifier cannot be expected to absorb an appreciable additional sulfur in the combustor/sulfator at an acceptable SO₂ leakage; and therefore, sufficient fresh sorbent needs to be added to the combustor/sulfator to absorb all the sulfur (to assure low SO₂ leakage) that is either evolved from carbon combustion or recycled to the unit from an external desulfurizer.

1.3 Characterization of LASHs/DASHs and Sorbents by Mercury Porosimetry

Calcined sorbents and carbon-free LASHs and DASHs were characterized by mercury porosimetry to measure the variation of pore surface area and pore volume as a function of pore size. The measurements were performed on a Micromeritics Autopore II 9220. The pressure was increased from 1.6 to 60,000 psia that covers pores from about 117 microns to 0.003 micron (30 angstroms) in diameter.

Based on these results, pores of about 0.05 to 0.5 micron in diameter found in fresh sorbents, that appear to be beneficial for SO₂ absorption, are not present in the KRW LASH, and KRW and Tampella DASHs contributing to poor SO₂ absorption capacity of these solids. Pores of about 0.05 to 0.5 micron in diameter, found in fresh sorbents, are however present in FW DASH and TRTU LASH. The good SO₂ absorption capacity of these solids may be attributed to the presence of these pores. Although FW LASH contains pores in the above range, it did not absorb SO₂ as well as these solids.

1.4 LASH/DASH Oxidation Studies in TRTU

1.4.1 Oxidation of KRW LASH

The Transport Reactor Test Unit (TRTU) is a circulating fluidized bed reactor capable of continuous operation. It consists of a riser which is 0.5 inch Schedule 40 pipe and 30-ft tall located inside a 3-inch ID pipe that serves as a pressure vessel. The riser is equipped with a cone valve-eductor solids circulation control device at the bottom. The annulus between the pressure vessel and the riser is used as the solids downcomer leg from which heated solids are circulated into the riser and mixed with fresh feeds. Reactions occur in the riser. Solids are educted into the riser by the high velocity gas entering the bottom of the riser.

Batch oxidation of the fine KRW LASH in the TRTU at 1600°F yielded oxidation levels up to 80%. For the batch oxidation of the coarse KRW LASH also at 1600°F, an oxidation level of 66% was obtained. The difference in the oxidation of the fine and the coarse KRW LASH may be attributed primarily to the difference in the particle size.

1.4.2 Continuous Oxidation of KRW LASH

Comparison of results of steady-state periods for the coarse and fine LASHs indicates that the oxidation level was about the same ($\sim 40\%$) in both cases, although the riser bed density was 4.6 lb/ft^3 for the fine LASH versus 12.7 lb/ft^3 for the coarse LASH, showing that better performance was achieved with the fine LASH. With an increase in the riser bed density from 4.6 to 11.5 lb/ft^3 for the fine KRW LASH, an increase in the oxidation level from 40 to 62% was obtained. With an increase in the partial pressure of O_2 from 1.7 to 4.5 psi at the riser exit, the oxidation level of fine LASH increased from 52 to 74% , as can be expected from the nature of the reaction. For the coarse KRW LASH, a slightly higher oxidation level (50%) was obtained in the annulus compared to that of the riser (46%).

Oxidized KRW LASH was found to have negligible capacity to absorb SO_2 .

Solid residence time per pass in the riser varied over a narrow range of 1.3 to 1.9 seconds and the number of passes varied from 105 to 470 with the assumption of a slip ratio (ratio of actual gas velocity to the actual solid velocity) of 2 based on previous experience.

1.4.3 Oxidation of FW LASH/DASH

Batch Oxidation of FW LASH and FW DASH in TRTU

The testing of FW LASH and DASH in the TRTU can be summarized as follows:

- Oxidation of the FW LASH was poor. Final oxidation levels of only $20\text{-}30\%$ were achieved.
- Oxidation of the FW DASH was much better than LASH oxidation. The data indicated that $70\text{-}90\%$ oxidation could be achieved.
- Both materials readily absorbed SO_2 .
- Oxidation of both materials at temperatures approaching 1600°F at zero oxygen partial pressure in the outlet gas (essentially all the oxygen fed was consumed in the TRTU prior to the outlet gas oxygen measurement) resulted in appreciable evolution of SO_2 .

1.5 Testing of LASHs/DASHs As Per Interim EPA Test

Samples of LASHs and DASHs were tested as per the EPA interim test to evaluate solid wastes in terms of the amount of H_2S released upon contact with an aqueous acid. The following is a summary of the results:

- Both AR and oxidized CF KRW LASHs passed the test although they contained fairly high amounts of CaS (6.1 and 15.2% respectively) as a result of higher temperatures to which they were exposed compared to the other LASHs resulting in poorer oxidation levels.
- The AR FW LASH passed the test while the CF solids from a different batch failed the test as a result of higher CaS (7.5%) content. The AR TRTU LASH failed the test, as it was more reactive, due to the lower temperature at which this was produced compared to the KRW and FW LASHs, and the appreciable CaS (6.3%) content.
- As-received and partially oxidized KRW DASH and AR FW DASH failed the test. The partially oxidized KRW DASH contained a high amount of CaS (15.8%) and, hence, failed the test despite the higher temperature at which it was produced. The oxidized FW DASH (2% CaS) passed the test.

The limited database of materials tested prevents drawing general conclusions about whether a specific material will pass or fail the interim EPA test. It would appear that the properties of the initial sorbent, level of oxidation and/or CaS level, and the materials processing temperature history in the gasifier/carbonizer have an impact on the materials propensity to release H_2S under the conditions of the interim EPA test.

SECTION 2.0 - INTRODUCTION

All of the emerging coal gasification technologies under development that use calcium-based sorbents for sulfur control have a common problem, i.e., the disposal of CaS produced in the gasification step by absorption of H_2S . Since the CaS is not a suitable waste material, due to the potential release of H_2S upon inadvertent acidification in the waste disposal area, the material must be treated to render it inert. Although several different concepts are potentially feasible, a direct approach to the problem is oxidation at high temperature to $CaSO_4$, an acceptable waste product. This approach is attractive, since it eliminates the need for any further processing. The major effort of this study was devoted to investigate the feasibility of this approach and to determine the conditions that lead to a high degree of oxidation.

In general, studies done to date have shown the difficulty of converting CaS to $CaSO_4$ due to coating of micron-size grains of the sulfide with reaction product.^{1,2,3,4,5} Heavily-sulfided limestones, in particular, are difficult to sulfate. As the degree of sorbent sulfidation is reduced, the sulfide oxidation becomes easier since it is being confined increasingly to the solid surfaces and does not have to penetrate the grains. Sulfided dolomitic sorbents are also more easily oxidized, presumably due to the effect of the inert magnesium oxide in increasing the porosity of solids. Prior to this study, only limited testing was done on actual pilot plant solids.^{1,4,5}

The technologies referred to previously include both advanced coal gasification processes and second generation pressurized fluid bed combustion systems, that combine coal gasification with coal/char combustion. Consequently, the conditions under which the sulfide-bearing material is produced may vary considerably. In addition, the options for oxidation of the sulfide may be restricted by the process concept, as, for example, in the case of PFBC systems wherein the oxidation must occur within the coal/char combustor. These constraints defined the boundaries within which the experimental program was carried out.

To carry out the experimental investigations, CaS-containing materials from existing pilot plants or development units were used. This was in contrast to the original experimental approach to produce materials for Task 5 oxidation by simulating experimentally gasifier/carbonizer conditions on the bench-scale to make CaS-containing samples directly from representative fresh sorbents and coals. It was concluded that materials from larger scale units would be produced in a localized environment more representative of commercial gasifier/carbonizer operations than could be obtained on the bench-scale; however, it was also recognized that the selection of materials from these larger units would be limited in terms of range of stoichiometry, sorbents, coals, and overall operating conditions under which they were produced. Tests with these materials were supplemented by additional tests, as needed, with these materials modified to better reflect the expected range of commercial operation. Several candidates were identified for testing in the experimental study. These were solids that were produced in the KRW Gasifier Process Development Unit, Kellogg's Transport Reactor Test Unit, Foster Wheeler's carbonizer, and the Tampella pilot plant (Finland). Samples from all the four

units were available for the test program. The sample from the Tampella unit was a DASH produced from an unidentified dolomite. Table 2.1 compares some of the relevant expected commercial operating conditions for these systems.

Table 2.1 – Commercial Conditions in Gasifier Systems

<u>TECHNOLOGY</u>	<u>KRW/U-GAS</u>	<u>MWK</u>	<u>FW</u>
Gasifier Type	agglomerating fluid bed	transport bed	fluid bed carbonizer
Operating Temperature	high	moderate	moderate
Feed Particle Size	-1/4"	100-500 μ	-1/8"
Coal Conversion (gasifier)	90+ %	60-90+ %	50-70%
Ca/S, overall (typical)	1.5-2	1.5-2	1.5-2
Sulfidation level in gasifier	45-60%	25-60%	20-30%

Project Description

The project was a 40-month effort to investigate the complex influence of calcium-based sorbents on coal conversion. The work was divided into six tasks. Tasks 1 and 2 dealt mostly with overall project related activities, with preparation of test equipment, and with preparation of a literature search on the subjects of the three experimental tasks. The experimental part of the project was separated into three tasks: Task 3 – studies on sulfidation of calcium-based sorbents, Task 4 – kinetic studies to understand the mechanisms of calcium-catalyzed carbon gasification reactions, and Task 5 – studies on oxidation of CaS to CaSO₄ in order to identify and investigate different methods to oxidize the sulfide and to further develop a promising method. Task 6 was the economic evaluation of the most promising sulfide oxidation technique developed under this program. The knowledge to be obtained from Task 5 activities were judged to be critical to the successful commercialization of the associated coal technologies; therefore, major emphasis in terms of resources was directed to this task.

A condensed version of the literature review, performed under Task 1, is presented in Appendix A. The literature search was used to determine the status of current knowledge of the technologies associated with the three experimental Tasks to provide guidance in proposing the detailed experimental test plans for the project.

2.1 Introduction To Testing

As mentioned earlier, the R&D work performed prior to this study has not resulted in any definitively attractive method to achieve an acceptable conversion of CaS to CaSO_4 . The test philosophy placed a greater emphasis on problem solving rather than on fundamental aspects.

The main objective of the study was to oxidize the CaS produced in the units listed below, typical of fluid bed gasifiers and carbonizers to achieve high conversion (>90%) as part of Task 5:

- a fluid bed gasifier such as the KRW pilot plant or the Tampella pilot plant,
- a fluid bed carbonizer of the Foster Wheeler second generation Pressurized Fluidized Bed combustion system, and
- a Kellogg's transport gasifier.

Additional objectives were to obtain fundamental kinetic information on sulfidation reactions and to produce sulfided samples, if necessary, as part of Task 3, and to study the catalytic effect of calcium on carbon gasification reactions as part of Task 4.

In the first two types of reactors, the particle size distributions are about the same and the mean size is about 1000–200 microns. The difference between the two types of reactors is the level of sulfidation and the presence of an appreciable quantity of unconverted carbon in the FW unit. In the transport reactor, the mean particle size is in the range of about 100–500 microns. Thus, it is important to investigate the effect of particle size on the oxidation of sulfide in addition to the operating parameters such as temperature, pressure, and O_2 concentration. Two bench-scale facilities were used for this testing in the batch mode: the Bench-scale Reactor Unit (BRU), and the Atmospheric Thermogravimetric Analyzer (ATGA). A sub-pilot scale facility, the Transport Reactor Test Unit (TRTU), was used for testing in the batch and continuous modes.

Several investigators have reported catalytic enhancement of gasification due to the presence of calcium in the carbon matrix.^{6,7,8,9} Since coal devolatilization and gasification take place in the presence of calcium in all the above three processes, it is important to investigate the effect of calcium on carbon gasification reactions and devolatilization. The study of the catalytic effect may be important only for the two fluid bed gasification technologies where the presence of a central jet (the bed temperatures are substantially higher in the central jet than in the rest of the bed) appears to contribute to calcium impregnation of char. The catalytic effect of calcium may not be as pronounced or significant either in the transport gasifier or in the FW carbonizer since calcium may not be embedded in the carbon matrix and thus may not have an appreciable effect on gasification.

2.2 Description of Tests

Oxidation of LASHs/DASHs (Task 5)

As part of Task 5, studies were conducted on the oxidation of CaS to develop a viable technique to achieve high levels of oxidation (>90%) using LASH and DASH samples produced in the various pilot plants (TP and KRW pilot plants, FW carbonizer, and TRTU). Samples representative of the FW carbonizer, the KRW gasifier, and the transport gasifier were used to perform LASH/DASH oxidation studies to develop viable techniques suitable for application to the three technologies.

Prior to oxidizing the solids from various pilot plants, unconverted carbon was combusted from these solids. In some of the tests, the sulfidation level in these samples was increased to nominally 60%, that is typical of expected level in a commercial unit, in the quartz reactor prior to conducting the oxidation studies. Samples from the various pilot plants were found to be suitable. There were no problems either due to aging or low levels of sulfidation of the samples. Samples with a low sulfidation level such as 20 to 30% were shown to be oxidized to fairly high levels in the earlier studies performed at KRW Energy Systems, Inc.⁵ A general description of the tests is given below.

- (1) Selected samples from the KRW pilot plant, TP pilot plant, FW carbonizer, and Kellogg's TRTU were oxidized in the BRU. Samples were injected batchwise into the BRU reactor in an oxidizing atmosphere to oxidize the sulfide. Oxidation of the samples was performed after combusting the carbon present in the sample since the carbon-containing samples could not be processed in the BRU since temperature control was a problem while maintaining an oxidizing environment. Selected samples were ground to about 70x140 mesh to determine the effect of grinding. This was necessary since the average size of particles that could be processed in the TRTU was about 100-300 microns.
- (2) Simultaneous oxidation of CaS ($\text{CaS} + 2\text{O}_2 \rightleftharpoons \text{CaSO}_4$) and the sulfation of CaO ($\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{CaO} \rightleftharpoons \text{CaSO}_4$) were studied in order to simulate the operation of the sulfator/combustor that is proposed for the SPPCo Project. The SPPCo Piñon Pine Power Project is a demonstration project based on the IGCC concept using the KRW air-blown, pressurized, fluidized-bed coal gasification system. In the project, a nominal 800 tons/day of coal is converted into 86 MW_e (gross) of electrical power. Crushed limestone is added to the gasifier to capture a portion of the sulfur that reacts with the limestone to form CaS, which, after oxidation, exits along with coal ash in the form of agglomerated particles suitable for landfill. This plant is being built at Tracy Station, near Reno, Nevada.

SO₂ absorption capacity of the fresh and partially sulfided forms of the sorbent proposed for this project has been studied since the external desulfurizer regeneration offgas will be recycled to the sulfator/combustor for absorption of additional sulfur by the sorbent. In addition, the oxidation of KRW LASH is

relevant to the project since the LASH produced in this plant is expected to possess similar characteristics.

These tests were done in the quartz reactor to determine the extent of oxidation and the extent of absorption of SO_2 that could be achieved over a range of operating conditions.

- (3) A promising technique appeared to be additive oxidation (oxidation of LASHs after adding an additive) based on earlier studies performed at KRW Energy Systems. The effect of adding an alkali (sodium carbonate) to the sulfided material was investigated. Poorly oxidized materials in the above tests were selected for this study. The BRU was used for conducting these studies supplemented by tests on an atmospheric thermogravimetric analyzer (ATGA). The additive investigated in this study was selected based on prior studies and its possible effect on leachates to meet environmental regulations was not studied. The amount of additive required was not investigated. In addition to oxidation with the selected samples, limited testing was done to examine the effect of grinding on additive oxidation.
- (4) The effect of "weathering" (oxidation in the presence of saturated air) was studied using a sample that was partially oxidized to determine its viability. The effect of moisture content was not investigated.
- (5) Based on the results of the studies that were performed in the BRU, a limited number of tests were carried out in the Transport Reactor Test Unit (TRTU) to demonstrate the concept in a continuous mode and to establish optimum operating conditions (temperature, pressure, O_2 concentration, etc.) and to obtain data required for process design.

Sulfidation Kinetics (Task 3)

Sulfidation kinetics studies were assigned a lower priority and subsequently were not studied due to constraints of time and money.

Gasification Kinetics (Task 4)

Determination of the possible catalytic effect of calcium on carbon gasification and coal devolatilization was assigned a lower priority and subsequently was not studied due to constraints of time and money.

SECTION 3.0 - EXPERIMENTAL

3.1 Introduction

The test facilities include a pressurized thermogravimetric analyzer (PTGA), an atmospheric thermogravimetric analyzer (ATGA), a bench-scale reactor unit (BRU), a horizontal quartz reactor consisting of a fixed bed, and a transport reactor test unit (TRTU). A brief description of these units is given in this section and the test programs accomplished in these facilities are discussed separately in other sections.

Depending upon specific test objectives, solids were used either as received, or ground to a mean size of about 150 to 250 microns. The materials were modified, as needed, to increase the level of sulfidation to be more representative of expected commercial operating conditions and to remove the carbon from the solids. Some samples were additionally treated with an alkali (sodium carbonate) as per test objectives. In the following description, DASH represents a mixture of dolomite and ash and LASH represents a mixture of limestone and ash. Solid samples were analyzed for calcium compounds, carbon content, and sulfur content to determine the utilization of calcium and the sulfidation level of the sample. Carbon-free LASH and DASH were produced in a muffle furnace by burning off carbon at a temperature of about 1200°F in 8-10% O₂. The temperature was monitored to ensure that the temperature of solids did not exceed about 1400°F by monitoring the bed temperature to prevent any sintering during preparation. The muffle furnace is equipped with a gas sparger for distributing the oxidant evenly in a tray used for processing solids.

3.2 Description of Bench-scale Reactor Unit (BRU)

The BRU facility, shown in Figure 3.1, consists of a 2-inch ID reactor made of Incoloy 800H contained in a cool-wall pressure vessel and ancillary gaseous feed, steam, and product recovery systems. Bed solids are supported on the distributor plate within the reactor. The reactor is surrounded by electric heaters for temperature control. Reacting solids can either be placed inside the reactor prior to assembly or can be subsequently injected under pressure during a test. The feed gases are electrically preheated. If required, water is injected into the gas stream and vaporized. The resulting gas stream enters the reactor through the bottom and fluidizes the material. The BRU facility can be operated at temperatures up to 1950°F at pressures up to 450 psig.

Sand was found to be a suitable inert bed material for the experiments. Based on a few shakedown runs in the BRU and fluidization studies performed in a cold flow model, it was determined that the sand had good fluidization properties and was still separable from the injected solids by simple screening. This has the advantage of moderating the temperature increase due to the exothermic reactions and stabilizing the bed temperature in a relatively short period of time. A known amount of inert bed material was used, and the expanded bed height was maintained such that the height to diameter was in the range of 1-2. The reactor was pressurized to a desired level and

then heated to a desired operating temperature at which time air was introduced and fluidization velocity was maintained at a U/U_{cf} ratio (operating superficial velocity/complete fluidization velocity) of between 1-2. The U_{cf} determined at ambient conditions was used to estimate the U_{cf} at operating conditions. When the fluidized bed reached a desired temperature, air flowrate was reduced so that about 25-30 grams of CaS-containing solids could be injected into the bed. The experiment was continued to oxidize the CaS for a desired time period while monitoring the SO_2 concentration with an online SO_2 analyzer and bed temperatures near the bottom and the top. At the end of the experiment, all gas flows were shut off; and the reactor was allowed to cool in order to prevent any possible decomposition of Ca-S compounds in a N_2 atmosphere. The unit has significant thermal inertia, taking overnight to cool sufficiently to be re-opened.

3.3 Description of Pressurized Thermogravimetric Analyzer (PTGA)

The PTGA facility consists of a 2-inch ID quartz reactor tube. The solid sample needed for the reaction under study is placed in a platinum mesh basket located in the center of the reactor tube and suspended from a weighing head. A variety of sample baskets can be used in the reactor. The unit can be operated up to temperatures of 2000°F at pressures up to about 1000 psig.

3.4 Description of Atmospheric Thermogravimetric Analyzer (ATGA)

An atmospheric thermogravimetric analyzer (ATGA) was used to study the fundamental kinetics of oxidation of LASH (18x100 mesh) at 1700°F in air. It consists of a DuPont 951 thermobalance, a DuPont 9000 console for controlling the heating rate and run time, a data acquisition system, and a personal computer for data storage, retrieval and analysis. Data acquisition is accomplished using Lotus Measure software, a Lotus Corporation product. Samples are placed in a platinum-mesh screen shaped into the form of a basket and suspended from the balance arm.

3.5 Description of Quartz Reactor

The experimental apparatus consists of a quartz reactor (1.65-inch I.D. and 15 inches long), in a horizontal fixed bed configuration, with a quartz fritted disc for gas distribution, that is heated by an electrical furnace. The outlet of the quartz reactor has a ball and socket joint with an O-ring for a gas-tight connection and easy replacement of solids. The reactor was packed with the desired solids, and quartz wool was then placed in both ends to hold the solids firmly in position. The length of the bed generally ranged from 10-12 inches. The wall temperature was monitored near the inlet, the middle, and the outlet locations of the bed by means of thermocouples strapped to the outside of the reactor. The gas leaving the packed bed was passed through bubblers to scrub the gas of any sulfur compounds present before venting it to the atmosphere. There was a provision to measure the concentration of H_2S or SO_2 by means of Draeger tubes before the gas entered the bubblers. All experiments were performed at atmospheric pressure.

Figure 3.1 Sketch of Bench-Scale Reactor Unit (BRU)

3.6 Description of Transport Reactor Test Unit (TRTU)

The TRTU is a circulating fluidized bed reactor, shown in Figure 3.2, capable of continuous operation. It consists of a riser which is 0.5-inch Schedule 40 pipe and 30-foot tall located inside a 3-inch ID pipe that serves as a pressure vessel. Both pipes are made of Incoloy 800HT that is resistant to both H_2S and SO_2 at operating temperature. The riser is equipped with a cone valve-eductor solids circulation control device at the bottom and is contained in an outer pressure vessel. The annulus between the pressure vessel and the riser is used as the solids downcomer leg from which heated solids are circulated into the riser and mixed with fresh feeds. Reactions occur in the riser and solids and gases are injected into the riser at the bottom and flow upward through the tube. Perforations are provided through the bottom flange for sparging N_2 and to fluidize solids in the annular space, coal feed gun, and eductor feed line. Heat to the unit is supplied by six zone electric heaters, each of which is separately controlled. The TRTU can be operated at temperatures up to 1950°F and pressures up to 90 psig (300 psig with some additional equipment).

3.7 Summary of Tests

Conditions for the tests performed on LASH/DASH oxidation in the BRU and SO_2 and H_2S absorption in the quartz reactor are summarized in Tables 3.1 to 3.3.

Table 3.1 - Tests Performed on LASH/DASH Oxidation in the BRU

Material	Temperature, °F	Test No. 5-
LSCF KRW LASH	1500, 1600, 1700	6, 5, 9
LSCF FW LASH	1500, 1600, 1700	8, 7, 10
LSCF ground KRW LASH	1700	19
LSCF doped KRW LASH	1700	20
LSCF ground and doped KRW LASH	1700	21
LSCF Tampella DASH	1700	12
HSCF KRW LASH	1700, 1800	14, 15
HSCF ground KRW LASH	1600, 1700	18, 16
HSCF ground and doped KRW LASH	1700	17
HSCF FW LASH	1600, 1700	11, 13
CFHS FW LASH	1700	22
CFHS ground FW LASH	1700	24
CFHS doped FW LASH	1700	23
CFHS ground and doped FW LASH	1700	25
CFHS KRW LASH	1700	26

(cont'd)

Table 3.1 – Tests Performed on LASH/DASH Oxidation in the BRU (cont'd)

Material	Temperature, °F	Test No. 5-
CFHS ground KRW LASH	1700	28
CFHS doped KRW LASH	1700	29
CFHS ground and doped KRW LASH	1700	27
CFHS ground KRW LASH soaked in H ₂ O	1700	30
HSCF TRTU LASH	1700	31
HSCF doped TRTU LASH	1700	32
CFHS KRW LASH-repeat	1700	33
LSAR KRW LASH	1800	34
CFHS KRW LASH	1700	35
CFHS KRW LASH	1700	36
LSCF FW DASH	1700	37

Table 3.2 – Tests on SO₂ Absorption by Sorbents* in the Quartz Reactor

Sorbent	Temperature, °F
SP limestone	1600, 1700, 1800
Greer limestone	1600, 1700
Longview limestone	1600
LSCF KRW LASH	1600
LSCF KRW LASH (Doped)	1600
LSCF FW LASH	1600
LSCF FW DASH	1600
LSCF TRTU LASH	1600
TP DASH	1600
Sulfided (10%) SP limestone	1600
Sulfided (10%) Greer limestone	1600
Sulfided (15%) PR dolomite	1600
Mixture of KRW LASH-Greer limestone	1600
Mixture of FW LASH-Longview limestone	1600
Sulfated (20%) Greer limestone	1600
Sulfated (20%) SP limestone	1600
Mixture of FW DASH-PR dolomite	1600
Sulfated (40%) PR dolomite	1600
LSCF KRW DASH	1600

* For solids containing CaS, sufficient time was allowed to oxidize the sulfide to sulfate or sufficient additional O₂ was supplied for studies on simultaneous oxidation and SO₂ absorption.

Figure 3.2 Transport Reactor Test Unit Configuration

Table 3.3 - H₂S Absorption by Sorbents in the Quartz Reactor

Sorbent	Temperature, °F
SP limestone	1800
Greer limestone	1800
KRW LASH	1800
FW LASH	1800
TP DASH	1800

3.8 Analytical Aspects

Calibration of SO₂ Analyzer

The online SO₂ analyzer was calibrated using certified gases of SO₂ in nitrogen at different concentrations in order to determine the accuracy of the instrument, particularly at low concentrations that are more pertinent to the studies. Also, the response time of the SO₂ analyzer was found to be less than one minute when the SO₂ concentration was changed from 927 to 12 ppm. The results of the calibration are given in Table 3.4.

Table 3.4 - Calibration of SO₂ Analyzer

SO ₂ conc. certified, ppm	SO ₂ conc. as measured, ppm
12	12 ¹
100	100
0	0 ²
12	11
498	497
927	934

¹ Zeroed with air and spanned with calibration gas of 927 ppm of SO₂ in N₂.

² Zeroed with air and spanned with calibration gas of 100 ppm of SO₂ in N₂.

Note that the accuracy of the instrument is about one ppm for SO₂ concentration of less than 500 ppm. The SO₂ concentration was recorded during each run on a

personal computer and the %CaS decomposed was computed at the end of each test based on integrated values of the SO₂ concentration profile measured during the test. The SO₂ concentration as measured by the on-line analyzer, at a level of about 250 ppm, was also confirmed by analysis done by means of a Draeger tube.

Blank Run to determine SO₂ absorption in BRU

A blank run was made in the BRU following test 5-33 (description of the test is given in Section 4.0). The reactor containing a bed of sand was heated by flowing air through the reactor as normally done in a typical test. In the temperature range of 1460 to 1685°F and over a period of 42 minutes, the SO₂ concentration varied with a maximum value of 13 ppm. The quantity of SO₂ evolved, obtained by integrating the SO₂ concentration profile over this period, amounted to 0.36% of CaS present in the sample oxidized during test 5-33. This is negligible. At 1700°F, calibration gases containing SO₂ at different concentrations were introduced and the SO₂ concentration in the offgas was measured by the SO₂ analyzer. Table 3.5 shows a comparison of the SO₂ concentration in the calibration gas (as measured by the analyzer) before introducing it into the BRU and SO₂ concentration in the offgas downstream of the reactor.

Table 3.5 - Absorption of SO₂ Downstream of Reactor

SO ₂ conc. in calibration gas, ppm	SO ₂ conc. in offgas, ppm	Difference in SO ₂ conc., ppm
9	9	0
99	95	4
496	483	13
937	925	12

At 10 ppm level of SO₂ concentration, no SO₂ absorption was observed. At 496 ppm level of SO₂ concentration, a small, but appreciable amount of SO₂ was absorbed downstream of the reactor. At the 99 ppm level, the difference of 4 ppm would amount to 0.36% of CaS converting to CaO in the case of test 5-33. This is negligible. In some of the actual tests, the SO₂ concentration was about 10 ppm for an extended period of time. A sustained SO₂ concentration of 100 ppm or higher was never observed in any of the tests. Thus, the blank run showed that negligible SO₂ absorption took place on the reactor wall or downstream of the reactor during the tests.

3.9 Properties of Feedstocks

The composition in weight per cent of LASHs and DASHs used in this study, and the average and maximum bed temperatures to which these solids were exposed in the units in which they were originally produced are given in Table 3.6. If a different batch of solids is used for any particular study, its composition is given in the relevant section.

Table 3.6 – Composition of LASHs and DASHs

AL No.	4592	4926			
Material	KRW	FW	FW	TRTU	TP
	LASH	LASH	DASH	LASH	DASH
Sulfide Level	AR	AR	AR	AR	LSCF
CaO, %	23.50	1.63	5.36	1.57	15.71
CaSO ₄ , %	0.51	0.76	0.55	0.55	6.28
CaS, %	15.20	4.14	18.47	6.01	0.00
MgO, %	13.60	0.35	18.24	0.21	11.14
Inerts, %	46.79	25.27	21.64	68.82	66.87
CaCO ₃ , %	0.00	18.59	10.84	3.52	0.00
carbon, %	0.40	49.25	24.90	19.32	0.00
Ca Ut., %	35.00	23.00	56.00	58.00	14.13
Bed Temp., °F	1858- 1950	1605	1698	1850	-
Max Bed Temp., °F	2111- 2268	-	-	1850	-

Max Bed Temp. – maximum temperature to which the solids were exposed.

AL No. – refers to a traceable reference number assigned to the material prior to chemical analysis.

A range of temperatures indicates variation with time.

The composition of the limestones and the dolomite used in SO₂ absorption studies is given in Table 3.7.

The size distribution of carbon-free KRW LASH (carbon had to be combusted prior to gas absorption studies since the objective was to study SO₂ absorption only) is given in Table 3.8.

Table 3.7 – Composition of Fresh Sorbents

Comp. wt%	NE limestone	Longview limestone	Greer limestone	SP limestone	PR dolomite
CaCO ₃	66.80	97.45	77.45	97.85	54.22
MgCO ₃	18.80	1.58	4.05	1.44	45.78
SiO ₂	10.01	0.20	12.60	0.55	0.00
Al ₂ O ₃	1.76	0.74	3.00	0.15	0.00
Others	2.63	0.03	2.90	0.01	0.00

Table 3.8 – Size Distribution of CF KRW LASH

Sieve size, mesh	wt%
+18	18.2
18x30	49.2
30x40	16.2
40x50	12.1
-50	4.2

The size distribution of KRW LASH used in the BRU for LASH oxidation studies, except when studying the effect of grinding, was -18 mesh in order to separate it from the inert bed material.

SECTION 4.0 - LASH/DASH OXIDATION STUDIES IN BRU

4.1 Introduction

The effect of bed temperature, grinding the LASHs, and impregnating the ground- and unground LASHs with an alkali on the oxidation of CaS was studied using both KRW and FW LASHs. These solids were formed at different gasification conditions that are relevant in studying their oxidation ($\text{CaS} + 2\text{O}_2 \rightleftharpoons \text{CaSO}_4$) and sulfation ($\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{CaO} \rightleftharpoons \text{CaSO}_4$) characteristics. KRW LASH was formed in a fluidized bed with a central jet where the temperatures were substantially higher than in the fluidized bed utilized by the FW process. The feedstocks used to produce KRW LASH were Upper Freeport coal and NE limestone that is of dolomitic type. The feedstocks used to produce FW LASH were Illinois No.6 coal and Longview limestone that is a high-calcium type. Thus, studies on both materials were expected to show the effect of these differences on oxidation. Only carbon-free materials could be processed in the BRU since temperature control was a problem while maintaining an oxidizing environment if appreciable carbon was present in the sample. Oxidation level is defined as the fraction of CaS converted to CaSO_4 during oxidation. Inerts reported in the various tables include the ash from coal and inert material from limestone or dolomite. Calcium utilization is calculated as the sum of moles of CaSO_4 and CaS divided by total moles of calcium in sample. The standard experimental conditions used in the BRU are given in Table 4.1.

Table 4.1 - Experimental Conditions in the BRU

Particle size	18x100 mesh for LASHs and DASHs
Distribution	(149 to 1000 microns) 80x270 mesh for TRTU LASH (53 to 177 microns) 70x140 mesh for ground solids (105 to 210 microns)
Gas composition	air
Operating temp.	1500-1700°F
Operating Pressure	atmospheric

4.2 Results and Discussion

4.2.1 Effect of Temperature

The effect of temperature on the oxidation of as-received (lightly sulfided) and carbon-free KRW LASH was studied over the temperature range of 1500 to 1700°F in air for a period of an hour. Oxidation achieved in the BRU as a function of temperature is shown in Figure 4.1. Oxidation is calculated based upon CaS content in the material

produced in the PRU and that of the feed. A conversion of about 20% was obtained during carbon burn-off in the muffle furnace. Based on these results, the temperature of 1700°F appears to be the most preferred, giving the highest level of oxidation.

Figure 4.1 Effect of Temperature on Oxidation of KRW and FW LASHs

The effect of temperature on the oxidation of as-received (lightly sulfided) and carbon-free FW LASH was also studied over the temperature range of 1500 to 1700°F in air over a period of an hour. The effect of temperature on oxidation achieved in the BRU for FW LASH is also shown in Figure 4.1. Oxidation is calculated based on the CaS content in the material before and after processing in the BRU. Based on these results, the highest level of oxidation for the FW LASH was also obtained at 1700°F, the highest temperature studied. The reason for appreciably lower conversions for FW LASH compared to KRW LASH may be attributed to the differences in the characteristics of the limestones used and the process conditions at which the LASHs were formed. No appreciable SO₂ evolution was observed in any of these tests, based on SO₂ on-line analyzer. All the subsequent tests were performed at 1700°F in order to investigate the effect of sulfidation level, grinding and impregnating with an alkali with both KRW and FW LASHs.

4.2.2 Effect of Grinding and Alkali Impregnation

The effect of impregnating the solids with 2 wt% Na_2CO_3 solution was studied using both KRW and FW LASHs. In order to study the effect of grinding, samples were ground to a size distribution of 70x140 mesh. The concept of adding an alkali to LASHs originated with the reporting of numerous studies on catalytic gasification of coals and chars. A variety of alkali-impregnation techniques were employed by various researchers and no single technique emerged as the best.

The oxidation of heavily-sulfided materials was studied by processing the solids by two methods. In the first method, the as-received LASHs were first sulfided in a quartz reactor, in a fixed bed mode, to increase the sulfidation level and then processed in a muffle furnace to burn off the carbon since only carbon-free solids can be oxidized in the fluidized bed. These materials are denoted as HSCF LASHs. The sulfidation levels achieved for KRW and FW LASHs are given in Section 3.0. These solids were oxidized in the BRU at 1700°F and atmospheric pressure for an hour. In the second method, carbon present in the solids was first burnt off and then the solids were sulfided in the quartz reactor to increase the sulfide level. These materials are denoted as CFHS LASHs. The sulfided solids were used to study the effect of alkali impregnation on the oxidation of both ground and unground solids. The alkali level in the sample was determined by gravimetric analysis.

The oxidation levels achieved for ground and impregnated samples of both HSCF KRW LASH and CFHS FW LASH are about the same. This suggests that it might be difficult to oxidize the last remaining CaS in the samples at the conditions studied. However, the oxidation of the untreated samples appears to be different. Grinding the FW LASH enhanced the oxidation level while it showed no effect on the KRW LASH. A detailed description of these tests is given in sections 4.2.3 and 4.2.4.

4.2.3 Oxidation of KRW LASH

A detailed description of all the tests performed with KRW LASH is given in this section.

Test 5-5 was conducted at a nominal temperature of 1600°F and atmospheric pressure. A 25-gram sample of carbon-free LASH was injected into a 200-gram bed of sand (Red Flint #30) in this test. No SO_2 evolution was observed at any time during the test. Test 5-6 was conducted in the BRU using the same procedure as that of test 5-5 to oxidize the KRW LASH at a nominal temperature of 1500°F and at about 25 psig in air. No SO_2 evolution was observed. It took about 10 minutes to stabilize the bed temperature after injecting solids into the bed in this test. Test 5-9 was conducted with the KRW LASH at a nominal temperature of 1700°F to determine an optimum temperature from these tests. The solids analyses are given in Table 4.2. The size distribution of KRW LASH used in the BRU was 18x100 mesh in order to separate it from the inert bed material (+18 mesh) by simple screening.

Table 4.2 - Results on Oxidation of KRW LASH

AL No.	4873	4882*	4887	4889+	4901
Test No.	Start	5-4	5-5	5-6	5-9
Material	KRW LASH	KRW LASH	KRW LASH	KRW LASH	KRW LASH
Temp, °F	-	1700	1600	1500	1700
CaO, %	23.04	27.33	20.60	24.45	20.53
CaSO ₄ , %	5.14	17.23	13.37	11.59	18.55
CaS, %	13.34	4.32	8.30	9.74	5.42
MgO, %	16.21	14.64	13.90	14.17	13.62
Inerts, %	42.23	36.48	43.83	40.05	41.78
Ca Ut., %	35.12	27.65	36.71	33.53	36.58
S Conv, %	-	52.29	34.90	27.11	58.39

*There was some sulfur loss during the test. Not corrected for sulfur loss.

+This test was conducted at 25 psig.

Test 5-14 was conducted with carbon-free and heavily-sulfided (CFHS) KRW LASH at a nominal temperature of 1700°F. There was no temperature increase during this test. During the first minute of the test, SO₂ evolved at 70 ppm level and rapidly decreased to about 7 ppm; and then it slowly decreased to about 1 ppm at the end of the test.

Test 5-15 was conducted to oxidize heavily-sulfided and carbon-free (HSCF) KRW LASH at a nominal temperature of 1800°F for an hour. The bed temperature decreased from 1800°F to 1762°F after injecting solids and then it increased slowly and steadily to 1780°F toward the end of the run. During the first minute of the test, SO₂ concentration increased to 425 ppm and then decreased to 21 ppm rapidly. It decreased gradually to about 3 ppm towards the end. The total loss of sulfur in the test was minimal. Based on this small temperature increase, appreciable oxidation was not expected.

Test 5-16 was conducted with finely ground (70x140 mesh) HSCF KRW LASH at 1700°F for an hour. The LASH was injected into a bed of -140 mesh sand (Pioneer #5 ground to this size). For the test, the fluidization velocities measured in a cold flow unit were used to calculate the flows required to fluidize the bed in the BRU. There was an appreciable temperature increase during this test. The temperature increased up to 1778°F and was reduced to about 1700°F. The evolution of SO₂ was minimal in the test. SO₂ concentration was initially at 18 ppm level and then decreased to about 3 ppm in 10 minutes and later to one ppm.

Test 5-17 was conducted by injecting ground and alkali-impregnated HSCF KRW LASH (heavily-sulfided and carbon-free) into a bed of sand and oxidizing it at a nominal temperature of 1700°F for an hour. The bed temperature increased rapidly to about 1787°F in 3 minutes and further increased to about 1825°F in about 10 minutes and remained relatively constant at this temperature for the remainder of the test. The SO₂ concentration initially was about 12 ppm and later decreased to about 4 ppm and remained constant at this level for the rest of the test. The increase in bed temperature, in the absence of any significant SO₂ evolution, is an indication of appreciable oxidation level of the sample. The solids analysis in test 5-17 indicated that the sulfide was converted to oxide. However, no SO₂ evolution was observed (as measured by the SO₂ analyzer and confirmed by analysis using Draeger tubes) during the test to account for this conversion and at the flowrates used, this is expected to result in SO₂ concentration of about 140 ppm on the average for the test. In order to verify whether the sulfide was converted to sulfate or oxide and to confirm the level of oxidation achieved in the BRU, three tests were done on the ATGA with untreated, ground, ground and alkali-impregnated CFHS FW LASHs. All three tests showed that CaS present in the samples was oxidized to sulfate rather than to oxide (weight gain was observed). These results are discussed later in a separate section.

Test 5-18 was conducted with finely-ground HSCF KRW LASH (70x140 mesh) by injecting it into a bed of fine sand (-140 mesh) and oxidizing it at 1600°F. The temperature of the bed, after the usual initial drop, increased from 1610°F to 1634°F in about 7 minutes and then increased slowly to 1640°F toward the end of the test. The temperature increase in this test is much lower compared to the earlier two tests where samples of ground and alkali-impregnated KRW LASH and ground KRW LASH were oxidized at 1700°F. SO₂ evolved during the first minute at a level above 100 ppm and its concentration rapidly dropped to 5 ppm and then to one ppm gradually toward the end of the test.

For HSCF KRW LASH (tests 5-16 through 5-18), grinding alone did not increase the oxidation level. This solid is referred to as HSCF material although some of the sulfide was partially oxidized during carbon burn off. The analysis of the solids prior to carbon burn-off is also given in Table 4.3. However, grinding and impregnating the LASH with the alkali improved the oxidation (wt% of CaS was reduced to one per cent).

Test 5-19 was conducted with ground (70x140 mesh) and as-received KRW LASH (lightly sulfided) at 1700°F for an hour. The objective of the test was to investigate the effect of grinding the lightly-sulfided material on oxidation, and to afford a direct comparison with test 5-16 where ground and HSCF KRW LASH was oxidized at the same temperature. The material was oxidized by injecting it into a bed of -140 mesh sand. The bed temperature, after the normal decrease after solids injection, stabilized at 1689°F in about 4 minutes and then gradually decreased to 1647°F in about 25 minutes and then increased to 1674°F toward the end of the test. The SO₂ concentration was 20 ppm during the first minute and was zero during the remainder of the test. The temperature variation with time indicated that minimal oxidation took place.

Test 5-20 was performed with lightly-sulfided, and alkali-impregnated KRW LASH (-18 mesh) at 1700°F. Initially, the bed temperature increased from 1710°F to about 1797°F in 2 minutes and then decreased to about 1720°F in about 10 minutes and thereafter remained relatively constant, indicating that a good initial oxidation rate was sustained for only a short period. The SO₂ concentration during the first 2 minutes was 5 ppm and then dropped to zero. The analyses of solids obtained from tests 5-16 through 5-20 are given in Table 4.3 along with oxidation levels achieved. Regarding the oxidation of LSCF KRW LASH (tests 5-19 and 5-20), the solids analysis indicates clearly that the sulfide was converted to sulfate; and in test 5-20, 94% oxidation level was achieved, showing the advantage of impregnating the LASH with alkali. For LSCF KRW LASH, grinding alone improved the oxidation level; but for impregnated and unground material, the sulfide level was reduced to one per cent. This indicates that grinding the material prior to impregnation is not required.

Test 5-21 was conducted with lightly-sulfided, ground and alkali-impregnated KRW LASH (70x140 mesh) at 1700°F. The bed temperature increased from 1712°F to about 1785°F in about 8 minutes and then decreased slowly to about 1767°F toward the end of the test. SO₂ concentration ranged from 16 to 27 ppm during the first 6 minutes and then decreased to zero. The temperature change in this test indicates a higher level of oxidation than in Test 5-20. The solids analysis from this test is not presented due to unsatisfactory elemental balances.

Table 4.3 - Effect of Grinding and Alkali Impregnation on KRW LASHs

AL No.	4937	4965	4982	4984	4873	4987	4991
Test No.	Start	5-16	5-17	5-18	Start	5-19	5-20
Material	KRW LASH	KRW G LASH	KRW GD LASH	KRW G LASH	KRW LASH	KRW G LASH	KRW D LASH
Temp, °F	-	1700	1700	1600	-	1700	1700
Sulfide L	HSCF	HSCF	HSCF	HSCF	LSCF	LSCF	LSCF
CaO, %	12.20	10.62	12.24	14.84	23.04	23.17	24.52
CaSO ₄ , %	28.48	23.35	20.30	27.60	5.14	15.37	22.16
CaS, %	6.10	5.49	0.97	5.24	13.34	5.67	1.06
MgO, %	10.97	9.40	7.98	11.95	16.21	11.72	13.92
Inerts, %	42.25	51.14	58.51	40.37	42.23	44.07	38.34
Ca Ut., %	57.45	56.66	42.69	51.00	35.15	31.67	28.87

The solids analyses given in Table 4.3 were adjusted to maintain the same percentage of inerts content as that in the starting material in order to account for the differences in composition and are given in Table 4.4.

Table 4.4 - Analysis of Solids Adjusted for Inerts

AL No.		4937	4965	4982	4984	4592	4873	4987	4991.
Test No.	Feed	Start	5-16	5-17	5-18	Feed	Start	5-19	5-20
Material	KRW	KRW	KRW G	KRW GD	KRW G	KRW	KRW	KRW G	KRW D
	LASH	LASH	LASH	LASH	LASH	LASH	LASH	LASH	LASH
Temp, °F	-	-	1700	1700	1600	-	-	1700	1700
Sulfide L	HSCF	HSCF	HSCF	HSCF	HSCF	LSCF	LSCF	LSCF	LSCF
CaO, %	12.80	12.20	12.55	17.04	14.37	25.71	23.04	23.93	22.97
CaSO ₄ , %	0.31	28.48	27.60	28.26	26.73	0.56	5.14	15.88	20.76
CaS, %	29.78	6.10	6.49	1.35	5.07	16.63	13.34	5.86	0.99
MgO, %	14.87	10.97	11.11	11.11	11.57	14.88	16.21	12.11	13.04
Inerts, %	42.25	42.25	42.25	42.25	42.25	42.23	42.23	42.23	42.23
Ca Ut., %		57.43	56.64	42.67	50.97		35.12	31.65	28.85
S Conv. % ¹	-	-	0	77.87	0	-	-	56.10	92.60
S Conv. % ²	-	79.52	79.52	95.47	79.52	-	19.80	64.80	94.00

¹ oxidation based on material injected into BRU.

² oxidation based on material prior to preparation in muffle furnace.

Tests 5-26 through 5-29 were conducted in the BRU with CFHS KRW LASH to investigate the effect of grinding and impregnating the heavily-sulfided material with the alkali on oxidation.

Test 5-26 was conducted with CFHS KRW LASH at 1700°F. The bed temperature, after the usual drop, rose to 1700°F in 2 minutes and continued to rise very rapidly to 2025°F and then dropped to 1716°F in the next minute. After 3 minutes, the variation in temperature was small (first dropped to 1700°F in about 10 minutes and then slowly increased to 1720°F toward the end of the test). Two spikes of SO₂ concentration were observed. The SO₂ concentration rose from 225 ppm to 700 ppm in about a minute and then dropped to 225 ppm and then increased again to over 1000 ppm very rapidly and then dropped to about 142 ppm in a minute. Thus the change in SO₂ concentration was somewhat erratic. It dropped to zero toward the end of the test. The total loss of sulfur was negligible.

Test 5-27 was conducted with ground and impregnated CFHS KRW LASH at 1700°F for an hour. No appreciable temperature increase was observed during the test. SO₂ evolution was minimal. The SO₂ concentration was initially about 9 ppm and later decreased to zero. In this test, much of the material injected was elutriated (only about 5 grams were recovered). This coupled with a higher mixing rate might have contributed to a fairly constant temperature. The CaS content in the oxidized material was found to be 4.1%, about the same as that of the solids oxidized in test 5-26.

Test 5-28 was conducted with CFHS ground KRW LASH at 1700°F for an hour. No appreciable increase in temperature was observed during the test. The total amount of SO₂ evolved was minimal. SO₂ concentration initially rose to about 870 ppm and then rapidly decreased to zero.

Tests 5-29 and 5-30 were conducted in the BRU in order to investigate the effect of grinding and impregnating the heavily-sulfided material with the alkali on oxidation. Test 5-29 was conducted with alkali-impregnated CFHS KRW LASH at 1700°F for an hour. Temperature rose initially to about 1722°F and then stabilized around 1680°F after about 10 minutes and then remained at this level for the rest of the test. The SO₂ concentration increased to above 1000 ppm initially and then dropped to about 13 ppm in 4 minutes and was less than 2 ppm for the last 50 minutes of the test.

Test 5-30 was conducted with ground CFHS KRW LASH, which was soaked in water and then dried in a vacuum oven, at 1700°F for an hour. The objective of this test was to determine if soaking the LASH in water would enhance the oxidation and to serve as a blank run for the runs with alkali-impregnated LASHs. After a drop in bed temperature due to solid injection, the temperature remained at about 1680°F for the duration of the test. SO₂ concentration initially rose to about 1000 ppm and dropped rapidly in about 4 minutes and then gradually decreased to about 2 ppm by the end of the test. An oxidation level of 79% was obtained with ground CFHS KRW LASH. Thus, soaking in water did not contribute to any enhancement in oxidation level, as can be expected.

Table 4.5 - Analysis of KRW LASH from Tests 5-26 through 5-30

AL No.	5008	5043	5054	5059	5080	5086
Test No.	HS3	5-26	5-27	5-28	5-29	5-30
Material	KRW LASH	KRW LASH	KRW GD LASH	KRW G LASH	KRW D LASH	KRW GH LASH
Temp, F	-	1700	1700	1700	1700	1700
Sulfide L	HSAR	CFHS	CFHS	CFHS	CFHS	CFHS
CaO, %	14.21	23.26	13.75	17.51	17.98	16.37
CaSO ₄ , %	0.42	15.77	19.90	23.07	23.86	19.91
CaS, %	28.28	3.92	3.45	5.94	2.90	6.93
MgO, %	14.59	12.58	8.44	12.24	11.47	11.06
Inerts, %	42.50	44.47	54.46	41.24	43.79	45.73
Ca Ut., %	60.93	29.09	44.17	44.64	40.19	45.36
CaS level, %	60.45	9.29	10.89	14.60	7.50	17.98

Table 4.6 - Analysis of CFHS KRW LASH - Adjusted for Inerts

AL No.	5008	*	*	*	*	*
Test No.	HS3	5-26	5-27	5-28	5-29	5-30
Material	KRW	KRW	KRW GD	KRW G	KRW D	KRW GH
	LASH	LASH	LASH	LASH	LASH	LASH
Temp, °F	-	1700	1700	1700	1700	1700
Sulfide L	HSAR	CFHS	CFHS	CFHS	CFHS	CFHS
CaO, %	14.21	24.07	17.37	17.14	18.39	17.34
CaSO ₄ , %	0.42	16.32	25.13	22.59	24.41	21.09
CaS, %	28.28	4.06	4.36	5.82	2.97	7.34
MgO, %	14.59	13.02	10.66	11.98	11.73	11.72
Inerts, %	42.50	42.50	42.50	42.50	42.50	42.50
Ca Ut., %	60.89	29.07	44.15	44.62	40.17	45.33
S CONV, %	-	85.65	84.59	79.44	89.51	74.04
CaS level, %	60.42	9.28	10.88	14.58	7.49	17.97

Test 5-33 was conducted with CFHS KRW LASH at 1700°F for an hour to repeat test 5-26 since the material balance in test 5-26 did not appear to be correct, and to establish a baseline conversion for untreated CFHS KRW LASH in order to determine the benefit of impregnating the LASH with an alkali. The bed temperature dropped from 1709 to 1659°F in about 7 minutes and then gradually increased to 1682°F over the remaining period. During the first minute, the SO₂ concentration was in excess of 1000 ppm and later dropped to 22 ppm in 4 minutes. Thus, the SO₂ loss was small. Detailed solids analysis is given in Table 4.7. An oxidation level of 71.6% was obtained from this analysis. Conversions of 84.6% and 89.5% were obtained for KRW GD LASH and KRW D LASH, respectively. Thus, impregnation of the KRW LASH with an alkali enhanced the oxidation level considerably.

Test 5-34 was conducted with LSAR KRW LASH containing carbon, by modifying the normal procedure to avoid a high exotherm in order to determine if the same oxidation level could be achieved as that of the LSCF LASH. A much smaller amount of material (9.2 grams), than used normally, was injected into a 257-gram bed of sand (this is much larger than the normal weight of inert bed material) in order to reduce the potential exotherm to a manageable level. This test was conducted at a nominal 1800°F rather than at 1700°F. The bed temperature increased from 1779 to 1797°F gradually during the test. The SO₂ concentration during the first minute increased to 32 ppm and then dropped to zero and no SO₂ evolution was observed afterwards. An oxidation level of 69% was obtained that is in good agreement with the results from the earlier tests and confirms the validity of the experimental approach of burning off carbon prior to LASH oxidation in the BRU.

Test 5-35 was conducted with CFHS KRW LASH at 1700°F for an hour after modifying the reactor outlet in order to capture all the fines, and to study potential sulfur deposition in the outlet line and to make a sulfur balance. The modifications included a new product gas outlet line, an intermediate condenser and a final glass condenser and a bubbler with an impingement plate to capture the fines and a series of two bubblers containing aqueous solutions of hydrogen peroxide and sodium hydroxide in order to capture all the SO₂ evolved during the test. At the end of the test, the product gas exit line was cleaned with carbon disulfide to recover any elemental sulfur that might have deposited on the cooler surfaces. Only 5.9 milligrams of solids were recovered. This was a negligible overall loss of material if it were all sulfur. It was however not a sufficient quantity of material on which to perform any chemical analysis. This test clearly showed that essentially no sulfur loss occurred via deposition of elemental sulfur in the BRU outlet line. Sulfur and calcium balances on the run showed discrepancies of 1.7% in sulfur and 5.1% in calcium that are small.

Analyses of solids obtained from tests 5-33 through 5-35 with KRW LASH are given in Table 4.7. The composition of these solids after adjusting for inerts content to maintain the same level as that of the starting material along with oxidation level is given in this Table.

Table 4.7 - Analysis of KRW LASH from Tests 5-33, 5-34 and 5-35

AL No.	5120	5124	4891	5133	*	Feed ¹	*
Test No.	Start	5-33	Start	5-34	5-34	5-35	5-35
Material	KRW	KRW	KRW	KRW	KRW	KRW	KRW
	LASH	LASH	LASH	LASH	LASH	LASH	LASH
Temp, °F	-	1700	-	1700	1800	1700	1700
Sulfide L	CFHS	CFHS	LSAR	LSAR	LSAR	CFHS	CFHS
CaO, %	14.47	20.01	24.47	22.04	24.06	18.74	19.45
CaSO ₄ , %	0.30	17.96	0.13	15.58	17.01	19.93	20.69
CaS, %	31.14	8.48	19.06	5.42	5.92	6.44	6.68
MgO, %	16.94	13.73	16.56	12.36	13.50	13.17	13.67
Inerts, %	37.16	39.81	39.51	44.60	39.51	41.72	39.51
Ca Ut., %	62.67	41.12	37.77	32.52	32.52	41.33	41.33
S Conv, %		71.60			68.90		65.00

* Analysis adjusted to maintain the same percentage of inerts as in the starting material.

¹ Combined analysis of -25 mesh and +25 mesh of the feed.

4.2.4 Oxidation of FW LASH

A detailed description of all the tests performed with FW LASH is given in this section.

Carbon-free FW LASH was prepared in a muffle furnace at a temperature of 1200°F in the presence of about 8% O₂ in N₂. The carbon present in the LASH was combusted for about four days in order to limit the temperature increase. The solids temperature increased to about 1360°F and remained constant at this level for an extended period of time before it dropped gradually to 1200°F. By slightly modifying the injection procedure used initially for KRW LASH, the transition period was reduced to about 5 minutes in subsequent tests.

Test 5-7 was conducted with carbon-free FW LASH at a nominal temperature of 1600°F. The temperature increased from 1600 to about 1700°F during this test. The sample was oxidized for an hour. The variation of sample temperature was in sharp contrast to that of the KRW LASH and based on this temperature increase, a higher oxidation level with the FW LASH was expected. Test 5-8 was conducted by injecting about 24 grams of CF-FW LASH into a fluidized bed of sand at 1500°F and oxidizing it for an hour. The temperature of the lower part of the bed increased from 1500 to 1560°F during the test. The upper part of the bed remained at a relatively constant temperature. Test 5-10 was conducted with the same material at a nominal temperature of 1700°F. There was a modest temperature increase (20°F) during the test. No SO₂ evolution was observed during these tests. The analysis of the solids is given in Table 4.8.

Test 5-11 was conducted with heavily sulfided and carbon-free (HSCF) FW LASH at a nominal temperature of 1600°F for an hour. The temperature increase during the test was small. The temperature increased by about 12°F over the run. The SO₂ evolution was negligible. In the initial 10-minute period, the SO₂ concentration varied from about 4 ppm to one ppm and later decreased to zero. Test 5-13 was conducted with heavily-sulfided and carbon-free (HSCF) FW LASH at a nominal temperature of 1700°F and 50 psig. The temperature gradually increased to 1864°F toward the end of the test. This represents a large temperature increase and is an indication that the extent of oxidation was good. A very small amount of SO₂ evolved during the test. It varied from about 5 ppm at the beginning to about one ppm at the end of the test. Results from these two tests were inconclusive and, hence, the solids analyses are not presented. The tests were not repeated since the solids did not contain the desired sulfide level.

Beginning from test 5-22, the heavily-sulfided LASHs were produced by first burning off the carbon from the as-received materials and then by sulfiding them in the quartz reactor to increase the sulfidation level. These are denoted as CFHS materials. The heavily-sulfided LASHs used in the BRU tests up to test 5-21 were produced by first sulfiding the as-received materials in the quartz reactor and then by burning off the carbon in a muffle furnace. These are denoted as HSCF materials. Tests 5-22 through 5-25 were performed with CFHS FW LASH (sulfided to about 60% after carbon burn off). The solids analyses from these tests are given following the description of the tests.

Table 4.8 – Results on Oxidation of FW LASH From Tests 5-7, 5-8 and 5-10

AL No.	4852	4890*	4893	4897	4907
Test No.	As Rec.	start	5-7	5-8	5-10
Material	FW LASH	FW LASH	FW LASH	FW LASH	FW LASH
Temp, °F	-	-	1600	1500	1700
CaO, %	9.39	25.29	32.84	33.98	36.87
CaSO ₄ , %	0.76	15.32	19.61	18.63	23.13
CaS, %	4.14	13.73	12.92	13.93	15.75
MgO, %	0.35	0.76	0.71	0.76	1.13
Inerts, %	33.86	41.17	32.42	31.95	22.80
carbon, %	51.50				
Ca Ut., %	27.39	40.15	35.53	35.23	37.10
S Conv., %	-	-	18.25	14.01	33.84

*The size distribution of FW LASH used in the BRU was -18 mesh in order to separate it from the inert bed material. As-received FW LASH consisted of both -18 mesh and +18 mesh fractions.

In test 5-22, CFHS FW LASH was oxidized at 1700°F. The bed temperature dropped from 1698°F, after the usual decrease associated with solid injection, to 1673°F in 2 minutes and then decreased steadily to 1640°F in about 12 minutes and then slowly increased to 1650°F toward the end of the test. During the first minute, the SO₂ concentration was above 200 ppm and then rapidly reduced to zero. Based on this temperature variation, it appears that no appreciable oxidation took place. The temperature drop in the test was due to significant heat losses from the reactor.

In test 5-23, CFHS FW LASH impregnated with the alkali was oxidized at 1700°F. The bed temperature, after the usual drop (to 1681°F), stabilized at 1707°F and gradually decreased to 1632°F in about 12 minutes and then increased steadily to 1668°F toward the end of the test. The SO₂ concentration was initially above 1000 ppm and then quickly dropped to about one ppm. The temperature variation indicates a small increase in oxidation level compared to test 5-22.

Test 5-24 was done with finely-ground (70x140 mesh) CFHS FW LASH at 1700°F for an hour. The bed temperature, after normal drop after solid injection, steadily increased to 1750°F toward the end of the test. During the first 2 minutes, the SO₂ concentration in the exit gas rose above 1000 ppm, then after 10 minutes had declined to 777 ppm, and then after 20 minutes had further decreased to 173 ppm. It then decreased gradually to 4 ppm at the end of the test. The high concentration of SO₂ for an extended period is in sharp contrast with that observed in the earlier tests and may be attributed to both grinding and the high sulfide content, about 70%, of the solids re-

established after carbon burn off. The appreciable temperature increase accompanied by evolution of SO_2 is an indication that the sulfide was converted to oxide.

Test 5-25 was conducted with finely-ground (70x140 mesh) and alkali-impregnated CFHS FW LASH at 1700°F for an hour. The bed temperature increased gradually, after the normal drop after solid injection, to 1841°F in about 35 minutes and then dropped rapidly to 1745°F in 5 minutes and after that steadily decreased to 1729°F by the end of the test. The SO_2 concentration was fairly steady for about 40 minutes at about 16 ppm and then rapidly dropped to zero. The end of the reaction was marked by a sudden drop in temperature as well as a drop in SO_2 concentration. The results of this test are in sharp contrast with those of test 5-24 where ground CFHS FW LASH was oxidized. This test clearly demonstrated the advantage of grinding the FW LASH and then impregnating it with an alkali.

The composition of solids from tests 5-22 through 5-25 along with the composition of as-received, carbon-free and sulfided FW LASH is given in Table 4.9.

Table 4.9 - Analysis of CFHS FW LASH in tests 5-22 through 5-25

AL No.	4852	4890	4999	5000	5003	5014	5017
Test No.	As Rec	muffle	Start	5-22	5-23	5-24	5-25
Material	FW LASH	FW LASH	FW LASH	FW LASH	FW D LASH	FW G LASH	FW GD LASH
Temp, °F	-	-	-	1700	1700	1700	1700
Sulfide L	LSAR	LSCF	CFHS	CFHS	CFHS	CFHS	CFHS
CaO, %	28.31	32.73	35.09	32.25	27.86	26.61	17.05
CaSO ₄ , %	1.80	17.34	2.72	14.69	41.19	41.02	34.01
CaS, %	9.72	15.53	32.83	26.78	4.68	8.71	1.46
MgO, %	0.82	0.86	0.84	0.98	0.79	0.79	0.56
Inerts, %	59.35	33.53	28.52	25.30	25.48	22.87	46.92
CaCO ₃ , %							
Ca Ut., %	40.15	40.15	43.12	45.42	42.50	47.05	47.02

The composition of the solids is adjusted to have the same percentage of inerts as that of the starting material for comparison of the analysis of the solids from these tests and is given in Table 4.10.

Table 4.10 – Analysis of CFHS FW LASH Adjusted For Inerts

AL No.	4852 ¹	4890 ²	4999	*	*	*	*
Test No.	As Rec	muffle	Start	5-22	5-23	5-24	5-25
Material	FW	FW	FW	FW	FW D	FW G	FW GD
	LASH	LASH	LASH	LASH	LASH	LASH	LASH
Temp, °F	-	-	-	1700	1700	1700	1700
Sulfide L	LSAR	LSCF	CFHS	CFHS	CFHS	CFHS	CFHS
CaO, %	28.31	32.73	35.09	30.86	26.72	24.66	22.96
CaSO ₄ , %	1.80	17.34	2.72	14.06	39.51	38.02	45.80
CaS, %	9.72	15.53	32.83	25.63	4.49	8.07	1.97
MgO, %	0.82	0.86	0.84	0.94	0.76	0.73	0.75
Inerts, %	59.35	33.53	28.52	28.52	28.52	28.52	28.52
CaCO ₃ , %							
Ca Ut., %	40.15	40.15	43.12	45.42	42.50	47.05	47.02
S Conv, %	-	-	-	21.9	86.3	75.4	94.0

¹ The analysis is reported on a carbon-free and carbonate-free basis although the as-received FW LASH contained carbon and CaCO₃ in order to compare the sulfide and sulfate content with that of materials processed in the BRU.

² The analysis is reported on a carbonate-free basis although the LASH contained CaCO₃.

The analysis given in Table 4.9 indicates that during carbon burn-off, CaO was converted to CaSO₄ but no CaS was oxidized. There appears to be enough sulfur in the carbon present in the as-received FW LASH to convert the CaO to CaSO₄. This is in sharp contrast to the results obtained with KRW LASH. The difference between the two LASHs may be attributed to the differences between the dolomitic limestone and the high-calcium limestone that were used in producing these LASHs. The composition of the two limestones is given in Section 3.0. The reduction in CaSO₄ during sulfidation might be due to the solid-state reaction between CaS and CaSO₄ that releases SO₂.

4.2.5 Oxidation of TRTU LASH

Two tests (5-31 and 5-32) were performed with TRTU LASH that was produced in the TRTU using Longview limestone and these tests are described below.

Test 5-31 was conducted with HSCF TRTU LASH at 1700°F for an hour. Because of the smaller size distribution (80x270 mesh) of this material compared to the ground LASHs, a bed of pure hollow alumina spheres of +80 mesh with nearly the same fluidization velocity as that of the TRTU LASH was used for this test. The size

distribution of the TRTU LASH was measured on a Microtrac Model N° 7995-11 laser-based particle size analyzer due to the small size of the particles. Note that the size distribution of ground LASHs used in some of the earlier tests was 70x140 mesh. In this test, the bed temperature dropped to 1627°F after the solids were injected and then increased to 1676°F in about 5 minutes and then gradually dropped to about 1665°F toward the end of the test. The SO₂ concentration initially was 81 ppm and then gradually decreased to about 10 ppm. Thus the SO₂ evolution in this test was much higher compared to most of the earlier tests. CaS content in the LASH prior to the test on carbon and carbonate-free basis was 7.6 wt%. Based on these analyses, an oxidation level of 40% was obtained. Analyses of the solids is presented in Table 4.9 and the oxidation level was calculated taking into account the different inerts content in the two samples. This conversion is lower than that of the HSCF or the CFHS KRW LASH possibly due to the relatively less reactive Longview limestone (compared to the NE limestone used in producing KRW LASH) used in producing the TRTU LASH, despite the much smaller particle size distribution of solids.

Test 5-32 was conducted with alkali-impregnated HSCF TRTU LASH at 1700°F for an hour with the same bed material as used in test 5-31. In this test, the bed temperature dropped to 1651°F after the solids were injected and then increased to 1683°F in about 5 minutes and then gradually dropped to about 1668°F toward the end of the test. The SO₂ concentration initially was 87 ppm and then gradually decreased to about 4 ppm toward the end of the test. The amount of SO₂ evolved in this test was appreciably lower than in test 5-31. An oxidation level of 79% was obtained for the alkali-impregnated TRTU LASH in contrast to an oxidation level of 40% for the untreated LASH in test 5-31. These conversions include the conversion achieved during carbon burn-off (12%) in the muffle furnace. This shows that alkali-impregnation increased the oxidation of TRTU LASH substantially, just as it did for KRW and FW LASHs. Note that Longview limestone was used in producing both the FW and TRTU LASHs. The analyses of solids in the feed and the products of tests 5-31 and 5-32 are presented in Table 4.11.

4.2.6 Oxidation of TP and FW DASHs

A detailed description of the tests performed with TP (5-12) and FW DASHs (5-37) is given in this section.

In test 5-12, TP DASH was oxidized at a nominal temperature of 1700°F for an hour after injecting carbon-free material into a fluidized bed of sand. The temperature of the lower part of the bed increased up to 1873°F and remained above 1840°F during most of the test. No explanation can be offered for the observed temperature increase during this test. A small amount of SO₂ evolved at a level of about 3 ppm during the initial part of the test and was zero during half the test (the accuracy of the SO₂ analyzer is about one ppm). The temperature increase in this test was also one of the largest observed and is an indication of the extent of oxidation in the absence of any carbon combustion.

Table 4.11 - Results on Oxidation of TRTU LASH from Tests 5-31 and 5-32

AL No.	5062 ¹	5066	*	5168	5166	*	*
Test No.	Start	Start	Start	5-31	5-32	5-31	5-32
Material	TRTU LASH	TRTU LASH	TRTU LASH	TRTU LASH	TRTU D LASH	TRTU LASH	TRTU D LASH
Temp, °F	-	-	-	1700	1700	1700	1700
Sulfide L	HSAR	HSCF	HSAR	HSCF	HSCF	HSCF	HSCF
CaO, %	4.48	4.05	5.66	3.48	3.09	5.91	5.22
CaSO ₄ , %	0.70	3.69	0.88	2.67	5.31	4.54	8.97
CaS, %	7.59	8.44	9.59	3.39	1.22	5.76	2.06
MgO, %	0.26	0.27	0.33	0.14	0.13	0.24	0.22
Inerts, %	86.97	83.54	83.54	90.31	90.26	83.54	83.54
CaCO ₃ , % carbon, %							
Ca Ut., %	57.97	66.59	57.97	51.74	50.34	51.76	50.34
S Conv., %	-	-	-	-	-	39.90	78.50

* indicates that the analysis was adjusted to contain the same amount of inerts present in the sample injected into the BRU reactor.

¹ The analysis is on a carbon-free and CaCO₃-free basis although the sample contains carbon and CaCO₃.

The oxidation of LSCF FW DASH was conducted in test 5-37 at a nominal temperature of 1700°F and atmospheric pressure using air by injecting a sample of the DASH into a bed of sand. The bed temperature decreased from 1750°F to 1675°F after the sample injection. After the bed temperature recovered, the temperature decreased to 1725°F and thereafter remained relatively constant. The SO₂ concentration in the offgas was 3 ppm after a minute and was zero during the rest of the test. This is negligible. Much of the CaS present in the DASH was oxidized during carbon burn-off in the muffle furnace. The detailed analyses of the solids as-received, after carbon burn-off, and after oxidation in the BRU are given in Table 4.12. These results show that an oxidation level of 92.4% was achieved during carbon burn-off and that oxidation in the BRU was negligible.

Table 4.12 - Results on Oxidation of FW DASH

AL No.	4853	4853#	*	5251	5281	*
Test No.	Start	Start	Start	Muffle	5-37	5-37
Material	FW	FW	FW	FW	FW	FW
	DASH	DASH	DASH	DASH	DASH	DASH
Temp, °F	-	-	-		1700	1700
Sulfide L	HSAR	HSAR	HSAR	HSCF	HSCF	HSCF
CaO, %	5.36	16.25	17.44	13.71	13.83	13.17
CaSO ₄ , %	0.55	0.78	0.84	36.85	40.89	38.93
CaS, %	18.47	26.27	28.19	2.14	1.96	1.87
MgO, %	18.24	25.93	27.82	21.59	21.37	20.34
Inerts, %	21.64	30.77	25.70	25.70	21.96	25.70
CaCO ₃ , %	10.84	-	-	-	-	-
carbon, %	24.90	-	-	-	-	-
Ca Ut., %	56.05	56.07	56.07	55.13	57.05	57.05
S Conv, %				92.4		93.0

Analysis is on a carbon and carbonate-free basis

* Analysis is adjusted to have same % of inerts as in the starting solids

4.3 Weathering Study

The objective of the weathering study was to determine if the oxidation of a LASH sample, partially oxidized in the BRU, could be further increased by "weathering". Weathering study was conducted with CFHS KRW LASH that was partially oxidized in test 5-36 in the BRU to determine if the weathering of oxidized samples at 70°F further increases the oxidation level of the LASH sample. The sample was divided into three batches. One of the batches was impregnated with Na₂CO₃ solution, to 2% by wt of alkali, in order to determine the effect of the alkali on weathering. Two batches including the above sample were exposed to saturated air for 60 days. The third batch was a control sample. Complete analyses of the weathered and unweathered solids are reported in Table 4.13 along with the oxidation level. CaS content in the sample prior to oxidation in the BRU was 24.25 wt%.

Test 5-36 was conducted at pressure of 3 psig using air to prepare a desired amount of partially oxidized sample using CFHS KRW LASH for weathering study. The procedure employed in this test was slightly different from the normal procedure in that a bed of about 220 grams of KRW LASH was heated to the reaction temperature without flowing any gas through the bed, and then at the operating temperature, air was introduced for oxidation. The sample was oxidized at 1600°F for an hour followed by

oxidation at 1700°F for another hour to achieve higher conversion than before and to look at the effect of extended time on oxidation.

Weathering study was conducted with CFHS KRW LASH that was oxidized in test 5-36 to determine if the "weathering" of oxidized samples increases the level of oxidation of CaS present in the LASH sample. The procedure used for the study is given below.

The oxidized LASH was divided into 3 batches. One of the batches was impregnated with Na_2CO_3 solution so that the alkali added was 2% by wt of the sample. This batch and a second batch were subjected to "weathering" by flowing saturated air (air is bubbled through water) through a fixed bed of solids spread on a 140-mesh screen. It was assured that there was no preferential flow of air through any particular part of the bed. The third batch was a control sample and was stored in a vial that was blanketed in a N_2 atmosphere. Samples from the two batches, that were oxidized in air, were analyzed for CaS content by the Draeger Tube (DT) method at intervals of about 10 days to determine if appreciable oxidation occurred. Based upon these results, weathering of these samples for a period longer than 60 days was judged to have little potential benefit, and the testing was terminated.

Table 4.13 - Results on Oxidation of KRW LASH Due to Weathering

AL No.	5244	5397	*	5398	*	5399	*
Test No.	5-36	weath	weath	weath	weath	weath	weath
Material	KRW	KRW	KRW	KRW	KRW	KRW D	KRW D
	LASH	LASH	LASH	LASH	LASH	LASH	LASH
Temp, °F	1600	ctrl	ctrl	70	70	70	70
Sulfide L	CFHS	CFHS	CFHS	CFHS	CFHS	CFHS	CFHS
CaO, %	19.45	18.29	17.14	19.13	18.10	19.25	18.98
CaSO ₄ , %	18.31	21.41	20.06	21.01	19.88	21.96	21.65
CaS, %	6.55	7.81	7.32	7.26	6.87	4.49	4.43
MgO, %	12.14	12.73	11.93	12.25	11.59	11.55	11.39
Inerts, %	43.55	39.75	43.55	40.34	43.55	42.74	43.55
Ca Ut., %	39.38	44.88	44.88	42.77	42.77	39.44	39.44
S Conv., %		0.0		0.0		32.4	

weath - indicates that the samples were from the weathering study.

* Analysis adjusted to maintain same amount of inerts as in starting solids.

ctrl - control sample that was stored in an inert atmosphere.

KRW D - LASH impregnated with Na_2CO_3 to 2 wt%.

These results clearly show that the weathering of KRW LASH did not reduce the sulfide level. The LASH sample impregnated with Na_2CO_3 shows a 32% oxidation level. The sulfide level (4.5%) in this sample may not be satisfactory. Hence, it is concluded that weathering is not as effective a technique as was originally anticipated to stabilize the solid waste.

4.4 Fundamental Kinetic Studies on ATGA

The oxidation of CFHS FW LASH was studied on the atmospheric thermogravimetric analyzer (ATGA) at atmospheric pressure and the results are plotted to show the CaS oxidation level as a function of time. The conversion profiles for the FW LASH are shown in Figure 4.2. It can be seen that much of the conversion occurred in less than 20 minutes. These fundamental studies show that after a certain oxidation level is achieved, the rate slows down substantially as a result of diffusional resistance in the product layer. The oxidation rate increased with grinding the solids and also with grinding and impregnating the solids with the alkali.

4.5 Analytical Aspects

4.5.1 Sodium Content in LASH Samples

Wt% of Na_2CO_3 in selected LASH samples after testing in the BRU is given in Table 4.14 with the assumption that sodium is present as carbonate. The analysis was done by means of Inductively Coupled Plasma (ICP) spectroscopy.

Table 4.14 - Sodium Content in Selected LASHs After Testing in BRU

Material	wt% of Na	wt% of Na_2CO_3	Test 5-
LSCF impregnated KRW LASH	0.26	0.60	20
LSCF ground and impregnated KRW LASH	0.22	0.51	21
HSCF ground and impregnated KRW LASH	0.16	0.37	17
CFHS KRW LASH Untreated	0.00	0.00	26
CFHS ground KRW LASH	0.13	0.30*	28
CFHS ground and impregnated KRW LASH	0.17	0.39	27
CFHS impregnated FW LASH	0.43	0.99	23
CFHS ground and impregnated FW LASH	0.20	0.46	25

* Does not appear to be correct

Figure 4.2 Effect of Grinding and Doping on Oxidation of CFHS FW LASH

4.5.2 Change in CaS content with Grinding and Alkali Impregnation

The weight percentage of CaS present in various samples was determined by a quick analytical method, the results of which are well correlated with those of the detailed gravimetric method that is used for the complete analysis of solids. The results presented below show that the CaS content varied after grinding and alkali impregnation. These results were completely unexpected.

(1) LSCF KRW LASH 18x100 mesh (CaS -> 13.3%)	impregnated and dried	CaS -> 13.4%
	----->	
	ground (70x140 mesh)	CaS -> 14.6
	----->	
(2) CFHS KRW LASH 18x100 mesh (CaS -> 28.3%)	ground (70x140 mesh)	CaS -> 24.8%, 20.2%
	----->	(avg. 22.5%)

ground, impregnated
and dried

----->

CaS -> 15.0%,
15.9%
(avg. 15.5%)

(3) CFHS FW LASH
18x100 mesh
(CaS -> 32.8%)

ground (70x140 mesh)
----->

CaS -> 36.0%

ground, impregnated and dried

----->

CaS -> 16.0%

(CaS in -140 mesh -> 20.2%)

Additional information on change in CaS content as a result of grinding, impregnating with the alkali and then drying is given below. CFHS KRW LASH was ground, soaked in 2% Na₂CO₃ solution and then dried in a vacuum oven.

Start
(18x100 mesh)

grinding CaS -> 22.5%
in vacuum

----->

impregnated & dried

----->

CaS -> 20.8%

CaS in spent Na₂CO₃ solution -> 2.8%

Thus, grinding the LASH reduced the CaS content from 28.3% to 22.5%. Drying in air at 230°F reduced the CaS content further to 15.5%. The change in CaS content with grinding and drying can not be explained without additional studies. It appears that it is better experimentally to impregnate the samples with Na₂CO₃ by incipient wetting technique. If this technique is employed, they should be dried in vacuum to prevent any oxidation. However, these results do not impact on the oxidation levels reported here since the latter include the conversions achieved during processing of the sample prior to oxidation in the BRU.

The %CaS converted to CaO in various tests is given in Table 4.15 and is calculated on the assumption that the following reaction takes place:

This calculation is based on the CaS content in the sample after carbon burn-off as per the gravimetric method and the integrated SO₂ concentration profile measured in the offgas, as a function of time, during the test. These results show that the percentage of CaS oxidized to CaO during the tests was negligible.

The oxidation levels achieved for all the solids tested in the BRU, including the oxidation level achieved in the muffle furnace, are shown in Table 1.1 of the Summary section.

Table 4.15 – Per cent CaS Oxidized to CaO

Test No. 5-	%CaS decomposed
12	0.19
13	0.12
14	0.56
15	1.53
16	0.25
17	0.08
18	0.19
19	0.02
20	0.04
21	0.08
22	0.39
23	0.88
24	1.27
25	0.08
26	3.79
27	0.03
28	0.40
29	4.28
30	0.41
31*	1.11

* conversion based on CaS content before muffling.

SECTION 5.0 - GAS ABSORPTION STUDIES

5.1 Introduction

The objective of the gas absorption studies was to investigate the ability of various fresh sorbents and KRW and FW LASHs to react with (termed absorption here) SO_2 over the temperature range of 1600 to 1800°F and at atmospheric pressure to enhance fundamental understanding of the sulfation reaction ($\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{CaO} = \text{CaSO}_4$) and to simulate the operation of a combustor/sulfator in an IGCC plant. The latter has to absorb the SO_2 evolved from the combustion of carbon as well as SO_2 that is present in the regeneration offgas from an external desulfurizer if it is recycled to the sulfator.

Longview, SP, and Greer limestones and PR dolomite were selected in addition to the LASHs and DASHs for these studies. The quartz reactor was utilized to perform these studies. This study was undertaken to determine the relative capacities of the LASHs, DASHs and fresh limestones and a dolomite to absorb SO_2 and H_2S rather than investigating the fundamental aspects of the reactions involved. The effects of recrystallization and sintering that are affected by calcination conditions were not examined in this study.

The absorption of H_2S and SO_2 was studied to investigate the differences between fresh sorbents and LASHs and to gain a perspective on whether gasifier conditions have contributed to any changes in the nature of LASHs. The outlet concentration of H_2S and SO_2 was measured by means of Draeger tubes to monitor the reaction of H_2S and SO_2 with these materials. In general, the same superficial velocity and amount of bed material were used for both sulfidation ($\text{CaO} + \text{H}_2\text{S}$) and sulfation ($\text{CaO} + \text{SO}_2 + \text{O}_2$) studies so that a direct comparison could be made between the results of the two studies.

5.2 Experimental

The experimental apparatus consists of a quartz reactor (1.65-inch I.D. and 15-inch long) in a horizontal fixed bed configuration, with a quartz fritted disc for gas distribution, that is heated by an electrical furnace. The outlet of the quartz reactor has a ball and socket joint with an O-ring for a gas-tight connection and easy replacement of solids. The reactor was packed with the desired solids and quartz wool was placed in both ends such that the solids were held firmly in position. The length of the bed generally ranged from 10 to 12 inches. The wall temperature was monitored near the inlet, the middle, and the outlet locations of the bed by means of thermocouples strapped to the outside of the reactor. The gas leaving the packed bed was passed through bubblers to scrub the gas of any sulfur compounds present before venting it to the atmosphere. There was a provision to measure the concentration of H_2S or SO_2 by means of Draeger tubes before the gas entered the bubblers. All the experiments were performed at atmospheric pressure. The standard experimental conditions are given in Table 5.1.

Table 5.1 – Experimental Conditions for SO₂ Absorption

Particle size	18x80 mesh for fresh sorbents (177 to 1000 microns) 18x100 mesh for LASHs and DASHs (149 to 1000 microns)
Gas composition	1.5% SO ₂ , 3% O ₂ , balance N ₂
Linear velocity at temperature	0.43 ft/s
Temperature	1600°F
Pressure	atmospheric

The outlet concentration of SO₂ or H₂S was measured by means of Draeger tubes that were specific for the appropriate range of concentration of the component being measured. At the end of each test, the bed was examined to ensure that there was no channeling or bypassing of the gas and that no solids caking took place during the test. If a malfunction contributing to poor gas distribution occurred during a test, the test was repeated, and only the results of the final test were considered. For the study of SO₂ absorption by alkali-impregnated KRW LASH, the LASH was soaked in 2% aqueous Na₂CO₃ solution for about 22 hours and then dried in an oven.

The compositions of the two limestones used in these studies and of the NE and Longview limestones that were used in producing KRW LASH and FW LASH, respectively, are reported in Table 3.5.

5.3 Absorption of SO₂ in Quartz Reactor

The results obtained in individual tests with various solids are presented in this section. Fresh sorbents, LASHs, DASHs, sulfided sorbents, and mixtures of LASHs/DASHs and fresh sorbents were used for these studies. Most of these tests were done at 1600°F since the operation of a sulfator/combustor in a commercial plant is envisioned at this temperature. For selected sorbents, absorption of SO₂ was studied over the temperature range of 1600 to 1800°F.

5.3.1 Absorption of SO₂ by Fresh Sorbents

The reaction rate of SP limestone with SO₂ was studied at 1600°F, 1700°F and 1800°F in the quartz reactor, in a fixed bed mode. The concentration of SO₂ in the outlet gas as a function of time at 1600°F for both SP and Greer limestones is shown in Table 5.2.

Table 5.2 – Absorption of SO₂ by SP and Greer limestones at 1600°F

SP Limestone at 1600°F		Greer Limestone at 1600°F	
Time, hours	Outlet SO ₂ conc. ppm	Time, hours	Outlet SO ₂ conc., ppm
0.0 - 4.7	< 20	0.0 - 8.5	< 20
6.0	200	12.5	100

At 1600°F, Greer limestone absorbed SO₂ much better than SP limestone. Note that in the case of Greer limestone, it took 12.5 hours to reach SO₂ exit concentration of 100 ppm.

The concentration of SO₂ in the outlet gas at 1700°F as a function of time is shown in Table 5.3. The results obtained with SP limestone at 1800°F are given in Table 5.4.

Table 5.3 – Absorption of SO₂ by SP and Greer limestones at 1700°F

SP Limestone at 1700°F		Greer Limestone at 1700°F	
Time, hours	Outlet SO ₂ conc., ppm	Time, hours	Outlet SO ₂ conc., ppm
0 - 9.5	5	0 - 13.3	5
10.8	15	14.8	500
11.0	90		
11.5	150		

Table 5.4 – Absorption of SO₂ by SP limestone at 1800°F

Time, hours	Outlet SO ₂ conc., ppm
0.0 - 2.8	5
4.0	15
4.5	210

Absorption of SO₂ by SP limestone in the temperature range of 1600 to 1800°F shows that maximum amount of absorption occurred at 1700°F. Greer limestone appears to be more reactive than SP limestone based on these results.

The absorption of SO₂ was studied on calcined Longview limestone at 1600°F. The breakthrough period for this sorbent at 150 ppm of SO₂ is about 11.5 hours. The concentration of SO₂ as a function of time is shown in Table 5.5.

Table 5.5 - SO₂ Absorption by Longview limestone at 1600°F

Time, hr	SO ₂ conc. in exit, ppm
0	0
10.5	5
11.0	10
11.5	170

5.3.2 Absorption of SO₂ by LASHs and DASHs

Absorption of SO₂ by KRW LASH

The SO₂ absorption by carbon-free KRW LASH at 1600°F was found to be poor at the standard test conditions as shown in Table 5.6.

Table 5.6 - Absorption of SO₂ by KRW LASH at 1600°F

Time, min.	Outlet SO ₂ conc., ppm
20	< 20
40	5900

SO₂ absorption by KRW LASH was repeated in the quartz reactor at 1600°F. The KRW LASH was oxidized in air for 2 hours at 1600°F to convert the CaS to CaSO₄ prior to SO₂ absorption. The SO₂ concentration in the exit rose to 0.5% within 30 minutes confirming the earlier observation with this material that the SO₂ absorption

was poor. This poor absorption might be attributed to the high temperature at which the KRW LASH was processed.

Absorption of SO₂ by KRW DASH

SO₂ absorption by carbon-free KRW DASH was studied at standard test conditions after oxidizing the CaS present in the DASH. Table 5.7 shows the SO₂ concentration at the exit during the oxidation of KRW DASH.

Table 5.7 – SO₂ Release During Oxidation of KRW DASH

Time, hours	SO ₂ outlet conc., ppm
0.00	> 120
0.08	10800
0.50	8100
0.75	60
1.25	35
2.00	20

Following the oxidation of KRW DASH, SO₂ absorption was studied. There was SO₂ breakthrough almost immediately showing the poor absorption of SO₂ by KRW DASH. The results on SO₂ absorption are presented in Table 5.8.

Table 5.8 – Absorption of SO₂ by KRW DASH

Time, min.	SO ₂ outlet conc., ppm
0	> 120
5	6500
25	> 5000

At the end of the experiment, the bed thermocouple (T.C.) was removed and the solids were rearranged to eliminate any possibility of gas bypassing around the T.C. and the SO₂ absorption study was continued. There was immediate breakthrough of SO₂ at >4000 ppm showing that the capacity of KRW DASH to absorb SO₂ is very poor just as KRW LASH. The implication of this observation is very clear. The discharge

product from a KRW gasifier cannot be expected to absorb appreciable additional sulfur in the combustor/sulfator at an acceptable SO₂ leakage; and, therefore, fresh sorbent needs to be added to absorb all the sulfur that is either evolved from carbon combustion or recycled to the unit from an external desulfurizer.

Absorption of SO₂ by FW LASH and DASH

The absorption of SO₂ by FW DASH and FW LASH in the presence of O₂ was studied at 1600°F and atmospheric pressure in the quartz reactor, in the fixed bed mode, at the standard test conditions. Much of the CaS present in FW DASH was oxidized during carbon burn-off in the muffle furnace. The CaS remaining in the DASH was determined to be about 2 wt% by the Draeger Tube method. The concentration of SO₂ in the outlet gas as a function of time at 1600°F for LSCF FW LASH is shown in Table 5.9.

Table 5.9 - Absorption of SO₂ by LSCF FW LASH

O ₂ conc. %	SO ₂ inlet conc., %	Time, hr.	Outlet SO ₂ conc., ppm
3.0	1.50	0.25	600
		0.50	500
		1.00	500
		1.50	500
		3.00	400
10.0	1.38	3.17	750
		4.00	4000
		5.00	>4000
21.0	1.22	5.10	-
		5.50	7000
		6.00	9000

Absorption of SO₂ by FW LASH is, thus, similar to that of KRW LASH at SO₂ leakage of 150 ppm. Absorption of SO₂ by LSCF FW LASH was repeated in the quartz reactor at standard test conditions after oxidizing the LASH in air for 2 hours with negligible SO₂ evolution and with no appreciable temperature increase. Table 5.10 shows the results obtained for SO₂ absorption.

Table 5.10 - Absorption of SO₂ by FW LASH

Time, min.	Outlet SO ₂ conc., ppm
2	1
15	2000
30	4000
45	9700

These results show that the absorption of SO₂ by FW LASH is poor at SO₂ leakage of 150 ppm and confirm the earlier results obtained with this LASH. This poor absorption may be attributed to the temperature at which the LASH was prepared. The usage of a jetting fluidized bed to promote high solid circulation rate in a gasifier results in substantially higher temperatures in the jet due to the combustion of gases and solids taking place in a confined region. This was substantiated by temperature measurements performed in the KRW pilot plant.¹⁰

The results obtained for FW DASH are shown in Table 5.11.

Table 5.11 - Absorption of SO₂ by FW DASH

O ₂ conc. %	SO ₂ inlet conc., %	Time, hours	Outlet SO ₂ conc., ppm
3.0	1.50	0.23	2500
		0.58	2500
10.0	1.38	0.65	-
		0.90	20
		1.40	8
		1.63	5
3.0	1.50	1.63	-
		2.03	5
		2.75	5
		4.50	3800
10.0	1.38	4.60	-
		4.93	4000
		5.18	4000

Table 5.11 shows that at 3% O₂ concentration level, there was insufficient O₂ for both oxidation and SO₂ absorption as evidenced by the high SO₂ concentration in the exit gas. When the O₂ concentration was increased to 10% and maintained at this level for about 1.6 hour and then switched back to 3%, SO₂ concentration decreased to low levels showing that most of the CaS had been oxidized by this time and that sufficient O₂ was available for SO₂ absorption. The O₂ concentration was later increased to 10% to investigate its effect on SO₂ absorption. There was no further SO₂ absorption. The breakthrough period at SO₂ concentration of 150 ppm was about 2.75 hours.

Absorption of SO₂ by TRTU LASH

Absorption of SO₂ by lightly sulfided and carbon-free TRTU LASH (produced in the TRTU using Longview limestone over the temperature range of 1800-1850°F) was studied after burning off the carbon followed by oxidation of the solids in air at 1600°F for 3 hours. The sample was oxidized first in order to convert the CaS to CaSO₄ so that there would be no competition for O₂ during the absorption of SO₂ and to determine if any SO₂ would evolve during oxidation. The size distribution of carbon-free TRTU LASH was as follows:

Size, mesh	+70	70x100	100x140	-140
wt%	1.9	1.5	23.9	72.7

SO₂ absorption on the +140 mesh fraction of these solids was studied in the quartz reactor at the conditions given in Table 5.12. The -140 mesh fraction was removed in order to limit the pressure drop across the bed.

5.12 - Experimental Conditions for Absorption of SO₂ by TRTU LASH

Bed material	+140 mesh of solids from TRTU
Linear velocity at temperature, ft/s	0.25
Bed temperature, °F	1600

The concentration of SO₂ in the offgas was measured during the oxidation step and was found to be negligible as shown in Table 5.13.

Table 5.13 – SO₂ Release During Oxidation of TRTU LASH

Time, hours	Outlet SO ₂ conc., ppm
0.17	5
1.33	5
3.00	10

A lower operating velocity than normal was used in this test in order to limit the pressure drop across the bed due to the smaller size distribution of the solids compared to the other solids. The breakthrough period for SO₂ in the test was 6.25 hours, during which the SO₂ concentration in the exit was less than 5 ppm. Thus, the absorption of SO₂ by the TRTU LASH was quite good and can be attributed to the lower temperature (temperature increase was very small due to high solid circulation rate) at which this was produced compared to the KRW and FW LASHs.

Analysis of TRTU LASH of full size distribution, +140 mesh used prior to and after SO₂ absorption studies is given in Table 5.14. The calcium utilization increased from 7.6% to 73.7% and even after muffling, the TRTU LASH contained an appreciable percentage of carbonate, but at the end of SO₂ absorption, no carbonate was left.

Table 5.14 – Analysis of TRTU LASH Before and After SO₂ absorption

AL No.	5292	5292#	5293	5293#	5294
Test No.	Start	Start	Muff.	Muff.	QR31
Material	TRTU LASH	TRTU LASH	TRTU LASH	TRTU LASH	TRTU LASH
	-	-	+140 m	+140 m	-
Sulfide L	LSAR	LSAR	LSCF	LSCF	LSCF
CaO, %	0.78	5.09	9.27	12.40	2.52
CaSO ₄ , %	0.34	0.43	2.25	2.30	17.11
CaS, %	0.50	0.63	0.09	0.09	0.00
MgO, %	0.35	0.45	0.32	0.33	0.27
Inerts, %	72.93	93.39	82.97	84.87	80.10
CaCO ₃ , %	5.71		5.09		
carbon, %	19.40		0.00		
Ca Ut., %		11.58		7.58	73.66

- analysis on carbon and carbonate-free basis

+140 m represents +140 mesh.

Muff - represents the sample after carbon burn-off in a muffle furnace.

5.3.3 Absorption of SO₂ by Sulfided Sorbents

Absorption of SO₂ by Sulfided PR dolomite

SO₂ absorption by PR dolomite, that was lightly-sulfided and then oxidized, was studied at 1600°F. Size distribution used was 18x80 mesh. Results of this study are given in Table 5.15 showing the O₂ concentration in the inlet and the SO₂ concentration in the outlet gas. The SO₂ concentration in the inlet gas corresponding to different levels of O₂ concentration is given in Table 5.9.

Table 5.15 – Absorption of SO₂ by PR dolomite

O ₂ conc. %	Time, hours	Outlet SO ₂ conc., ppm
3.0	0.13	120
	0.17	200
10.0	0.25	175
	0.75	2500
21.0	1.33	-
	3.00	<5
3.0	3.00	2
	12.75	5
	14.75	170
	15.25	800

Table 5.15 shows that PR dolomite, that was sulfided and then oxidized, absorbed SO₂ very well and the breakthrough period was about 15 hours. At the end of the test, the whole bed formed a soft single mass which had to be taken out, part by part, by using a spatula. The solids could be easily crushed into original particles with a little bit of force. This shows that slight sintering occurred in this test that is not expected in a fluidized bed.

Absorption of SO₂ by Sulfided SP Limestone

The SO₂ absorption by sulfided SP limestone was studied at 1600°F. The calcined sorbent was first sulfided at 1800°F using 1% H₂S (balance N₂) gas mixture. At the end of sulfidation, a sample from the bed was analyzed and was found to contain 8.7 wt% of CaS by the Draeger Tube method. Following sulfidation, absorption of SO₂ was studied at the standard test conditions and the results are presented in Table 5.16. The

SO₂ concentration in the inlet gas corresponding to different levels of O₂ concentration is given in Table 5.9.

Table 5.16 – Absorption of SO₂ by sulfided SP limestone

O ₂ conc. %	Time, hours	Outlet SO ₂ conc., ppm
21.0	<7.00	0
	7.50	25
10.0	7.50	-
	7.88	22
	9.25	10
	10.25	8
	13.62	5
3.0	14.67	5

These results show that the SO₂ absorption by the solids is very good. This test was not continued until SO₂ breakthrough was observed since the expected breakthrough period was quite high. The calcium utilization in the solids prior to and after the test is reported elsewhere.

Absorption of SO₂ by Sulfided Greer limestone (10% sulfide level)

Calcined Greer limestone was first sulfided to about 10% level (10% of CaO was converted to CaS) at 1600°F using 1% H₂S gas mixture. Following sulfidation, the sorbent was oxidized for three hours to convert the CaS to CaSO₄. The internal bed temperature was monitored at about 1.5 inch from the inlet of the bed during oxidation and subsequent SO₂ absorption. Table 5.17 shows the SO₂ concentration in the exit gas during oxidation.

The O₂ concentration was reduced from 22% to 6% to prevent the bed temperature from becoming high so as not to sinter the sorbent. The bed temperature reached a maximum of 1874°F before it stabilized and the temperature exotherm passed the measurement location. The high levels of SO₂ concentration in the exit gas were due to the high bed temperature that is expected to result in converting the CaS to CaO in addition to the oxidation of the CaS to CaSO₄. This is in sharp contrast to the test on SO₂ absorption on TRTU LASH where the SO₂ evolution during oxidation was negligible and the temperature increase was modest (74°F). This may be attributed to the difference in the rate of oxidation (of CaS to CaSO₄) of the two solids and points out the importance of conducting oxidation and SO₂ absorption tests separately.

Table 5.17 - SO₂ Release During Oxidation of Sulfided Greer limestone

O ₂ conc. %	Time, hours	SO ₂ conc. ppm
21.9	0.08	120
0.0	0.17	700
7.9	0.58	500
5.7	0.75	600
	1.00	1500
	1.25	2500
	1.75	500
	2.25	2
	2.75	7
	3.25	6

Following oxidation, SO₂ absorption was studied using a mixture of 1.5% SO₂ and 3% O₂ in N₂ and the results are given in Table 5.18. The breakthrough period at SO₂ concentration of 150 ppm was about 6 hours. This compares very well with the absorption of SO₂ by fresh (unsulfided, but calcined) Greer limestone which was studied earlier and shows that the amount of sulfide or sulfate (10% level) present in this sorbent has little effect on SO₂ absorption.

Table 5.18 - Absorption of SO₂ by Sulfided/Oxidized Greer limestone

Time, hours	SO ₂ conc. in exit, ppm
0	0
6.17	< 5
7.17	900

Absorption of SO₂ by Sulfided Greer limestone (20% Sulfide level)

The absorption of SO₂ on Greer limestone containing about 20 wt% CaS was studied at standard conditions in order to determine the effect of sulfide level on SO₂ absorption by comparing with the results on SO₂ absorption by Greer limestone containing 10 wt% CaS. The sulfided sorbent was oxidized with 6% O₂ except for a brief period in order to limit the temperature increase followed by SO₂ absorption.

Calcined Greer limestone was first sulfided in two campaigns similar to the previous sulfidations (in order to sulfide it more uniformly). Following sulfidation, O₂ was introduced at 21 mole% and the bed temperature near the inlet increased up to 1838°F. Oxygen was shut off for a brief period to reduce the bed temperature to 1600°F and then it was reintroduced at 6 mole%. The bed temperature increased to 1715°F before it stabilized. The sorbent was oxidized (for about 3.75 hours) until the SO₂ concentration in the exit was negligible and then the SO₂ absorption was studied. The results on exit concentration of SO₂ during oxidation is given in Table 5.19. The high concentration of SO₂ in the exit gas (as a result of the conversion of CaS to CaO) compared to any of the earlier tests may be attributed to the combined effect of the high sulfide level of the sorbent and the low O₂ concentration.

Table 5.19 – SO₂ Release During Oxidation of Sulfided Greer limestone

Time, hours	O ₂ conc. %	SO ₂ exit conc., ppm
0.0	21.0	200
0.08	21.0	250
0.25	6.0	500
0.42		500
0.75		300
1.25		7000
1.25		1000
2.08		1000
3.25		125
3.75		2

The results on SO₂ absorption by the Greer limestone, that was sulfided and then oxidized, are shown in Table 5.20.

Table 5.20 – Absorption of SO₂ by Sulfided/Oxidized Greer limestone

Time, hours	SO ₂ exit conc., ppm
0.00	3
3.00	3
3.50	800
3.75	1600

SO₂ breakthrough period at 150 ppm was about 3 hours while the expected breakthrough period from the previous test on Greer limestone containing 10 wt% CaS is about 4.3 hours (based on the available CaO). The significant reduction in the absorption of SO₂ by the 20%-CaS sorbent may be due to the higher level of sulfide/sulfate present in the sorbent. A comparison of the analysis and calcium utilization of the Greer limestone used in this test with that of the KRW and FW LASHs is given in Table 5.21. The sulfided sorbent was oxidized prior to SO₂ absorption and the level of oxidation is unknown.

Table 5.21 – Composition of Solids

Solids	wt% of CaS	wt% of CaSO ₄	Ca Ut., %
LSCF KRW LASH	13	5	35
LSCF FW LASH	14	15	40
Greer limestone (sulfided)	21	0	25

Absorption of SO₂ by Sulfided SP limestone (20% Sulfide level)

Absorption of SO₂ on SP limestone containing about 20 wt% CaS was studied at standard conditions in order to determine the effect of sulfide level on SO₂ absorption by comparing with that of SP limestone containing 10 wt% CaS. The sulfided sorbent was oxidized with 6% O₂ to limit the temperature increase followed by SO₂ absorption.

Calcined SP limestone was first sulfided in two campaigns (in order to sulfide it more uniformly). Following sulfidation, O₂ was introduced at 6 vol% and the bed temperature near the inlet increased to 2060°F. This is a large temperature increase and no attempt was made to change the O₂ concentration. The sorbent was oxidized until the SO₂ concentration in the exit was negligible (for 2 hours) and then the SO₂ absorption was studied. The exit concentration of SO₂ during oxidation is given in Table 5.22. The concentration of SO₂ in the exit gas (as a result of the conversion of CaS to CaO) was not appreciable. The difference between SP and Greer limestones, in terms of SO₂ release during oxidation, is remarkable and no explanation for this can be offered at this time. The SO₂ evolved during oxidation was captured in two bubblers in order to determine the total amount that evolved and to calculate the CaS that was converted to CaO. The results on absorption of SO₂ on sulfided-and-then-oxidized SP limestone are given in Table 5.23.

Table 5.22 - SO₂ Release During Oxidation of Sulfided SP limestone

Time, hours	SO ₂ exit conc., ppm
0	80
0.25	200
0.50	35
1.00	0
2.00	3

Table 5.23 - Absorption of SO₂ by Sulfided/Oxidized SP limestone

Time, hours	SO ₂ exit conc., ppm
0	0
5.50	<5
6.17	25
6.50	64
6.75	100
7.00	130

The breakthrough period of 7 hours for 20%-sulfided SP limestone is very good and compares well with that of the test with 10%-sulfided SP limestone and is in sharp contrast with that of Greer limestone.

Absorption of SO₂ by Sulfided PR dolomite

SO₂ absorption on PR dolomite, that was sulfided and then oxidized, was studied at standard test conditions. The dolomite was sulfided for 4 hours using 5% H₂S in N₂ to sulfide the sorbent to about 40% CaS level. The sulfided dolomite was oxidized (for 7.5 hours) until the SO₂ concentration in the exit gas, shown in Table 5.24 became negligible.

Table 5.24 - SO₂ Release During Oxidation of Sulfided PR Dolomite

Time, hours	SO ₂ conc. at exit, ppm
0.25	500
0.75	200
1.75	900
2.00	900
3.0-6.0	500
7.00	180
7.50	3

O₂ concentration was maintained at 3.9% during oxidation except for a few minutes. The bed temperature increased to 2039°F, as a result of the oxidation of CaS, prior to stabilizing at the operating temperature. Results on SO₂ absorption are shown in Table 5.25.

Table 5.25 - Absorption of SO₂ by 40% CaS - PR dolomite

Time, hours	SO ₂ outlet conc., ppm
0.0	0
3.5	<5
4.5	200
5.0	800

The breakthrough period for the 40% CaS-PR dolomite at SO₂ concentration of 150 ppm was about 4.5 hours. Expected breakthrough period based on results from 20% CaS-PR dolomite is 4.7 hours. There is no appreciable reduction in the SO₂ absorption capacity with an increase in sulfide level from 20% to 40%. An increase in bed temperature to 2039°F did not appear to have sintered the sorbent.

5.3.4 Absorption of SO₂ by Mixtures of LASH/DASH and Fresh Sorbents

Absorption of SO₂ by Mixture of KRW LASH and Greer limestone

Absorption of SO₂ on a mixture of calcined Greer limestone and LSCF KRW LASH containing equal amounts of CaO was studied at standard conditions after oxidation in air for three hours. The reason for using Greer limestone in this mixture is that it is a dolomitic limestone and KRW LASH was produced using a dolomitic limestone. During oxidation, negligible amount of SO₂ (<2 ppm) evolved and the increase in bed temperature was modest. Table 5.26 shows the SO₂ concentration in the exit gas as a function of time during absorption of SO₂.

Table 5.26 – Absorption of SO₂ by Mixture of KRW LASH and Greer limestone

Time, hours	Outlet SO ₂ conc., ppm
<4	<1
4.25	3
4.50	40
4.75	100
5.00	170

Expected breakthrough period at SO₂ concentration of 150 ppm for the mixture is 2.2 hours based on SO₂ absorption by the calcined Greer limestone and its fraction in the bed with the breakthrough period for the KRW LASH as zero. The observed breakthrough period for the mixture was 5 hours. Hence the mixture performed much better than that of the individual solids at low SO₂ leakage. This improvement in performance is due to the absorption of SO₂, that escaped the LASH, by the limestone. The separation of active material by the less active material might have also contributed to the improvement in performance of the active material.

Absorption of SO₂ by Mixture of Longview limestone and FW LASH

The absorption of SO₂ on a mixture, containing LSCF FW LASH and calcined Longview limestone such that the wt of CaO in both was about the same (73.5 grams), was studied at standard conditions and the results are presented in Table 5.27. Longview limestone was used in this mixture since FW LASH was produced using this limestone.

Table 5.27 – Absorption of SO₂ by Mixture of FW LASH and Longview limestone

Time, hours	SO ₂ conc. in exit, ppm
0.0	0
4.0	<5
4.5	170
5.0	1500

Expected breakthrough period for this mixture is 3 hours since the breakthrough period for FW LASH at 150 ppm of SO₂ was zero. Hence the improvement in performance is about 50%. This is not as good as that of the mixture of KRW LASH and Greer limestone.

Absorption of SO₂ by Mixture of FW DASH and PR dolomite

Absorption of SO₂ on a mixture of calcined PR dolomite and LSCF FW DASH (about 21% and 79% by wt., respectively) containing equal amounts of CaO was studied at standard conditions to investigate if the addition of a less active material to an active material would enhance the SO₂ absorption capacity of the latter. Table 5.28 shows the SO₂ exit concentration as a function of time during the absorption of SO₂.

Table 5.28 – Absorption of SO₂ by Mixture of FW DASH and PR dolomite

Time, hours	Outlet SO ₂ conc., ppm
0.0	0
5.0	<5
6.0	1000
6.2	2000

Expected breakthrough period at SO₂ concentration of 150 ppm for the mixture is 5.8 hours based on the SO₂ absorption capacity of the calcined PR dolomite and FW DASH and their relative amounts in the bed. The observed breakthrough period for the mixture was 5.2 hours. Hence the performance of the mixture is about the same as that expected based on the performance of the individual solids. The lack of any improvement in the performance can be expected since both solids performed well individually.

Absorption of SO₂ by Mixture of KRW DASH and PR dolomite

SO₂ absorption by a mixture of carbon-free KRW DASH and PR dolomite, both consisting of equal amounts of CaO, was studied at standard test conditions after oxidizing the CaS present (17 wt% as per the DT method) in the DASH to investigate if SO₂ absorption by an active material can be increased by mixing it with an inactive material. Table 5.29 shows the SO₂ concentration at the exit during the oxidation step.

Table 5.29 – SO₂ Release During Oxidation of Mixture of KRW DASH and PR dolomite

Time, hours	SO ₂ outlet conc., ppm
0.0	1000
0.5	400
1.0	> 4000
1.5	> 4000
3.0	12
3.5	> 120
4.25	15
4.9	15

The SO₂ release during oxidation of the mixture was appreciable. Following the oxidation of the mixture, SO₂ absorption was studied and the results are shown in Table 5.30.

Table 5.30 – Absorption of SO₂ by Mixture of KRW DASH and PR dolomite

Time, hours	SO ₂ outlet conc., ppm
0.0	5
0.5	15
1.0	7
1.5	12
2.0	1600
2.5	> 4000

Thus the breakthrough period for the mixture of KRW DASH and PR dolomite at SO_2 concentration of 150 ppm was about 1.5 hour. This is much less than the expected breakthrough period of 4.5 hours.

5.4 SO_2 Absorption Studies in PTGA

The rate of sulfation reaction was studied in a PTGA with various limestones, dolomites, and LASHs and DASHs used in this program to determine their reactivities. The kinetic data are needed to predict the performance of a sulfator/combustor. The experimental conditions used on the PTGA are given in Table 5.31.

Table 5.31 - Experimental Conditions on PTGA

Particle size	18x25 mesh (707 to 1000 microns)
Gas composition	1.5% SO_2 , 3% O_2 , balance N_2
Gas flowrate	2.0 liters/minute
Temperature	1600°F
Pressure	atmospheric

The sample weight and gas flowrate required to obtain a true kinetic rate that is free from the gas film diffusional effect were established by studying the rate of CaO sulfation reaction at 1600°F and atmospheric pressure on a PTGA using PR dolomite (18x25 mesh) and these conditions were employed for all the subsequent tests. The reaction rate at any time is defined as the weight of CaO reacting per minute per unit weight of CaO present at this time. In the case of LASHs, DASHs and fresh sorbents, the composition of the solids, as determined from gravimetric analysis, was used in calculating the reaction rate. The sample basket is made of 140-mesh platinum screen and is hung by means of a hangdown wire (made of Rolled Alloys 330) that is resistant to gases containing SO_2 and H_2S .

The sorbent calcination was done at 1600°F in a N_2 atmosphere containing 10% CO_2 since this represents gas composition typical of a sulfator/combustor and since the presence of CO_2 during calcination was shown to have a beneficial effect on the reactivity of calcined sorbents.^{11,12} The sample was heated at the rate of 25°C per minute and a gas flowrate of 2 liters/minute was used.

Sulfation Rate of KRW, FW and TRTU LASHs

The sulfation rate ($\text{CaO-SO}_2\text{-O}_2$ reaction) of the KRW, FW and TRTU LASHs was studied at standard conditions and the results are presented in Figures 5.1 and 5.2

showing the CaO conversion as a function of time and the reaction rate as a function of CaO conversion, respectively. For the various solids studied in the PTGA for reaction with SO₂, the PTGA results are in qualitative agreement with the results obtained in the quartz reactor. The reaction rate of FW LASH appears to be good, but is not in agreement with the results obtained in the quartz reactor, possibly due to gas maldistribution in the test with FW LASH.

The reaction rate of TRTU LASH is much higher than that of the KRW and FW LASHs. This higher rate may be attributed to the mild conditions at which the TRTU LASH was prepared in the TRTU since the same sorbent was used in the preparation of FW LASH as well. Due to high solid circulation rate and the absence of a high-temperature jet in the TRTU, the LASH is not exposed to localized temperatures as high as in fluidized beds.

Sulfation Rate of FW, TP, and KRW DASHs

The sulfation rate of FW, TP, and KRW DASHs was studied at standard conditions. The results are presented in Figures 5.3 and 5.4 showing the CaO conversion as a function of time and the reaction rate as a function of CaO conversion, respectively. The poor reaction rates of KRW and TP DASHs corroborate the SO₂ absorption results obtained in the quartz reactor. The reaction rate of the KRW DASH is just as poor as that of the TP DASH and the KRW LASH.

Based on the qualitative agreement between the results obtained in the quartz reactor and in the PTGA, it appears that, if a suitable model is developed, the SO₂ absorption capacity of a sorbent in either the quartz reactor or in a fluidized bed reactor can be predicted from the results of fundamental tests on the PTGA.

Effect of Heat Treatment Temperature (HTT) on Absorption of SO₂

Fresh sorbents were exposed to different temperatures in the range of 1600 to 2100°F and then their reactivities were studied in the PTGA at standard conditions. At about 2100°F, SO₂ absorption capacity was appreciably reduced for both Longview limestone and PR dolomite. The conversion of CaO from 20 to 80 minutes at different HTTs for the Longview limestone and PR dolomite are presented in Tables 5.32 and 5.33, respectively. The data on CaO conversion as a function of time for both of these solids are shown in Figures 5.5 and 5.6, respectively.

Figure 5.1 Sulfation of KRW, FW, and TRTU LASHs—Conversion vs. Time

Figure 5.2 Sulfation of KRW, FW, and TRTU LASHs—Rate vs. Conversion

Figure 5.3 Sulfation of DASHs and PR Dolomite—Conversion vs. Time

Figure 5.4 Sulfation of DASHs and PR Dolomite—Rate vs. Conversion

Figure 5.5 Effect of HTT on Sulfation of Longview Limestone—Conversion vs. Time

Figure 5.6 Effect of HTT on Sulfation of PR Dolomite—Conversion vs. Time

Table 5.32 - Effect of HTT on SO₂ Absorption by Longview limestone

Time, min.	Calcium Conversion, %			
	2130°F	2024°F	1900°F	1600°F
20	16.9	35.7	40.4	36.7
40	21.5	44.3	49.9	39.9
60	24.7	49.2	54.8	41.1
80	27.2	52.4	57.7	41.6

Table 5.33 - Effect of HTT on SO₂ Absorption by PR dolomite

Time, min.	Calcium Conversion, %	
	2100°F	1600°F
20	20.4	73.9
40	23.9	83.5
60	26.4	88.6
80	28.5	92.0

5.5 H₂S Absorption Studies in Quartz Reactor

Sulfidation of LASHs was carried out in the quartz reactor in order to increase the fraction of CaS present in LASHs and to determine the extent of absorption of H₂S by LASHs and fresh limestones. Except for the bed temperature, generally same experimental conditions (velocity and the amount of bed material) as used for the SO₂ absorption study were maintained so that a direct comparison could be made between the results of the two studies. The standard test conditions for these studies are given in Table 5.34. The reaction rate of Greer limestone with H₂S was studied at 1800°F. The results are shown in Table 5.35.

Table 5.34 - Experimental Conditions for H₂S Absorption

Particle size	18x80 mesh
Gas composition	1% H ₂ S, balance N ₂
Linear velocity at operating temp.	0.43 ft/s

Table 5.35 - H₂S Absorption by Greer limestone at 1800°F

Time, hours	Outlet H ₂ S conc. ppm
<4.0	10
5.5	80
6.5	140
7.4	200

Thus the absorption of H₂S at 1800°F was not as good as the absorption of SO₂ at 1600°F. The absorption of H₂S by KRW and FW LASHs at 1800°F is shown in Table 5.36.

Table 5.36 - H₂S Absorption by KRW and FW LASHs at 1800°F

KRW LASH at 1800°F		FW LASH at 1800°F	
Time, hours	Outlet H ₂ S conc., ppm	Time, hours	Outlet H ₂ S conc., ppm
<4.0	0	<1.5	0
6.75	100	3	30
8.25	900	4	250
12.0	3500	6	1000

The superior H₂S absorption by KRW LASH compared to FW LASH may be attributed to the differences in the sorbents used in producing these LASHs. KRW LASH was produced from NE limestone, a dolomitic limestone, whereas FW LASH was produced from Longview limestone, a high-calcium limestone.

The TP DASH was sulfided in the quartz reactor at standard test conditions for a total period of seven hours. The concentration of H₂S in the outlet as a function of time is shown in Table 5.37. The TP DASH compares poorly with KRW LASH for the absorption of H₂S.

Table 5.37 - H₂S Absorption by TP DASH at 1800°F

Time, hours	Outlet H ₂ S conc., %
<4.0	0.4
5.75	0.4
7.00	0.5

Summary

A summary of calcium utilization of the solids after SO₂ absorption is given in Table 5.38 with nominal weight per cent of CaS after sulfidation in those cases where sulfided solids were used. As discussed earlier, the sulfided solids were either oxidized separately or enough O₂ was supplied to convert the sulfide to sulfate prior to SO₂ absorption.

These results show that PR dolomite absorbed SO₂ much better than the other solids. The sulfide level did not affect its SO₂ absorption capacity. Among the LASHs, TRTU LASH absorbed the maximum amount of SO₂ leading to high calcium utilization.

The results on SO₂ absorption can be summarized as follows:

- The absorption of SO₂ in the presence of O₂ by fresh sorbents was very good with breakthrough periods at SO₂ concentration of 100 ppm up to 12 hours with a maximum observed at 1700°F for Greer limestone. The performance of the latter was appreciably better than that of SP limestone.
- The absorption of SO₂ by lightly-sulfided as well as heavily-sulfided SP and Greer limestones, and PR dolomite was very good after exposing the sorbents to 10-21 % O₂ for a period of time sufficient for the conversion of most CaS to CaSO₄ or after they were oxidized in a separate step.
- The absorption of SO₂ by KRW LASH, and KRW and TP DASHs was very poor. This may be attributed to the relatively high temperatures at which these solids were processed in the gasifiers. The absorption of SO₂ by FW DASH was very good, after converting most CaS to CaSO₄, reflecting the advantage of using a dolomite over a limestone in the FW carbonizer. The absorption of SO₂ by FW LASH was poor, but better compared to KRW LASH.

- The absorption of SO_2 by mixtures of LASHs and limestones was synergistic compared to the performance of individual solids. The absorption of SO_2 by a mixture of FW DASH and PR dolomite was about the same as that expected from individual solids.
- The absorption of SO_2 by fresh limestones in the absence of O_2 was poor, possibly due to the absence of a stable product.
- The absorption of H_2S by KRW LASH was as good as that observed for the two fresh limestones, used in this study, with a breakthrough period at H_2S concentration of 100 ppm up to 7 hours.

Table 5.38 - Summary of Calcium Utilization in SO_2 Absorption Studies

Material	B.T. period, hours	SO_2^* abs., % of CaO	Ca Ut. mole % Feed	Ca Ut. mole % Product
SP limestone	6.00	12.9	0	11 ⁺
Greer limestone	12.50	31.0	0	27
Longview limestone	11.44	27.2	0	24
Greer-10% CaS	6.00	27.5	10	34
PR dolomite-10% CaS	14.51	78.1	23	76
PR dolomite-40% CaS	4.50	114.2	73	100
LSCF KRW LASH	0.33	2.3	35	36
LSCF FW LASH	0.00	0.0	23	23
LSCF TRTU LASH	6.25	10.0	12	74
TP DASH	0.06	1.0	14	15
FW DASH	2.00	45.8	56	71
Mix. KRW LASH-Greer	4.93	30.8	26	53
Mix. FW LASH-Longview	4.50	20.1	17	28
Mix. FW DASH-PR dolomite	5.15	49.0	51	86

B.T. - Breakthrough period corresponds to 150 ppm of SO_2 at the exit

* grams of SO_2 absorbed per 100 grams of CaO

⁺ Calcium utilization appears to be low.

SECTION 6.0-PHYSICAL CHARACTERIZATION OF LASHS, DASHS AND SORBENTS

6.1 Mercury Porosimetry

Calcined sorbents and carbon-free LASHs and DASHs were characterized by mercury porosimetry to measure the variation of pore surface area and pore volume as a function of pore size. The measurements were performed on a Micromeritics Autopore II 9220. The pressure was increased from 1.6 to 60,000 psia that covers pores from about 117 microns to 0.003 micron (30 angstroms) in diameter.

The results on total pore volume and total pore surface area of various solids are given in Table 6.1. The results were calculated using a contact angle of 130 degrees and a surface tension of 485 dynes/centimeter for mercury. The average pore diameter is calculated from the relation $4V/A$ where V is the total pore volume and A is the total pore surface area.

Table 6.1 - Pore Characteristics of Calcined Sorbents and LASHs/DASHs

Solid Type	Pore Surf. Area, m ² /gm	Pore dia. (Average) micron	Porosity, Fraction	Pore volume, cc/gm
PR dolomite	7.50	0.21	0.53	0.39
Longview limestone	6.00	0.19	0.47	0.29
SP limestone	11.78	0.10	0.46	0.30
KRW LASH-AR	3.45	0.22	0.36	0.19
KRW LASH-CF	5.62	0.11	0.30	0.15
KRW DASH-CF	6.41	0.06	0.23	0.10
FW LASH-CF	9.54	0.11	0.40	0.26
FW DASH-CF	10.11	0.10	0.42	0.25
TP DASH-CF	9.57	0.22	0.57	0.52
KRW LASH (oxidized)	4.6	0.13	0.30	0.15
TRTU LASH	8.9	0.34	0.66	0.76

AR - as received (containing carbon)

CF - carbon-free

Based on the SO₂ absorption capacity of the various solids, reported in Section 5.0, and the above information on pore characteristics, no correlation appears to exist between either the total pore surface area or the total pore volume and SO₂ absorption capacity.

The differential pore volume divided by differential pore size for each incremental change in pressure, called differential intrusion, is plotted as a function of pore diameter in Figures 6.1 to 6.7 for LASHs, DASHs and fresh sorbents. Among the various types of plots drawn generally from mercury porosimetry data, this particular plot appears to be the best in discerning the differences in SO₂ absorption capacity of these solids. In the discussion given below, large pores refer to pores of 0.05 to 0.5 micron in diameter and small pores refer to pores less than 0.01 micron in diameter.

By comparing the pore characteristics of KRW LASH with Longview limestone (Figures 6.1 and 6.2) and KRW DASH with PR dolomite (Figures 6.3 and 6.4), it can be noted that large pores (0.05 to 0.5 micron in diameter) present in the fresh sorbents are not present in the KRW LASH and DASH. Characteristics of TP DASH are similar to those of KRW DASH. This suggests that large pores that are beneficial for SO₂ absorption disappeared from the sorbents when they were processed in the KRW and TP gasifiers. In the case of FW LASH (Figure 6.6), there is a partial loss of large pores and its SO₂ absorption capacity did not correlate well with the observed pore size distribution.

Examination of the data on TRTU LASH (Figure 6.7) indicates that there is appreciable volume in pores of 0.02 to 0.1 micron in diameter. Although this range is smaller than the range observed for fresh sorbents, it is larger than the small pores (<0.01 micron in diameter). The good SO₂ absorption capacity of the TRTU LASH may be attributed to the presence of these pores.

Table 6.2 - Pore Characteristics of Calcined Sorbents and LASHs/DASHs

Solid Type (HTT) ¹	Pore Surf. Area, m ² /gm	Pore dia. (Average) micron	Poro- sity, Fraction	Pore volume, cc/gm
PR dolomite (2100°F)	1.5	1.25	0.59	0.47
PR dolomite (1600°F)	7.5	0.21	0.53	0.39
Longview limestone (2130°F)	1.7	0.71	0.49	0.31
Longview limestone (2024°F)	6.0	0.24	0.53	0.36
Longview limestone (1600°F)	6.0	0.19	0.47	0.29

¹ Temperatures given in parentheses are heat treatment temperatures.

Figure 6.1 Characterization of KRW LASH

Figure 6.2 Characterization of Longview limestone

Figure 6.3 Characterization of KRW DASH

Figure 6.4 Characterization of PR dolomite

Figure 6.5 Characterization of TP DASH

Figure 6.6 Characterization of FW LASH

Figure 6.7 Characterization of TRTU LASH

The pore surface areas of both PR dolomite and Longview limestone decreased substantially with an increase in HTT to about 2100°F. Based on the SO₂ absorption capacity of the various solids and the above information on pore characteristics, no correlation appears to exist between either the total pore surface area or the total pore volume and SO₂ absorption capacity. Although there is no good correlation between the pore surface area and SO₂ absorption for the wide array of solids studied; for the same solid, however, there appears to be a good correlation between these two parameters. But average pore diameter, porosity and pore volume do not correlate with SO₂ absorption capacity.

The differential intrusion is plotted as a function of pore diameter in Figures 6.8 and 6.9 for Longview limestone and PR dolomite exposed to 2100°F, respectively. Comparison of data on PR dolomite with a HTT of 2100°F (Figure 6.9) with that at 1600°F (Figure 6.7), there is a substantial reduction in the volume of pores of 0.05 to 0.5 micron in diameter (corresponding to a reduction in the maximum value of differential intrusion), indicating that heating the sorbent to 2100°F reduced the volume of these pores. Comparison of Figures 6.8 and 6.6 on Longview limestone, showing the effect of HTT of 2130°F, indicates that there is a significant reduction in the volume of pores of 0.05 to 0.5 micron in diameter with an increase in the HTT, confirming the above observation with PR dolomite and the observation that large pores disappeared when sorbents were processed in the KRW and TP gasifiers. There is a reduction in the

volume of smaller pores, but this appears to be of no consequence to SO₂ absorption capacity.

6.2 N₂ Pore Surface Areas as per BET method

Pore surface areas of various calcined, sulfided and sulfated sorbents and LASHs were measured using N₂ on a BET analyzer and are given in Table 6.3.

Table 6.3 - N₂ Pore surface areas as per BET method

LASH/Sorbent	Surface area, m ² /gm
LSCF FW LASH	2.9
LSAR KRW LASH	0.6
LSCF KRW LASH	0.4
LSCF KRW LASH oxidized	0.5
SP limestone calcined	7.9
LSCF TP DASH	2.1
PR dolomite calcined	5.0
PR dolomite sulfided	4.8
Greer limestone calcined	1.4
Greer limestone sulfided (17% CaS)	2.0
Longview limestone (sulfated)	3.9

No clear trends on change in pore surface areas with sulfidation and sulfation can be noticed from the above results. There appears to be no correlation between the SO₂ absorption capacity and the N₂ surface areas. Measurement of pore size distribution by means of mercury porosimetry is the preferred method to understand the SO₂ absorption behavior of the various sorbents.

Figure 6.8 Characterization of Longview limestone Exposed to 2100°F

Figure 6.9 Characterization of PR dolomite Exposed to 2100°F

SECTION 7.0 - LASH/DASH OXIDATION STUDIES IN TRTU

7.1 Introduction

Oxidation tests on KRW and TRTU LASHs, FW LASH and DASH were conducted in the Transport Reactor Test Unit (TRTU). Tests on the KRW LASH were conducted to determine the effect of bed temperature, oxygen level, riser bed density and particle size. Oxidation was performed in the riser as well as in the annulus. The operation was performed in both batch and continuous feed modes. Oxidation of the TRTU LASH was conducted in the batch mode at selected conditions. Although attempted, absorption of SO_2 on KRW and TRTU LASHs was not as successful as hoped due to operating problems in the SO_2 delivery system. The TRTU LASH was produced using Longview limestone that is a high calcium-type whereas KRW LASH was prepared using NE limestone that is a dolomitic type. FW LASH and DASH were oxidized in the batch mode.

Tests on KRW and TRTU LASHs

Each test was classified into steady-state periods based on the operating conditions of process variables. For each steady-state period, mass balances on both solids and gases were performed. Details of the run history, experimental procedure and data analysis are given here.

Table 7.1 - Summary of Operating Conditions For KRW LASH

Pressure, psig	35
Temperature, °F	1530 - 1663
Riser bed density, lb/ft ³	11.5 - 12.3*
Gas super. velocity, ft/s	30 - 42
LASH feedrate, lb/hr	0 - 14
Feedstocks	KRW and TRTU LASHs
Oxidation modes	continuous and batch Riser and annulus

* overall (average) riser bed density based on pressure differentials

Tests on FW LASH and DASH

A summary of the operating conditions used for the TRTU tests with FW LASH and DASH is given in Table 7.2. Lower riser densities were maintained in the case of

FW LASH and DASH as a result of lower solid inventory (of desired size distribution) used in the annulus.

Table 7.2 - Summary of Operating Conditions for FW LASH and DASH

Pressure, psig	35
Temperature, °F	1499 - 1608
Riser bed density, lb/ft ³	0.2 - 2.5*
Gas super. velocity, ft/s	11 - 25
Bed material	FW LASH and DASH
Oxidation mode	Batch (riser and annulus)
Sulfation mode	Batch (riser only)

* overall (average) riser bed density based on pressure differentials

7.2 Experimental

7.2.1 Description of TRTU

The TRTU is a circulating fluidized bed reactor capable of continuous operation. It consists of a riser which is 0.5-inch Schedule 40 pipe 30-ft tall located inside a 3-inch ID outer pipe which serves as the pressure vessel. Both pipes are made of Incoloy 800HT. The riser is equipped with a cone valve-eductor solids circulation control device at the bottom and is contained in the outer pressure vessel. The annulus between the pressure vessel and the riser is used as the solids downcomer leg from which heated solids are circulated into the riser and mixed with fresh feeds. Reactions occur in the riser and solids and gases are injected into the riser at the bottom and flow up through the tube. Perforations are provided through the bottom flange for N₂ sparging and to fluidize solids in the annular space, solid feed gun and eductor feed line. Heat to the unit is supplied by six zone electric heaters, each of which is separately controlled. The TRTU can be operated at temperatures up to 1950°F and pressures up to 300 psig.

LASH oxidation studies were performed in two modes of operation: (1) continuous feed and (2) batch feed of LASH. In the batch feed of LASH, the effect of solid residence time and temperature on sulfide oxidation was studied. In order to simulate the operation of a sulfator/combustor, the simultaneous oxidation of LASH and the absorption of SO₂ was attempted in the continuous feed mode, there was an immediate breakthrough of SO₂ from the TRTU.

7.2.2 Description of Tests

A summary of the tests with KRW LASH, FW LASH and FW DASH is given below.

Tests on KRW LASH

1. L00 KRW coarse LASH was oxidized in the riser for a total period of 13 hours in a batch mode.
2. L01 KRW fine LASH was oxidized in the riser in the continuous mode. LASH feed was steady. LASH feed was discontinued during SO₂ absorption test. Depending upon operating conditions, this series was divided into four steady-state periods:
 - L01A - High partial pressure of oxygen
 - L01B - Low partial pressure of oxygen
 - L01C - High temperature and high partial pressure of oxygen
 - L01D - Attempted SO₂ absorption
3. L02 KRW coarse LASH was oxidized. LASH feed was not as smooth as in the L01 series. The coal feed gun developed a blowthrough due to erosion from LASH particles and, hence, during this run, solid feed was discontinued. The oxidation of the LASH in the annular bed was conducted (bubbling bed mode) without feed. This series was divided into two periods depending upon the oxidation mode.
 - L02A - Oxidation in the riser with a continuous feed
 - L02B - Oxidation in the annulus and riser in the batch mode
4. L03A KRW fine LASH was oxidized in the riser. This was a repeat of the L01 series at a reduced bed density and corresponds to a high oxygen level at a reduced riser bed density.
5. L04A TRTU LASH was oxidized in this period in the batch mode.

Tests on FW LASH (All In Batch Mode)

1. FWL01A 17 lb of fresh LASH were charged, and the carbon in the LASH was burned off until oxygen breakthrough occurred.
2. FWL01B Oxidation was continued from the previous test until no carbon oxides were present in the exit gas and the oxygen concentration leveled off.

3. FWL02A 3 lb of fresh LASH were added and oxidation was run until oxygen breakthrough occurred.
4. FWL02B Oxidation was continued with concurrent injection of SO₂ (about 7500 ppm at inlet) until outlet SO₂ concentration exceeded 1000 ppm.
5. FWL03A 3 lb of fresh LASH were added and oxidation was run until oxygen breakthrough occurred.
6. FWL03B Repeat of test FWL02B.
7. FWL04 Annular oxidation of material remaining from FWL03B.

Tests on FW DASH

8. FWD01A 17 lb of fresh DASH was charged and the carbon in the DASH was burned off until oxygen breakthrough occurred.
9. FWD01B Oxidation was continued with concurrent injection of SO₂ (about 7500 ppm at inlet) until outlet SO₂ reached 185 ppm.
10. FWD02 Annular oxidation of material remaining from FWD01B.
11. FWD03A 3 lb of fresh DASH were added and oxidation was performed until oxygen breakthrough occurred.
12. FWD03B Oxidation was continued until no carbon oxides were present in the exit gas and the oxygen concentration leveled off.

7.3 Results and Discussion

7.3.1 Oxidation of KRW LASH

The results on KRW LASH are summarized in Table 7.3. Limited data obtained with TRTU LASH are also presented in this table. Operating data are presented in Table 7.4.

Table 7.3 - Summary of Test Results on KRW and TRTU LASHs

Run ID	L00	L01A	L01B	L01C
Material	Coarse	Fine	Fine	Fine
Test Mode	Riser	Riser	Riser	Riser
Temperature, °F	1540	1570	1563	1663
LASH Feed, lb/hr	0	8.5	9.4	10.4
O ₂ in Exit Gas, %	8.0	9.1	3.4	7.9
Gas vel., ft/s ¹	30.1	37.8	36.4	40.7
Riser dens. ² lb/ft ³	12.0	12.3	12.6	11.5
Time-Batch Oxid., hr	13.0	N.A.	N.A.	N.A.
Initial sulfide, %	4.7	7.7	7.7	7.7
Final sulfide, %	0.47	2.0	3.7	2.9
Conversion, %	90.0	74.0	52.0	62.3

Table 7.3 Summary of Test Results on KRW and TRTU LASHs (Cont'd)

Run ID	L01D	L02A	L02B	L03A	L04A
Material	Fine	Coarse	Coarse	Fine	TRTU
Test Mode	Riser	Riser	Annulus +Riser	Riser	Riser
Temperature, °F	1600	1600	1600	1650	1552
LASH Feed, lb/hr	0	13.1	0	13.7	0
O ₂ in Exit Gas, %	10.3	7.0	5.6	8.0	-
Gas vel., ft/s	30.1	41.1	32.7	41.0	41.6
Riser den., lb/ft ³	7.2	12.7	4.9	4.6	8.6
Time-Batch Oxid., hr	4.0	N.A.	4.5	N.A.	5.9
Initial sulfide, %	1.5	5.9	4.0	5.3	-
Final sulfide, %	0.3	3.2	2.0	3.2	-
Conversion, %	80.0	45.8	50.0	39.6	-

¹ Superficial gas velocity in the riser based on the inlet gas flow and conditions at the exit of the riser.

² Overall riser bed density

N.A. - not applicable

Table 7.4 - Summary of Operating Data on KRW and TRTU LASHs

Run Number	L00	L01A	L01B	L01C
Material	Coarse	Fine	Fine	Fine
Test Mode	Riser	Riser	Riser	Riser
Temperature, °F	1540	1570	1563	1663
Riser Velocity, ft/sec*	30.10	37.83	36.35	40.70
Annular Velocity, ft/sec	0.49	0.49	0.54	0.56
Annular bed ht., ft	12.70	10.96	12.30	13.16
Riser bed dens., lb/ft ³	10.78	12.27	12.63	11.50
Annular bed dens., lb/ft ³	53.64	66.87	61.46	57.75
Riser holdup, lb	0.68	0.77	0.79	0.72
Annulus holdup, lb	30.69	33.15	34.19	34.39
Oxidation, %	90.0	74.0	52.0	62.3
Time-Batch Oxid., hr	13.0	N.A.	N.A.	N.A.
Solids Velocity, ft/sec	16.5	21.0	20.3	22.5
Solid circ. rate, lb/hr	1355	1960	1945	1962
Solids residence time per pass				
Riser, sec	1.81	1.41	1.47	1.32
Annular Bed, sec	82.5	60.9	63.3	63.1
Time for S.S., hr	6.19	1.82	2.58	2.07
No. of passes to S.S.	272	105	144	115
Total solids res. time				
in riser, minutes	8.07	2.48	3.51	2.55
in annular bed, min.	363.4	106.52	151.49	121.45
Conv. of sulfide per pass (average), %	0.331	0.705	0.361	0.542

* - gas superficial velocity in the riser

S.S. - Steady state

circ. - circulation

N.A. - not applicable

Table 7.4 - Summary of Operating Data on KRW and TRTU LASHs (Cont'd)

Run Number	L01D	L02A	L02B	L03A	L04A
Material	Fine	Coarse	Coarse	Fine	TRTU
Test Mode	Riser	Riser	Annulus + Riser	Riser	Riser
Temperature, °F	1600	1600	1600	1650	1552
Riser Velocity, ft/sec	30.1	41.1	32.7	41.0	41.6
Annular Velocity, ft/sec	0.56	0.70	0.42	0.57	0.62
Annular bed ht., ft	6.52	11.86	6.64	6.75	10.74
Riser bed dens., lb/ft ³	7.15	12.67	4.96	4.61	8.62
Annular Bed dens., lb/ft ³	65.14	61.03	44.47	59.23	53.43
Riser holdup, lb	0.45	0.80	0.31	0.29	0.54
Annulus holdup, lb	19.21	32.75	13.36	18.09	25.97
Oxidation, %	80.0	45.8	50.0	39.6	33.8
Time-Batch Oxid., hr	4.0	N.A.	4.5	N.A.	5.9
Solids Velocity, ft/sec	16.0	22.9	17.0	21.3	22.4
Solid circ. rate, lb/hr	868	2204	641	746	1464
Solids residence time per pass					
Riser, sec	1.86	1.30	1.75	1.40	1.33
Annular Bed, sec	79.7	53.5	75.1	87.3	63.9
Time for S.S., hr	10.65	3.40	6.00	7.38	6.53
No. of Passes to S.S.	470	223	281	300	361
Total solids res. time					
in riser, minutes	14.6	4.8	8.2	7.0	8.0
in annular bed, min.	624.4	199.2	351.8	436.0	384.0
Conv. of Sulfide per pass (average), %	0.170	0.205	0.178	0.132	-

7.3.2 Oxidation of FW LASH and DASH

A limited number of oxidation tests and SO_2 absorption tests on FW LASH and DASH were conducted in the TRTU. The tests were done for purposes of comparison with earlier results on KRW and TRTU LASHs. Due to a leak on the water jacket surrounding the solids feed tube, it was not possible to conduct any tests in a continuous feed mode. Hence, all of the tests were done in a batch mode. Most of the runs were done in the riser, but two short-term oxidation tests were done in the annulus to determine whether annular oxidation could enhance the oxidation of material previously oxidized in the riser.

FW LASH and DASH were produced from Longview limestone and PR dolomite, respectively. The materials, as received, contained appreciable amounts of free carbon (char). Analysis of the LASH showed about 28% free carbon, whereas the DASH contained almost 20% free carbon. Both materials had a low calcium utilization of 25-28%. Free calcium in the LASH appeared to be present in the carbonate form, and the DASH analysis showed the calcium to be about 50% carbonated. Both feed materials were ground and screened to 40x325 mesh for use in the TRTU.

Tests on FW LASH

A total of seven LASH oxidation tests were conducted, all but one in the riser. During two of the riser oxidation tests, SO_2 was injected into the feed gas to determine whether the LASH was capable of absorbing any SO_2 . Both of these tests demonstrated that the LASH absorbed a significant quantity of SO_2 , as shown by the large increase in calcium utilization over the run.

The tests showed that an oxidation level of only about 20-30% could be achieved, with oxidation levels generally below 20%. The two runs done with SO_2 injection produced higher oxidation levels (40-50%), but this can be attributed to the SO_2 absorption rather than oxidation.

During run FWL03A, which was performed at a riser temperature of about 1600°F, SO_2 evolution was noted, at an average concentration of 500 ppm. None of the other runs, all of which were done at temperatures below 1600°F, experienced evolution of SO_2 .

A single annular oxidation test, FWL04, was done to determine whether the oxidation level of LASH previously oxidized in the riser could be increased. The results showed no change in oxidation level after 4 hours in the dense phase annulus.

Tests on FW DASH

The DASH oxidation tests consisted of four riser tests and one annular test. SO_2 was added to the feed gas during one riser test.

Run FWD01A resulted in an oxidation level of about 50%, but this run was terminated at oxygen breakthrough. Most of the oxygen was consumed by carbon oxidation. Run FWD01B, with SO₂ addition to the feed gas, resulted in a much higher final oxidation level. While this partially reflects the absorption of SO₂, it also demonstrates a high conversion, about 77%, of the residual sulfide from the previous run. The next run, FWD02, was oxidation in the dense phase annulus, and increased the oxidation level to almost 100%. The final two riser runs, after the addition of fresh material, showed final oxidation levels of 70-80%.

Oxidation of the DASH is much better than that of the LASH. The data indicate that 70-90% oxidation level was achieved for the DASH as compared to only 20-30% for the LASH.

During run FWD03A, which was done at a riser temperature of 1576°F, SO₂ evolution was observed, at a concentration of about 100 ppm. Since both materials evolved SO₂ at temperatures approaching 1600°F at zero oxygen concentration in the exit gas, oxidation should preferably be done at either lower temperatures or at higher oxygen concentration.

Test results on the FW materials are summarized in Table 7.5. Abbreviations used in the table are defined at the bottom of the tables.

Table 7.5 - Summary of Test Results on FW LASH and DASH

Run ID ¹	FWL01A	FWL01B	FWL02A	FWL02B
Test Mode	Riser	Riser	Riser	Riser
Temperature, °F	1512	1499	1528	1507
O ₂ in Exit Gas, %	0	14	0	6.45
Gas vel., ft/s	25.4	25.3	20.8	12.2
Riser density, lb/ft ³	2.49	0.42	1.16	0.79
Run Time, hr	2.83	5.00	0.67	2.08
Initial Conditions				
% Ca Utilization	25.2	23.3	21.8	22.4
% S Oxidation ²	3.1	19.3	3.8	20.6
Wt% Free C	28.3	0.2	6.9	0.0
Final Conditions				
% Ca Utilization	23.3	21.7	22.4	33.5
% S Oxidation	19.3	27.8	20.6	52.2
Wt% Free C	0.24	0.95	0.0	0.04
Oxidation, %	16.7	10.5	17.5	12.3 ³
SO ₂ Absorption, % of initial sulfur content	-	-	-	45.7

¹ FWL - FW LASH; FWD - FW DASH

² Sulfide oxidation is defined as moles of sulfate sulfur divided by total moles of sulfur.

³ Estimated by deducting the moles of SO₂ absorbed from the moles of sulfate at the end of the run. This difference is the net sulfide in the starting material which was oxidized during the run.

N/A - not available

* SO₂ evolution was noted at an average concentration of about 100 ppm.

Table 7.5 - Summary of Test Results on FW LASH and DASH (Cont'd)

Run ID	FWL03A*	FWL03B	FWL04	FWD01A
Test Mode	Riser	Riser	Annular	Riser
Temperature, °F	1608	1569	1545	1527
O ₂ in Exit Gas, %	0	5.35	3.4	0
Gas vel., ft/sec	22.6	12.0	0.32	21.1
Riser den., lb/ft ³	1.12	1.01	-	1.26
Run Time, hr	0.83	1.58	3.92	2.00
Initial Conditions				
% Ca Utilization	31.5	26.1	32.5	27.7
% S Oxidation	8.2	28.6	45.7	3.7
Wt% Free C	15.5	0.4	0.0	19.7
Final Conditions				
% Ca Utilization	22.9	32.5	31.5	N/A
% S Oxidation	32.7	42.0	48.7	52.3
Wt% Free C	0.38	0.0	0.0	0.83
Oxidation, %	26.7	N/A	5.5	50.5
SO ₂ Absorption, % of initial sulfur content	-	31.1	-	-

¹ FWL - FW LASH; FWD - FW DASH

² Sulfide oxidation is defined as moles of sulfate sulfur divided by total moles of sulfur.

³ Estimated by deducting the moles of SO₂ absorbed from the moles of sulfate at the end of the run. This difference is the net sulfide in the starting material which was oxidized during the run.

N/A - not available

* SO₂ evolution was noted at an average concentration of about 100 ppm.

Table 7.5 - Summary of Test Results on FW LASH and DASH (Cont'd)

Run ID	FWD01B	FWD02	FWD03A*	FWD03B
Test Mode	Riser	Annular	Riser	Riser
Temperature, °F	1531	1550	1576	1545
O ₂ in Exit Gas, %	4.95	3.35	0	12.6
Gas vel., ft/sec	11.4	0.33	21.8	24.3
Riser den., lb/ft ³	0.97	-	0.88	0.23
Run Time, hr	7.33	4.00	0.42	1.08
Initial Conditions				
% Ca Utilization	N/A	57.6	43.3	41.7
% S Oxidation	52.3	91.9	73.5	73.3
Wt% Free C	0.8	0.0	5.5	0.0
Final Conditions				
% Ca Utilization	57.6	54.9	41.6	41.7
% S Oxidation	91.9	97.4	74.8	79.3
Wt% Free C	0.0	0.0	1.7	0.0
Oxidation, %	76.9	67.8	4.9	22.5
SO ₂ Absorption, % of initial sulfur content	36.6	-	-	-

¹ FWL - FW LASH; FWD - FW DASH

² Sulfide oxidation is defined as moles of sulfate sulfur divided by total moles of sulfur.

³ Estimated by deducting the moles of SO₂ absorbed from the moles of sulfate at the end of the run. This difference is the net sulfide in the starting material which was oxidized during the run.

N/A - not available

* SO₂ evolution was noted at an average concentration of about 100 ppm.

7.4 Summary

The following can be summarized from the batch and continuous oxidation of the fine and the coarse KRW LASH, and the batch oxidation of FW LASH and DASH in the TRTU:

Batch Oxidation of KRW LASH

- Batch oxidation of the fine KRW LASH yielded an oxidation level as high as 80%.
- For the batch oxidation of the coarse KRW LASH at 1600°F, an oxidation level of 66% was obtained. The difference in the oxidation of the fine and the coarse KRW LASH tests may be attributed primarily to the difference in the particle size.

Continuous Oxidation of KRW LASH

- Comparison of steady-state periods of L02A and L03A for the coarse and fine LASHs indicates that the oxidation level is about the same in both cases, although the riser bed density was 4.6 lb/ft³ for the fine LASH versus 12.7 lb/ft³ for the coarse LASH, showing that better performance was achieved with the fine LASH.
- With an increase in the riser bed density from 4.6 to 11.5 lb/ft³ for the fine KRW LASH, an increase in the oxidation level from 40 to 62% was obtained (L03A versus L01C).
- With an increase in the partial pressure of O₂ from 1.7 to 4.5 psi at the riser exit, the oxidation level increased from 52 to 74%, as can be expected from the nature of the reaction (L01B versus L01A).
- For the coarse KRW LASH, a slightly higher oxidation level (50%) in test L02B was obtained in the annulus compared to that of the riser (46%) in test L02A.
- Results indicate that the oxidized KRW LASH had very little capacity to absorb SO₂.
- Solid residence time per pass in the riser varied over a narrow range of 1.3 to 1.9 seconds and the number of passes varied from 105 to 470 with the assumption of a slip ratio (ratio of actual gas velocity to the actual solid velocity) of 2 based on previous experience.

Batch Oxidation of FW LASH and DASH in TRTU

- Oxidation of the FW LASH was poor. Final oxidation levels of only 20-30% were obtained.
- Oxidation of the FW DASH was much better than for the FW LASH. The data indicate that 70-90% oxidation level was achieved.
- Both FW LASH and DASH readily absorbed SO_2 .
- Oxidation of both LASH and DASH at zero oxygen partial pressure in the outlet gas (essentially all the oxygen fed was consumed in the TRTU prior to the outlet gas oxygen measurement) resulted in appreciable evolution of SO_2 . Oxidation should be accomplished preferably at lower temperatures or higher residual oxygen concentration.

The lower oxidation levels obtained for the various LASHs and the FW DASH in the TRTU compared to the results obtained in the BRU may be attributed to the lower solid residence time in the TRTU. This suggests that a transport reactor, over the experimental range studied, may not be suitable for oxidation of LASHs and DASHs.

SECTION 8.0 - CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

LASH/DASH Oxidation in BRU

The following conclusions may be drawn from the study of LASH oxidation in the BRU (temperature of 1700°F and atmospheric pressure in air for an hour):

- Higher oxidation levels obtained with KRW LASH compared to FW and TRTU LASHs may be attributed to the dolomitic limestone used in producing the KRW LASH whereas a high calcium-limestone was used in producing the other two LASHs.
- The alkali impregnation increased the oxidation levels of both KRW and FW LASHs from 22% to 80% to 90 to 95%.
- High oxidation levels obtained with TP and FW DASHs (100% and 93%) clearly demonstrate the advantage of using a dolomite over a limestone in the gasifier.
- Fundamental kinetic studies conducted on the ATGA showed that after about 20 to 50% oxidation level was achieved, the rate slowed down substantially (due to diffusional resistance in the CaSO_4 layer) and hence residence times larger than about 15 minutes are marginally beneficial in LASH oxidation.

SO_2 Absorption Studies

The following conclusions may be drawn from the SO_2 absorption studies in the quartz fixed bed reactor and the PTGA.

- The absorption of SO_2 in the presence of O_2 by fresh sorbents was very good while the absorption of SO_2 by fresh limestones in the absence of O_2 was poor, possibly due to the absence of a stable product.
- The absorption of SO_2 by lightly-sulfided as well as heavily-sulfided SP and Greer limestones, and PR dolomite was very good after the conversion of most CaS present in the solid to CaSO_4 .
- The poor absorption of SO_2 by KRW LASH, and KRW and TP DASHs may be attributed to the relatively high temperatures at which these solids were processed.
- The good absorption of SO_2 by FW DASH showed the advantage of using a dolomite over a limestone in the FW carbonizer.

- The absorption of SO_2 by mixtures of LASHs and limestones was better than that of the individual solids. The absorption of SO_2 by a mixture of FW DASH and dolomite was about the same as that expected from individual solids.
- The absorption of H_2S by KRW LASH was as good as that observed for the SP and Greer limestones.

Pore Characterization of Solids

The following conclusions may be drawn from the pore characterization of the various solids by means of mercury porosimetry:

- Pores of about 0.05 to 0.5 micron in diameter found in fresh sorbents, are apparently beneficial for SO_2 absorption. These were not present in the KRW LASH, and KRW and TP DASHs, thus contributing to poor SO_2 absorption where as FW DASH and TRTU LASH absorbed SO_2 quite well due to the presence of these pores. But the SO_2 absorption capacity of FW LASH did not correlate well with the observed pore size distribution.

Batch Oxidation of KRW LASH in TRTU

The following can be summarized from the batch oxidation of the fine and the coarse KRW LASH in the TRTU:

- Batch oxidation of the fine KRW LASH yielded oxidation levels as high as 80%.
- For the batch oxidation of the coarse KRW LASH at 1600°F , an oxidation level of 66% was obtained. The difference in the oxidation of the fine and the coarse KRW LASH tests may be attributed primarily to the difference in the particle size and the consequent difference in gas diffusional resistance.

Continuous Oxidation of KRW LASH in TRTU

The following can be summarized from the continuous oxidation of the fine and the coarse KRW LASH in the TRTU:

- Comparison of steady-state periods L02A and L03A for the coarse and fine LASHs indicates that the oxidation level was about the same in both cases, although the riser bed density was 4.6 lb/ft^3 for the fine LASH versus 12.7 lb/ft^3 for the coarse LASH, showing that better performance was achieved with the fine LASH (oxidation is apparently enhanced by increasing bed density).
- With an increase in the riser bed density from 4.6 to 11.5 lb/ft^3 for the fine KRW LASH, an increase in the oxidation level from 40 to 62% was obtained.

- With an increase in the partial pressure of O_2 from 1.7 to 4.5 psi at the riser exit, the oxidation level increased from 52 to 74%, as can be expected from the nature of the reaction.
- For the coarse KRW LASH, a slightly higher oxidation level (50%) was obtained in the annulus compared to that of the riser (46%).
- The oxidized KRW LASH had negligible capacity to absorb SO_2 at a leakage of 150 ppm.

Batch Oxidation of FW LASH and FW DASH in TRTU

- Oxidation of the FW LASH was poor. Final oxidation levels of only 20-30% were achieved.
- Oxidation of the FW DASH was much better than that of LASH. The data indicated that 70-90% oxidation level was achieved.
- Both FW LASH and DASH readily absorbed SO_2 .
- Oxidation of both materials at temperatures approaching 1600°F at a zero oxygen partial pressure in the outlet gas (essentially all the oxygen fed was consumed in the TRTU prior to the outlet gas oxygen measurement) resulted in appreciable evolution of SO_2 . Oxidation should be accomplished either at lower temperatures or higher residual oxygen concentration.
- Based on the results achieved with the various solids in both batch and continuous modes of operation, transport reactor does not appear to be a viable device for oxidation of LASHs and DASHs as a result of low solid residence time in the riser.

Testing of LASHs/DASHs As Per Interim EPA Test

Samples of LASHs and DASHs were tested as per the EPA interim test to evaluate solid wastes in terms of the amount of H_2S released upon contact with an aqueous acid. The following is a summary of the results:

- Both AR and oxidized CF KRW LASHs passed the test although they contained fairly high amounts of CaS (6.1 and 15.2%) as a result of higher temperatures to which they were exposed compared to the other LASHs.
- The AR FW LASH passed the test while the oxidized CF solids from a different batch failed the test as a result of higher CaS (7.5%) content. The AR TRTU LASH failed the test, as it is more reactive, due to the lower temperature at which

this was produced compared to the KRW and FW LASHs, and the appreciable CaS (6.3%) content.

- AR and partially oxidized KRW DASHs and AR FW DASH failed the test. The partially oxidized KRW DASH contained a high amount of CaS (15.8%) and, hence, failed the test despite the higher temperature at which it was produced. The oxidized FW DASH (2% CaS) passed the test.

8.2 Recommendations

The following recommendations are made based on the results of this study:

- Consider using a dolomite in fluidized bed gasifiers as it is likely to result in a high degree of subsequent oxidation of CaS in the sulfator/combustor.
- Examine different options to reduce the HTT of the sorbent in the process design of the fluidized bed gasifier—such as not feeding limestone/dolomite directly into high-temperature jet—which is likely to enhance the SO₂ absorption capacity of the sorbent in the sulfator/combustor.
- Consider addition of a portion of fresh limestone/dolomite directly to the sulfator to reduce the leakage of SO₂.

SECTION 9.0 TESTING OF LASHS AND DASHS AS PER INTERIM EPA TEST

9.1 EPA Tests on LASHs and DASHs

Ten samples of LASHs and DASHs were tested as per the EPA interim test that was developed to evaluate solid wastes in terms of the amount of H_2S released upon contact with an aqueous acid. The limit for passing the test is 500 milligrams of H_2S released per kilogram of waste.¹³ The results are presented in Table 9.1. Previously, similar materials including which were only partially oxidized (as low as 20%) passed the less aggressive original EPA test method.¹⁴

Table 9.1 - Results of EPA Test on LASHs and DASHs

LASH or DASH	wt% of CaS	mg of H_2S per Kg	Recovery, %
KRW LASH AR	15.2	390	0.54
KRW LASH CF	6.1	108	0.37
KRW DASH AR (pulverized)	28.1	3614	2.70
KRW DASH CF	15.8	7121	9.46
FW LASH AR	4.1	269	1.38
FW LASH CF	7.5	631	1.77
FW DASH AR	18.5	3274	3.72
FW DASH Oxidized	2.0	80	0.84
TRTU LASH AR (G6A)*	6.3	2912	9.70
TRTU LASH CF (G3A)*	0.09	49	11.43

AR - as received (containing carbon and carbonate)

CF - carbon free

* - G3A and G6A refer to test periods when the TRTU LASH was produced in the transport reactor test unit (TRTU).

Recovery is defined as percentage of CaS present in the sample that is released in the test. The analysis of AR TRTU LASH and CF TRTU LASH should not be compared since the latter was not produced from the former. The AR TRTU LASH of G3A contained 0.5% CaS. During muffling, the CaS content decreased from 0.5% to 0.09%. This sample substitution had to be done due to the lack of a desired sample.

Both CF and AR KRW LASHs passed the test although they contained fairly high amounts of CaS (6.1 and 15.2%) as a result of higher temperatures to which they were exposed compared to the other LASHs. The AR FW LASH passed the test while the CF solids from a different batch failed the test as a result of higher CaS (7.5%) content. A comparison of KRW and FW LASHs shows that higher recovery was obtained with FW solids as they were processed at a significantly lower temperature than KRW solids. Among the LASHs, the AR TRTU LASH released the largest amount of H₂S. This may be attributed to the lower temperature at which this was processed compared to the KRW and FW LASHs and the appreciable CaS (6.3%) content.

AR and partially oxidized KRW DASH and AR FW DASH failed the test. The partially oxidized KRW DASH contained high amount of CaS (15.8%) and, hence, remained very active in releasing H₂S, despite the higher temperature at which it was processed. The oxidized FW DASH (2% CaS) passed the test.

CF KRW DASH and CF FW LASH were oxidized in a quartz fixed bed reactor (described in Section 5.0) at a nominal temperature of 1700°F for an hour at atmospheric pressure. Oxidized KRW DASH and oxidized FW LASH were tested as per the EPA interim test and the results are given in Table 9.2.

Table 9.2 - Results of EPA Test on FW LASH and KRW DASH

LASH or DASH	wt% of CaS	mg of H ₂ S per Kg	Recovery, %
KRW DASH oxidized	17.6	314	0.38
FW LASH oxidized	9.0	744	1.74

Oxidized KRW DASH passed the test while oxidized FW LASH failed the test. The appreciable CaS content in these solids indicate that these two solids were not oxidized as well as that achieved in the fluidized bed as a result of poorer gas-solid contacting.

The DASHs, in general, appear to be more reactive than the LASHs in releasing H₂S just as they are in absorbing SO₂ and during sulfide oxidation. Based on these results, it can be stated that the inherent reactivity of solids, temperature at which they were processed and the residual CaS content are major contributing factors to the behavior of these solids in the EPA test.

SECTION 10.0 - REFERENCES

1. Haldipur, G.B., D.K. Schmidt and K.J. Smith, "A 50-Month Gasifier Mechanistic Study and Downstream Unit Process Development Program for the Pressurized Ash-Agglomerating Fluidized Bed Gasification System: Final Report," Volumes 1 and 2, FE-21063-69 (1989).
2. Keairns, D.L. et al., "Evaluation of the FBC Process, Vol IV- Fluidized bed Oil Gasification/Desulfurization," EPA-650/2-73-048d (1973).
3. Rehmat, A. and M.J. Abbasian, "Reaction of Ca-based Sorbents with Sulfur Compounds during Gasification," Report No. GRI-88/0348 (1988).
4. Rogan, H.S., "Characterization of Sorbent Materials," Report to KRW Energy Systems, Inc. (1986).
5. Weldon, J. and G.B. Haldipur, "Preliminary Characterization of Solid Wastes Produced in the KRW Gasifier-Desulfurizer," DOE Report FE-21063-30 (1987).
6. Agrawal, R.K. and G.B. Haldipur, "Advanced Gasifier-Desulfurizer Process Development for SNG Application: KRW Bench-Scale Program," GRI-89/0011 (1989).
7. Lang, R.J. and R.C. Neavel, "Behavior of Ca as a Steam Gasification Catalyst," Fuel, **61**, 620 (1982).
8. Lecea, C.S., et al., "Ca-catalyzed Carbon Gasification in CO₂ and Steam," Fuel, **69**, 21 (1990).
9. Walker, P.L., Jr. et al., "Catalysis of Gasification of Coal-derived Cokes and Chars," Fuel, **62**, 140 (1983).
10. Katta, S., Principal Investigator, "Process Analysis Topical Report on Pressurized Ash-Agglomerating Fluidized-Bed Gasification System," FY-1984 & 1985, submitted by KRW Energy Systems to U.S. DOE, FE-21063-26 (1986).
11. E.P. O'Neill, D.L. Keairns and W.F. Kittle, *Thermochimica Acta*, **14**, 209-220 (1976).
12. N.H. Ulerich, E.P. O'Neill and D.L. Keairns, *Thermochimica Acta*, **26**, 269-282 (1978).
13. "Test Methods for Evaluating Solid Waste," Volume IC: Laboratory Manual Physical/Chemical Methods, Environmental Protection Agency (Revision 1, November 1990).
14. Weldon, J. and G.B. Haldipur, "Preliminary Characterization of Solid Wastes Produced in the KRW Gasifier-Desulfurizer," DOE Report FE-21063-30 (1987).

SECTION 11.0 - NOMENCLATURE AND ACRONYMS

AL No.	Identification number assigned to a sample submitted for chemical analysis
AR	As-Received solids
ATGA	Atmospheric Thermogravimetric Analyzer
BRU	Bench-scale Reactor Unit
CF	carbon-free
CFHS	processed in the muffle furnace first to burn off carbon and then sulfided in the quartz reactor
Conv.	conversion
DASH	mixture of dolomite and ash
DT method	Draeger Tube method to determine CaS content in solids
EDAX	Energy Dispersive X-ray Analysis
EPA	Environmental Protection Agency
FW LASH	LASH produced in the FW carbonizer using Longview limestone
FW DASH	DASH produced in the FW carbonizer using Plum Run dolomite
G	Ground to 70x140 mesh in LASH oxidation studies
GD	Ground and impregnated with an alkali
GH	Ground and soaked in distilled water
HSAR	Heavily sulfided and as received (carbon-containing)
HSCF	Heavily sulfided and carbon free
HTT	Heat treatment temperature
ICP	Inductively Coupled Plasma spectroscopy
IGCC	Integrated Gasifier Combined Cycle System
IGT	Institute of Gas Technology
KRW LASH	LASH produced in the KRW pilot plant using New Enterprise limestone (a dolomitic limestone)
KRW DASH	DASH produced in the KRW pilot plant using Plum Run dolomite
LASH	mixture of limestone and ash
LSCF	lightly sulfided and carbon-free
LSAR	lightly sulfided and as received (carbon-containing)
NE limestone	New Enterprise limestone (dolomitic type)
ppm	parts per million by volume
PFBC	Pressurized Fluidized Bed Combustor
PR dolomite	Plum Run dolomite
PTGA	Pressurized Thermogravimetric Analyzer
RCRA	Resource Conservation and Recovery Act
SEM	Scanning Electron Microscope
SP limestone	Sierra Pacific-supplied limestone
Sulfide L	sulfide level
T.C.	Thermocouple
TP DASH	DASH produced in the Tampella pilot plant gasifier using a dolomite
TRTU	Transport Reactor Test Unit

TRTU LASH

U

U_{cf}

UT

Ut.

LASH produced in the TRTU using Longview limestone
operating superficial velocity

complete fluidization velocity

untreated solids

Calcium utilization (mole % of calcium that is present as sulfide and
sulfate of total moles of calcium)

APPENDIX A - LITERATURE REVIEW

A.1 Literature Review on In-Situ Sulfur Capture (Task 3)

A.1.1 Introduction

An extensive literature review was conducted at KRW Energy Systems prior to the selection of the in-bed desulfurization concept for the KRW gasifier (Haldipur et al., 1989). This review encompassed reaction chemistry, thermodynamics, equilibrium, kinetics and related processes. Accordingly, pertinent studies performed in the past and relevant studies conducted since this review are discussed here.

High-temperature removal of H_2S in-situ by calcium-based sorbents provides an economical means of removing sulfur for fluidized bed coal gasification processes. Calcium-based sorbents that react with H_2S are: limestone ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), half-calcined dolomite ($CaCO_3 \cdot MgO$), and fully calcined limestone (CaO) or dolomite ($CaO \cdot MgO$). Based on the review of a number of important studies, the rate and extent of sulfidation reaction for calcium-based sorbents can be ranked as follows:

The relevant reactions of interest for in-situ sulfur capture are given below. Direct sulfidation reaction is represented by (1) and sequential sulfidation reactions are represented by (2) and (3):

In this review, for the limestone case, the above three reactions are referred to as L1, L2 and L3, and, for the dolomite case the reactions are referred to as D1, D2 and D3. The $MgCO_3$ portion of the dolomite always calcines at temperatures of interest in this study since its decomposition temperature in pure CO_2 is below 1100°F. It is inert and does not play a direct role in capturing H_2S . The nature of the sulfur capture reactions is determined by the temperature and CO_2 partial pressure. For direct sulfidation (reactions L1 and D1) to occur, the partial pressure of CO_2 should be greater than the equilibrium CO_2 partial pressure required to prevent the decomposition of $CaCO_3$. Therefore, direct sulfidation occurs at low temperatures and high CO_2 partial

pressures while sequential sulfidation (reactions L3 and D3) occurs at high temperatures and low CO₂ partial pressures.

The ultimate level to which sulfur can be removed depends upon the equilibrium properties of the gas mixture. However, the efficiency of sorbent utilization is determined by the overall rate of the gas-solid reactions involved. Several factors such as pore size distribution, porosity, surface area and presence of impurities and MgO content affect the reactivity and the extent of conversion of calcium-based sorbents. The various pertinent studies on direct and indirect sulfidation reactions at temperatures and pressures that are of interest to the project are reviewed below.

Results from sulfidation experiments indicate the possibility of H₂S decomposition depending upon temperature and gas composition during the course of the reaction. Freund (1981), Borgwardt and Roache (1984), and Rehmat (1987) found that H₂S decomposed to form H₂ and elemental sulfur. Thus, the partial pressure of H₂S is lowered due to decomposition of H₂S and could give erroneous results in any study, particularly if the concentration of H₂S is not measured in the exit gas stream.

Newby et al. (1987) studied the kinetics of sulfidation of a wide variety of sorbents over ranges of conditions applicable to fluidized and entrained bed processes and developed correlations for the effect of pressure, temperature and particle size.

A.1.2 Direct Sulfidation Reactions

Reactions With Limestone

Borgwardt and Roache (1984) conducted an extensive study on direct sulfidation of limestone over the temperature range of 1022 to 1598°F. The specific reaction rate was found to be directly proportional to the external surface area of the particles. Maximum reaction rate was obtained at 1382°F. Over the temperature range of 1382 to 1598°F, no increase in the reaction rate was observed, indicating that the reaction had become diffusion limited. Possible reasons for the change in rate-controlling step above 1382°F include sintering of CaCO₃, dissociation of H₂S, and product-layer diffusion to limit the rate and extent of CaS formation. At low temperatures, the initial reaction was found to be high within the internal pore structure and as the conversion increases, the pore volume occupied by the sulfide increases and the reaction becomes limited to the reaction interface resulting in a reduced reaction rate. They observed the particle size to be a critical variable affecting the reaction rate. The reaction L1 was found to be chemically controlled up to about 50% conversion compared to about 90% for reaction D1. This would vary with temperature and particle size.

Reactions With Dolomite

Ruth et al. (1972) observed that H₂S reacted more rapidly with half-calcined dolomite (D1) than with fully-calcined dolomite (D3) or limestone (L3). The rate became

extremely slow after 30% conversion. H_2S could be removed by dolomite at a considerably lower temperature than that required for limestone. The kinetics of reaction D1 was less than first order with respect to H_2S at temperatures over 1292°F and has a higher activation energy than both reactions D3 and L3.

For particle sizes ranging from 500 to 4000 microns and over the temperature range of 1600 to 1700°F, O'Neill (1977) observed the reaction D1 to be first order with respect to CaO (in the H_2S concentration range of 0.5 to 1.3%). The reaction was found to be weakly dependent on temperature and pressure. A two-fold increase in reaction rate was observed when the pressure was increased from 1 atm to 10 atm. Regenerated dolomite was found to have reduced reactivity.

A.1.3 Sequential Sulfidation Reactions

Reactions With Limestone

Abel and Fisher (1976) found that limestone showed little or no reactivity to H_2S until it was heated to above calcination temperatures and that the extent of sulfidation increased from 53% to 85% with an increase in temperature from 1400 to 1600°F for 450-micron particles. Keairns et al. (1976) reported that a sulfidation level up to 90% could be achieved for 500-micron particles.

Simons and Rawlins (1980) observed that the rate was proportional to H_2S concentration. They proposed a theory that is valid only during an initial period when the conversion is low. The activation energy of the reaction was found to be about 10 kcal/mol. They also reported that the rate of $\text{CaO-H}_2\text{S}$ reaction was of the same order of magnitude as CaO-SO_2 reaction. Predictions of the theory are in good agreement with the data of Keairns et al. (1976) during an initial period. Later Simons and Garman (1985) modified this theory to include the deactivation of surface due to the formation of CaS . The model predicts the data of Borgwardt et al. (1984) reasonably well. The improved model takes these phenomena into account: plugging of the smallest pores and subsequent loss in internal surface area, diffusion of sulfur gases through the product, and reduced intraparticle diffusion due to complete plugging of the largest pores. Plugging of the smallest pores was claimed by Simons and Garman (1986) to be the rate-controlling step although earlier model of Borgwardt and Roache (1984) attributed the deactivation of sorbent to diffusion through the product layer.

Borgwardt et al. (1984) found the reactivity of CaO to be more sensitive to surface area than that predicted by the grain model for pore diffusion control. Reactivity of CaO was found to have an exponential dependence on the surface area. The effect of surface area on the reactivity was claimed to be as high as that expected for pore diffusion control. Over the temperature range of 1112 to 1652°F, the activation energy was found to be 31.0 kcal/mol. The rate was observed to be limited by diffusion in the product layer surrounding individual CaO grains.

Attar and Dupis (1979) found that CaO reacted more rapidly with H_2S than CaCO_3 at temperatures above 1436°F and as soon as the oxides were formed, diffusion through the gas film became rate-controlling. Low values of activation energy (0-4 kcal/mol) were observed with carbonates while much higher values (10-25 kcal/mol) were observed with oxides, indicating that the H_2S reaction with carbonates is diffusion-controlled.

Reactions With Dolomites

For dolomites (particle size below 150 microns) and for H_2S concentration ranging from 0.3 to 20%, Pell et al. (1971) observed that the reaction occurs throughout the solid. H_2 was used in the gas stream to insure against dissociation of H_2S . The reaction was found to be first order with respect to both CaO and H_2S over the temperature range of 1292 to 1650°F for fully-calcined dolomite.

Freund (1981) found dolomite to be a better adsorbent than limestone and more resistant to sintering due to the presence of MgO over the temperature range of 1950 to 2390°F for particles of 69 microns. He showed that reactions L3 and D3 were first order with respect to calcium and half order with respect to H_2S which indicates diffusion control. Sintering was observed at 2390°F and resulted in reducing the reaction rate to a lower value than that at 1950°F with an activation energy of about 1000 cal/mol confirming diffusion limit. Recycled sorbent was found to be less reactive than fresh sorbent.

Rehmat (1987) found the rate of reaction D3 to be about twice that of reaction L3 and that both reactions, for 600-micron particles, were chemical-reaction controlled below 1500°F and 1700°F , respectively. Schreiber (1978) observed that the order of reaction was unity for calcined limestone and 0.85 for calcined dolomite for 389-micron particles in 0.1 to 5% H_2S range.

A.1.4 Effect of Environment

Borgwardt and Roache (1984) found that reaction L1 was inhibited by H_2 below 20% concentration and not affected at higher levels which was believed to be due to H_2 hindering the diffusion of H_2S through the product layer and not due to inhibition of the chemical reaction. H_2 was also reported to limit the extent of conversion. At 15% H_2 , the conversion was limited to about 20% compared to 65% when no H_2 was present. They suggested that the permeability of the product layer is reduced when CaS is formed in the presence of H_2 . For the reaction L3, they observed that H_2 retarded the reaction for low-surface-area particles while it had negligible effect for high-surface-area particles. The effect of H_2 was to change the reaction mechanism from reaction-rate-control to diffusion-control. Ruth et al. (1972) did not find H_2 to influence the rate of reaction D1 which was confirmed by Borgwardt and Roache (1984). Rehmat (1987) did not find any effect of gases such as H_2 , CO, CO_2 , and H_2O on both reactions L3 and D3 at 1800°F over a range of 6.7 to 26% H_2 . Thus, it appears that H_2 tends to decrease the rate and conversion of reaction L1, but has little effect on reaction L3 (depending on the surface area), D1 and D3. Ruth et al. (1972) showed that the reaction rate and the extent of

sulfidation of half-calcined dolomite greatly increased when CO_2 level in the reactant gas was increased from 3% to 60%.

Steam was observed to lower the decomposition temperature of CaCO_3 by Freund (1981). The results of Pell (1971) indicate that steam inhibits reaction D3 at temperatures over 1292°F . Ruth et al. (1972) found steam to be more effective than CO_2 in increasing the rate of reaction D1. No effect of steam was observed at 1292°F . Use of O_2 pulses was found to increase the rate and extent of conversion of reaction D1. They suggested the use of pulses of CO_2 , H_2O or O_2 to promote the formation of cracks in CaS layer in order to open the interior of the crystallites to reactions with H_2S . Schreiber (1978) did not find any effect of CO (up to concentrations of 35%) on the rate of reaction L3.

A.1.5 References

Abel, W.T. and E.P. Fisher, "Limestone to Remove H_2S from Hot Producer Gas," MERC/RI-75/3 (1976).

Attar, A. and F. Dupuis, "The Rate and the Fundamental Mechanisms of the Reaction of H_2S with the Basic Minerals in Coal," IEC Proc. Des. Dev., **18**, 607 (1979).

Borgwardt, R.H. and N.F. Roache, "Reaction of H_2S and Sulfur with Limestone Particles," IEC Process Des. Dev., **23**, 742 (1984).

Borgwardt, R.H., N.F. Roache and K.R. Bruce, "Surface Area of CaO and Kinetics of CaS Formation," Environmental Progress, **3**, 129 (1984).

Freund, H., "The Kinetics of Limestone/Dolomite with H_2S Under Rich Combustion Conditions," Combust. Sci. Technol., **26**, 83 (1981).

Haldipur, G.B., D.K. Schmidt and K.J. Smith, "A 50-Month Gasifier Mechanistic Study and Downstream Unit Process Development Program for the Pressurized Ash-Agglomerating Fluidized-Bed Gasification System," Final Report to METC No. FE-21063-69 (March 30, 1989).

Kaloidas, V. and N. Papayannakos, "Kinetics of Thermal, Non-Catalytic Decomposition of H_2S ," Chemical Eng. Sci., **44**, 2493 (1989).

Keairns, D.L., et al., "Eval. of FBC Process, Vol. 4: Fluidized Bed Oil Gasification/Desulfurization," EPA-650/2-73-048d (1973).

Newby, R.A., E.A. DeZubay and R.M. Chamberlin, "Laboratory Evaluation of High Temperature Sulfur Removal Sorbents for Direct Coal-Fired Turbines: Final Report," DOE/MC/22087-2543 (1987).

O'Neill, E.P. and D.L. Keairns, "Selection of Calcium-based Sorbents for High Temperature Fossil Fuel Desulfurization," AIChE Symp. Ser., **73** (No. 161), 100 (1977).

Pell, M., R.A. Graff and A.M. Squires, "Desulfurization of Fuels with Calcined Dolomite: II. Reaction of CaO with H₂S," Chem. Eng. Prog. Technical Manual, 151-57 (1971).

Rehmat, A. and M.J. Abbasian, "Reaction of Calcium-Based Sorbents with Sulfur Compounds during Gasification," Report No. GRI-88/0348 (1988).

Ruth, L.A., A.M. Squires and R.A. Graff, "Desulfurization of Fuels with Half-Calcined Dolomite: First Kinetic Data," Env. Sci. Tech., 6, 1009 (1972).

Schreiber, C.H. and T.W. Petrie, "Effect of CO on the Reaction of H₂S and CaO," J. Eng. Power, 100, 520 (1978).

Simons, G.A. and W.T. Rawlins, "Reaction of SO₂ and H₂S with Porous Calcined Limestone," IEC Proc. Des. Dev., 10, 565 (1980).

Simons, G.A. and A.R. Garman, "Intraparticle Mass Transfer During Sulfation by Calcined Limestone," in Heat Transfer in Fire & Combustion Systems, Ed. C.K. Law et al., ASME, Heat Transfer Division, Vol. 45, 9 (1985).

Simons, G.A. and A.R. Garman, "Small Pore Closure and the Deactivation of the Limestone Sulfation Reaction," AIChE J., 32, 1491 (1986).

A.2 Literature Review on Effect of Calcium on Carbon Conversion (Task 4)

A.2.1 Introduction

Calcium was observed to catalyze gasification reactions of carbon by several investigators [Essenhigh (1981), Lang (1982), McKee (1982), Walker (1983)]. Catalytic effect of calcium in gasification was reported to be a major cause for improved KRW gasifier performance and this was investigated and literature reviewed at KRW Energy Systems during the course of the development of KRW gasification technology [Agrawal (1989), Haldipur (1989), Schmidt (1989)].

The gasification rate of carbon depends on several factors including coal rank, pyrolysis conditions and gasification conditions. In most reactors, carbon gasification reactions are kinetically limited below temperatures of about 2000°F. Therefore for reactors operating below this temperature, catalytic coal gasification may provide an economic incentive for commercialization. Coal combustion reactions are diffusion-controlled above temperatures of about 1600°F and hence catalysis is expected to play little role in coal combustion processes.

Low rank coals such as lignites are well known to exhibit higher reactivities compared to higher rank bituminous coals. Walker and his coworkers (1978) found that the reactivity of U.S. coals increased by about 100 fold as the rank of coal decreased from anthracite to lignite. A factor influencing the reactivity of low rank coals is the presence of calcium in the carbon matrix which is due to the presence of carboxyl groups that readily exchange H₂ atoms for calcium in lignites. Kapteijn et al. (1986) found calcium to be the most effective alkali earth catalyst during gasification. They state that CaO is more active than CaCO₃. Thus at high CO₂ partial pressures, where equilibrium favors CaCO₃, catalytic effect of calcium would be much less. Jenkins et al. (1973) examined the effect of removal of K, Na, Ca and Fe on the gasification rate of lignites and found an increase in reactivity with an increase in Ca and Mg content. No such correlation was found with K, Na or Fe. Thus, they concluded that the presence of calcium was the probable cause for the increase in reactivity.

Bituminous coals contain little O₂ and therefore few carboxylic groups are present. Several studies in the literature showed that calcium enhanced the reactivity of bituminous coals [Agrawal (1991), Essenhigh (1981) and Sears (1980)], while earlier studies of Jenkins et al. (1973) and Johnson (1979) did not indicate any such effect. Marsh (1975) did not find any increase in reactivity with synthetic carbon made from furfural alcohol. Therefore, for bituminous coals, the method of addition of calcium appears to be very important. Various methods of impregnating calcium into bituminous coal matrix and their effect on coal reactivity are discussed below.

A.2.2 Methods of Impregnating Calcium into Char Matrix

The method of impregnating calcium into the char matrix is critical to obtain any catalytic effect. Calcium can be impregnated into the char matrix by the following

techniques: physical mixing of calcium salts with char, physical mixing of calcium salts with coal followed by pyrolysis, physical mixing of coal with limestone in a hot fluidized bed, and impregnating calcium into coal or char matrix by solution-impregnation techniques.

Physical mixing of CaO or CaCO₃ with char from bituminous coal did not increase the rate of C-H₂O reaction [Kayembe (1976)] or C-CO₂ reaction [Sears (1980)]. Similar results were obtained for chars prepared from sucrose for C-O₂ and C-CO₂ reactions [Floess (1988)]. Chars prepared by mixing bituminous coal with CaO or CaCO₃ at room temperature followed by pyrolysis, showed less than two-fold increase in the rates of C-H₂O [Lang (1982)] and C-CO₂ reactions [Sears (1980)]. Finely grinding bituminous coal and then mixing it with calcium acetate at room temperature was found to have little effect in enhancing the rate of C-O₂ reaction [Barthe (1986)]. The lack of intimate char-calcium contact obtained by the physical mixing of bituminous coal/char and calcium salts at low temperatures results in a limited enhancement in gasification rates. This result is supported by the observation of Lang and Neavel (1982) that calcium salts do not easily disperse in the char matrix. In all these studies, fixed beds were used which do not promote any carbon-calcium interaction. Since limited information is available on physical mixing at high temperature (where calcium salts may be mobile enough to diffuse into the char matrix or in fluidized bed reactors where carbon-calcium interactions are present), it cannot be ignored as a factor influencing catalysis.

It is shown from several studies, discussed below, that for calcium to be catalytically active during char gasification, it has to be finely dispersed into the char matrix. This can be achieved either by ion-exchange or solution-impregnation techniques. In these techniques, aqueous solutions of calcium salts such as Ca(NO₃)₂, Ca(OH)₂, CaCl₂ or Ca(CH₃OO)₂ are mixed with coal or char for different time periods followed by pyrolysis. Sears (1980) found about two- to four-fold increase in C-CO₂ reaction rate depending upon the calcium content of chars. Results of Joly (1990) indicate that although physical mixing with CaO does not enhance reactivity, impregnating low rank coals by ion exchange results in an increase in C-CO₂ rate. Walker (1983) showed that by varying the calcium content in lignitic chars using calcium-exchange technique, the gasification rate in O₂, H₂O or CO₂ could be increased almost proportionately by increasing calcium loading. These studies clearly demonstrate that calcium catalyzes carbon gasification reactions. However, solution-impregnation techniques are likely to be expensive due to increased costs in coal preparation, and hence are not regarded as economical for commercial applications.

Haynes (1979) observed that physical mixing of coal with dolomite or hydrated lime did not influence the gasification rate of carbon in a fixed bed reactor, while in a fluidized bed reactor, it increased the rate of carbon gasified. Calcium can also be dispersed into the char matrix by injecting coal into a fluidized bed of a mixture of char and limestone. Bituminous chars prepared by this method had calcium evenly distributed, as shown from EDAX (Energy Dispersive Analysis by X-ray) studies by Agrawal and Haldipur (1989), and exhibited a four-fold increase in C-H₂O reaction rate.

In fixed bed systems, calcium appears to be catalytically inactive because it does not impregnate char matrix. The pore structure and surface chemistry of coal affect dispersion of calcium into carbon matrix and play an important role in catalytic gasification processes. Small amounts of calcium can appreciably increase reactivity as in the case of native mineral matter and deeply-impregnated calcium in coal/char. During physical mixing in fixed bed systems, only the external particle surface is available, so little or no enhancement in reactivity is observed. In the case of fluidized beds, intimate mixing of char and CaO occurs, thus an increase in the mobility of CaO can be expected. Therefore, catalysis is expected to play a more important role in fluidized beds than in fixed beds.

A.2.3. Factors Promoting or Inhibiting Catalysis by Calcium

Since CO and H₂ are the gasification products, they are known to inhibit gasification reactions, especially at lower temperatures. Their influence on calcium-catalyzed reactions is less understood. During CO₂ gasification, Agrawal (1980) found that catalysis due to calcium was more pronounced in CO₂-CO gas mixtures than in CO₂. Walker (1983) reported that CO inhibits catalysis of C-H₂O reaction by calcium due to the following reaction:

Walker (1983) found H₂ to inhibit catalysis by calcium. This was claimed to be due to the absence of CaO[O] formation resulting from the following reaction:

Thus, the presence of H₂ retards both catalytic and non-catalytic gasification reactions, although data are limited for catalyzed reactions. This is consistent with the finding of Walker that calcium does not catalyze C-H₂ reaction.

A.2.4. Activity of Calcium as a Function of Carbon Conversion

Lang and Neavel (1982) and Kapteijn et al. (1986) observed that the initial activity of calcium was high but that it loses catalytic activity during gasification. Lecea et al. (1990) reported that the initial activity of calcium for both C-H₂O and C-CO₂ reactions was similar but decreased at higher conversions due to deactivation. They claim that deactivation is due to sintering of CaO via particle growth mechanism. Agrawal (1989) observed that the reactivity of C-H₂O reaction increased in the presence of calcium up to about 80% carbon conversion. Haga (1991) found that the effect of calcium on steam gasification was sensitive to char preparation temperature and coal rank.

The activity of calcium is sensitive to the initial dispersion of calcium in carbon, but a rapid loss in catalytic activity was observed during gasification. According to Haga, sintering of CaO alone does not explain the loss in catalytic activity during gasification. Levendis (1989) showed that, in the presence of calcium, the reactivity of low porosity chars dropped off after about 50% carbon conversion while no such drop in reactivity was observed for high porosity chars.

Results of these studies indicate that carbon-calcium interaction is very important for catalysis. Although the loss in activity of calcium during gasification may be partially explained by sintering, the drop in activity as a function of carbon conversion can be explained by the immobility of calcium to travel to the remaining carbon sites during gasification.

A.2.5 Enhancement in Reactivity as a Function of Calcium Content

Some investigators report a linear increase in reactivity from 2 to 4 wt% calcium, while others report a linear increase up to 12.9 wt% calcium [Lecea (1990) and Floess (1988)]. These discrepancies are believed to be due to the differences in preparation method and the extent of calcium dispersion in carbon. Lecea (1990) found that calcium was more active to C-CO₂ reaction compared to C-H₂O reaction. The gasification rate was found to increase linearly up to 4 wt% calcium. Sears (1980) reported an increase in C-CO₂ reaction rate by about four-fold as calcium content increased from 2 to 8 wt%. Ohtsuka (1986) found a linear increase in reaction rate up to about 5 wt% calcium. Floess (1988) found that addition of calcium, as verified through SEM/microprobe study, resulted in a linear increase in reactivity with calcium content. Dispersion of calcium at 1% level increases the C-O₂ reaction rate by about a factor of two and that of the C-CO₂ reaction rate by about a factor of three.

A.2.6 Mechanism of Calcium Catalysis

McKee (1982) concluded, in his review, that below temperatures of 1800°F, the following reactions are not favored:

CaO and MgO do not decompose in the presence of steam or CO₂ at elevated temperatures. Thus, mechanisms involving the decomposition of CaO are not applicable for reactions occurring below 2000°F. Formation of CaO[O] appears to be the only reasonable mechanism to explain the catalytic effect.

Walker et al. (1983) observed that calcium catalyzed C-O₂, C-CO₂ and C-H₂O reactions but did not catalyze C-H₂ reaction. Based on these studies, it appears that oxygen transfer plays a critical role during catalysis. McKee (1982) reported studies that indicated a tendency of CaO to form a superoxide CaO[O] at low temperatures. Sears et al. (1980) calculated the Gibbs free energy change for the formation of CaO[O] to be -64 kcal/mol. Thus, the activity of CaO[O] is high and it is possible for dissociative chemisorption of H₂O, CO₂ or O₂ to occur on CaO leading to enhanced gasification rate of carbon. CaO[O] thus formed could transfer the O₂ atom to the carbon site nearby to form CO. This is consistent with the findings in the literature which indicates a decrease in reactivity with carbon conversion. This decrease in reactivity would not have been observed if calcium were mobile to reach other carbon sites.

Based on these theories and observations, Sears et al. [1980] proposed the following reaction mechanism consisting of three steps to explain calcium catalysis of C-CO₂ reaction:

For C-H₂O and the C-O₂ reactions, they proposed the first steps to be:

with the second and third steps being the same for all the three reactions. They suggest that the desorption step leaves an activated carbon site.

Freund (1985) and Kapteijn et al. (1986) theorize that the rate determining step in CO₂ gasification is the desorption of CO from the carbon site which is consistent with their finding that the activation energy during catalysis does not change. Kapteijn et al. (1986) found that the activation energy of both C-CO₂ and C-H₂O reactions is not affected by calcium catalysis. Therefore, it was suggested that calcium increases the number of active sites. This is similar to the findings of Freund (1985) who found the activation energy for both catalyzed and uncatalyzed reactions to be similar indicating that calcium affects the active site density of the material but does not strongly interact with the desorption process.

In contrast to the above, another theory states that the chemisorption of O₂ is the rate limiting step [Floess (1988), Sears (1980) and Walker (1983)]. This theory implies

that the activation energy decreases during catalytic gasification. Sears (1980) found that calcium catalysis reduced the activation energy of C-CO₂ reaction from 70 to about 55 kcal/mol. According to Floess (1988), the increase in the reaction rate due to catalysis can be accounted for by a lower activation energy (a decrease from about 71 to 58 kcal/mol for C-CO₂ reaction and a decrease from 34 to 29 kcal/mol for C-O₂ reaction). For C-H₂O reaction, Agrawal (1989) observed a decrease in the activation energy from 73 to 41 kcal/mol.

A.2.7 References

- Agrawal, A.K. and J.T. Sears, "The Coal Char Reaction with CO₂-CO Gas Mixtures," IEC Proc. Des. Dev., **19**, 364-371 (1980).
- Agrawal, R.K. and G.B. Haldipur, "Advanced Gasifier-Desulfurizer Process Development for SNG Application: KRW Bench-Scale Program," GRI-89/0011 (1989).
- Agrawal, R.K., "Effect of Pyrolysis Conditions on Gasification Reactivity of Chars," Paper presented at the Eighth Annual International Pittsburgh Coal Conf., October 14-18 (1991).
- Barthe, P. et al., "Calcium Efficiency in the Low Temperature Gasification of Cokes in Air," Fuel, **65**, 1330 (1986).
- Essenhigh, R.H., "Fundamentals of Coal Combustion," in Chemistry of Coal utilization, 2nd Suppl. Vol, Ed. M.A. Elliott, Chapter 19, John Wiley (1981).
- Floess, J.K., J.P. Longwell and A.F. Sarofim, "Intrinsic Reaction Kinetics of Microporous Carbons. 2. Catalyzed Chars," Energy and Fuels, **2**, 756 (1988).
- Freund, H. "Kinetics of Carbon Gasification by CO₂," Fuel, **64**, 657 (1985).
- Haga, T. et al., "Influence of Structural Parameters on Coal Char on Potassium and Calcium Catalyzed Steam Gasification," Energy and Fuels, **5**, 317 (1991).
- Haldipur, G.B., D.K. Schmidt and K.J. Smith, "A 50-Month Gasifier Mechanistic Study and Downstream Unit Process Development Program for the Pressurized Ash-Agglomerating Fluidized-Bed Gasification System," Final Report to METC No. FE-21063-69 (March 30, 1989).
- Haynes, W.P., S.J. Gasior and A.J. Forney, "Catalysis of Coal Gasification at Elevated Pressures," ACS Adv. in Chemistry Series, **131**, 179 (1979).
- Jenkins, R.G., et al., "Reactivity of Heat Treated Coals in Air at 500°C," Fuel, **52**, 288 (1973).
- Johnson, J.L., "Kinetics of Coal Gasification," John Wiley, NY (1979).

- Joly, J.P. et al., "The state of Calcium as a Char Gasification Catalyst," *Fuel*, **69**, 878 (1990).
- Kayembe, N. and A.H. Pulsifer, "Kinetics and Catalysis of the Reaction of Coal Char and Steam," *Fuel*, **55**, 211 (1976).
- Kapteijn, F., H. Porre and J.A. Moulijn, "CO₂ Gasification of Activated Carbon Catalyzed by Earth Alkaline Elements," *AIChE J.*, **32**, 691 (1986).
- Lang, R.J. and R.C. Neavel, "Behavior of Ca as a Steam Gasification Catalyst," *Fuel*, **61**, 620 (1982).
- Lecea, C.S., et al., "Calcium Catalyzed Carbon Gasification in CO₂ and Steam," *Fuel*, **69**, 21 (1990).
- Levendis, Y.A., et al., "Catalysis of the Combustion of Synthetic Char Particles by Various Forms of Calcium Additives," *Energy and Fuels*, **3**, 28 (1989).
- Marsh, H. and R.R. Adair, "Catalytic Gasification of Doped Carbon- A Kinetic Study," *Carbon*, **13**, 327 (1975).
- McKee, D.W., "The Catalyzed Gasification Reactions of Carbon," *Chemistry and Physics of Carbon*, **16**, 1-118 (1982).
- Ohtsuka, Y. and A. Tomita, "Calcium-Catalyzed Steam Gasification of Yallourn brown Coal," *Fuel*, **65**, 1653 (1986).
- Schmidt, D.K., P. Sadhukhan and Y.Y. Lin, "Desulfurization using Ca-based Sorbents in Transport Bed Combustor and Fluidized Bed Gasifier," *Proceedings of the Sixth Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, **1**, 267 (1989).
- Sears J.T., H.S. Muralidhara and C.Y. Wen, "Reactivity Correlation for the Coal Char-CO₂ Reaction," *IEC Process. Des. Dev.*, **19**, 358 (1980).
- Walker, P.L., Jr. et al., "Catalysis of Gasification of Coal-derived Cokes and Chars," *Fuel*, **62**, 140 (1983).
- Walker, P.L., Jr., "Gasification Rates as Related to Coal Properties," in *Scientific Problems of Coal Utilization*, Ed. B.R. Cooper, 237-247 (1978).

A.3 Literature Review on Oxidation of CaS TO CaSO₄ (Task 5)

A.3.1 Introduction

During coal gasification, much of the sulfur in coal is released in the form of H₂S. Use of calcium-based sorbents to capture H₂S results in the formation of CaS. The CaS is not permitted to be disposed of in a landfill without further treatment. CaS is not inert because it has the potential of releasing H₂S in the presence of acid. Therefore, CaS is classified as a reactive sulfide under the RCRA (Resource Conservation and Recovery Act) definition for classifying materials as "hazardous wastes". Consequently the solid waste stream from gasifiers which utilize an in-situ sulfur control process using limestone or dolomite requires further processing to render it non-hazardous.

CaS can be processed either to recover sulfur (by decomposition of CaS in the presence of H₂O and/or CO₂ to obtain H₂S, or high temperature oxidation to obtain SO₂) or to "fix" the sulfur to form CaSO₄. The simplest method of rendering CaS innocuous is to convert it to CaSO₄ by oxidation in air which is the reaction of interest in this study. This approach has the additional advantage of recovering the combustion heat from any residual carbon in char which remains mixed with the spent sorbent. The sulfate thus produced in this "oxidation" step can be regarded and handled as an environmentally-acceptable waste. Limited fundamental information is available in the literature on the oxidation of CaS. When CaS reacts with O₂, the following reactions occur:

Reaction (14) is referred to as the oxidation reaction. Reactions (14) and (15) are highly competitive and are very sensitive to temperature and O₂ partial pressure. Both reactions are highly exothermic and result in high particle temperature that causes sintering and results in incomplete conversion of CaS. Studies of Keairns et al. (1973), Lynch and Elliott (1978 and 1980) and Weldon and Haldipur (1987) indicate that reaction (14) is favored at temperatures below 1800°F and high O₂ partial pressure while reaction (15) is favored above temperatures of 2000°F and low O₂ partial pressure. Reaction (15) is undesirable in the proposed process because it results in a net loss of sulfur at a concentration which is too low for further processing.

A.3.2 Oxidation of Calcium Sulfide

Studies of Lynch and Elliott (1978 and 1980) and Torres-Ordóñez (1989) were aimed at high-temperature oxidation of CaS. Their goal was to understand the fate of CaS formed during fuel-rich combustion of coal and the mechanism of reactions involved during sorbent injection. Lynch and Elliott found that at high temperatures (> 2500°F),

complete oxidation of CaS occurred via reaction (15). At temperatures below 2000°F, sulfate was produced in small amounts. In the intermediate temperature range (2100 to 2300°F), the conversion of CaS oscillated rapidly between the two reactions. Torres-Ordóñez (1989) reports that CaS oxidizes rapidly at a rate comparable to carbon oxidation to a limiting conversion due to the formation of CaO(s)-CaSO₄(s) eutectic. Thus, particle size, pore structure and temperature are important during the oxidation of CaS to CaO.

Keairns et al. (1973) found that CaS prepared from dolomite sulfidation could be readily oxidized to CaSO₄ and that the degree of conversion depended upon the extent to which the original stone was sulfided and the temperature of oxidation. The degree of oxidation was higher for lightly-sulfided samples and at higher temperatures (1472°F). Maximum sulfide conversion achieved was 92% for a 30%-sulfided Tymochtee dolomite in this study. They found that the limestone-based sorbents oxidized poorly which was attributed to pore blockage leading to a diffusional limit. Poor quality limestone containing impurities was found to yield greater conversion to sulfate. The behavior of low quality limestone was thought to be similar to that of the dolomites in that the inerts act as "spacers" which allow higher oxidation levels. Keairns et al. (1973) pointed out that CaS could not be directly oxidized in air to produce innocuous CaSO₄ for waste disposal. This can be attributed to the fact that they "totally" sulfided the limestone particles (extent of sulfidation >75%) and were able to achieve only 20 to 30% oxidation. Thus, the high sulfur loading on limestone was the limiting factor in their study.

Some work on oxidation was also conducted at the Institute of Gas Technology (IGT) by Rehmat (1987). This study was conducted over the temperature range of 1500 to 1900°F and up to pressures of 400 psig using both dolomite and limestone for an average particle size of 600 microns. Greater level of oxidation was reported for dolomites (83 to 100%) than for limestones (18 to 34%). The extent of sulfidation of these samples prior to oxidation was not reported. O₂ flow rate was found to have little effect on the conversion of limestone but partially improved the conversion of dolomite. This is not in agreement with the findings at KRW Energy Systems which show that the conversion increases with an increase in the O₂ partial pressure [Haldipur et al. (1989)]. Steam was found to have little effect on the reaction rate or conversion. This is difficult to explain because steam reacts with CaS to liberate SO₂ in this temperature range. Low temperatures result in greater oxidation of dolomite and the opposite is true for limestone. The reasons for these observations were claimed to be that, at higher temperatures, dolomite sinters causing a decrease in the reactive surface area and results in a decrease in oxidation. This explanation is not consistent with Freund's (1981) observation that dolomites are more resistant to sintering due to the presence of MgO. In the case of limestones, higher temperatures were proposed to increase the gas diffusion rate to result in additional oxidation [Rehmat (1987)].

Haldipur et al. (1989) have shown the difficulty in completing oxidation reaction. Low conversions of CaS was obtained at moderate temperatures (about 1500°F), and at high temperatures (1800°F), excessive evolution of SO₂ was observed (Note that the temperatures indicated are a function of O₂ partial pressure). These studies indicate that

O₂ starvation at the hot spots (created by the highly exothermic reaction) is a significant factor in causing the evolution of SO₂. SO₂ emission was also reported by Lyngfelt (1989). He states that CaS and CaSO₄ are stable under reducing and oxidizing conditions, respectively while CaO is stable at intermediate conditions. The size of the stable region for CaO increases with temperature. CaO in the stable region is relatively "inert" and does not capture sulfur gases. Thus, at O₂-starved conditions, SO₂ emissions would be observed.

Haldipur et al. (1989) showed that the mechanism for converting CaS to CaSO₄ involves the formation and growth of a product layer around the "grains" of CaS. This is analogous to the formation of product layers around CaO "grains" during the capture of either H₂S or SO₂. As the product layer of CaSO₄ around CaS becomes thicker, the reaction rate decreases dramatically. Attempts to increase the rate by using higher temperatures resulted in the evolution of SO₂. Oxidation tests were more successful with dolomites than with limestones. Difficulty in obtaining complete conversion of CaS is thought to be due to the size of the grains. Scanning Electron Microscope (SEM) studies of the material produced in the KRW coal gasification process with dolomite showed typical CaS grain sizes of less than one micron in diameter. Similar studies of the material produced from limestone have shown grain sizes of the order of 10 microns in diameter. Thus, lower size grains result in higher conversion of CaS to CaSO₄.

A.3.3 Oxidation of KRW LASH and DASH

In a study performed for KRW Energy Systems, Rogan (1986) investigated the oxidation characteristics of DASH samples. Oxidation studies with highly-sulfided DASH showed low conversions to sulfate, a maximum of 55% conversion was obtained at 1832°F. Higher levels of oxidation could be achieved with lightly-sulfided DASH. With 1% O₂ concentration, evolution of SO₂ was evident at temperature of 1832°F. At 1650°F, SO₂ evolution was not observed. An increase in O₂ concentration from 1 to 10% caused the SO₂ evolution to occur at temperature of 2000°F. Few runs were also conducted with LASH samples. Results indicate that the conversion is lower (20 to 30%) with LASH than with DASH samples. SEM studies with DASH indicate that CaS exists as tiny grains that are distributed throughout the rather porous matrix. Haldipur et al. (1989) observed the pore structure of LASH to be blocked. Low porosity in LASH is believed to be the cause for poor oxidation of CaS to CaSO₄. These studies indicate that the porosity of LASH and DASH particles is an important factor in promoting the oxidation of CaS.

With untreated LASH samples, Weldon and Haldipur (1987) reported that the quantity of sulfide released exceeded RCRA limits. Oxidation of LASH with air resulted in oxidation levels between 7 and 81%. The reactive sulfide levels were only about 5 milligrams per kilogram of waste. Regardless of the oxidation levels achieved in this study, all samples passed the original EPA's reactive sulfide test. LASH oxidized in the Dorr Oliver sulfator was found to achieve a conversion of about 20 to 30% which was found to satisfy the RCRA reactive sulfide requirement. The leachate from oxidized LASH and DASH samples was also found to meet RCRA's EP-toxicity test requirements.

In spite of the favorable results on H_2S release, since not all of the sulfide is converted to sulfate, this process is susceptible to any future changes in the RCRA requirements. Thus, low conversions during oxidation would present a potential risk.

Since oxidation of LASH resulted in only about 20 to 30% oxidation level, Haldipur et al. (1989) used an alkali to increase the conversion of sulfide. Tests conducted with Na_2CO_3 and KCO_3 additives showed that oxidation levels in the range of 60 to 86% could be obtained. Grinding the raw LASH before oxidation appears to enhance the extent of oxidation. This study recommended the use of Na_2CO_3 as it promotes near complete conversion of CaS in LASH to $CaSO_4$ without excessive evolution of SO_2 at temperatures below $1832^\circ F$ and an O_2 concentration of 10%.

A.3.4 References

Freund, H., "The Kinetics of Limestone/Dolomite with H_2S under Rich Combustion Conditions," *Combust. Sci. Technol.*, **26**, 83 (1981).

Haldipur, G.B., D.K. Schmidt and K.J. Smith, "A 50-Month Gasifier Mechanistic Study and Downstream Unit Process Development Program for the Pressurized Ash-Agglomerating Fluidized Bed Gasification System: Final Report," **1 and 2**, FE-21063-69 (1989).

Keairns, D.L. et al., "Evaluation of the FBC Process, Vol IV- Fluidized bed Oil Gasification/Desulfurization," EPA-650/2-73-048d (1973).

Lynch, D.C. and J.F. Elliott, "Kinetics of the Oxidation of CaS ," *Met. Trans.*, **9B**, 691 (1978).

Lynch, D.C. and J.F. Elliott, "Analysis of the Oxidation Reactions of CaS ," *Met. Trans.*, **11B**, 415 (1980).

Lyngfelt, A. and B. Leckner, "Sulfur Capture in Fluidized Bed Boilers: The Effect of Reductive Decomposition of $CaSO_4$," *Chem. Eng. J.*, **40**, 59 (1989).

Rehmat, A. and M.J. Abbasian, "Reaction of Ca-based Sorbents with Sulfur Compounds during Gasification," Report No. GRI-88/0348 (1988).

Rogan, H.S., "Characterization of Sorbent Materials," Report to KRW Energy Systems (1986).

Torres-Ordenez, R.J., J.P. Longwell and A.F. Sarofim, "Intrinsic Kinetics of CaS Oxidation," *Energy and Fuels*, **3**, 506 (1989).

Weldon, J. and G.B. Haldipur, "Preliminary Characterization of Solid Wastes Produced in the KRW Gasifier-Desulfurizer," DOE Report FE-21063-30 (1987).