

# ADVANCED COAL GASIFICATION AND DESULFURIZATION WITH CALCIUM BASED SORBENTS

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## 1.0 ABSTRACT

In-bed desulfurization using calcium based sorbents has been evaluated in the KRW pressurized fluidized bed gasifier as part of a joint program with KRW Energy Systems Inc. and the U. S. Department of Energy. For combined cycle power generation or synthesis gas applications such a system has large potential economic advantages over second generation gasifiers which use conventional cold gas cleanup.

In addition to achieving over 90% desulfurization, the process has also demonstrated significant gains in cold gas efficiency and fines consumption. Pilot plant performance data are presented for the KRW gasifier-desulfurizer process and the preliminary results of an in-bed waste characterization study are also presented. Though untreated in-bed wastes contain potentially hazardous calcium sulfide, laboratory-scale tests have shown that roasting processes can be adapted for converting the waste to a non-hazardous form.

## 2.0 INTRODUCTION

The production of low-Btu (120-160) Btu/scf gas from coal for use in combined cycle power generation is attractive to the utility industry because the feedstock is an abundant domestic natural resource and because it offers economic advantages over conventional coal fired steam plants.(1)

Conventional stack gas clean-up technologies are proving to be capital expensive and have the added disadvantage of poor thermal efficiency. In-bed clean-up with calcium sorbents offers an effective and economical method of removing the sulfur species from the product gas without pre-cooling. The particulate free hot gas can then be used directly in a gas turbine providing improved overall process efficiency.

The market incentive for an economical coal gasification combined cycle electric power generating plant will be substantial in the 1990's. According to the U. S. Department of Energy (1), 18% of the current U. S. generating capacity is greater than 25 years old. The KRW coal gasification combined cycle hot gas cleanup process is ideally suited to the needs of the electric power industry in the 1990's on the basis of environmental, cost and plant size considerations.

## 3.0 BACKGROUND

### 3.1 KRW Coal Gasifier

The KRW gasifier is a pressurized fluidized bed process which can convert a variety of solid carbonaceous feedstocks into low-Btu (100-160 Btu/scf) or medium-Btu (200-300 Btu/scf) gas. The essential features of the gasifier are shown in Figure 1. Run-of-mine coal or lignite in the size range of 1/4-inch x 0 is surface dried, pressurized in lockhoppers, and injected concentrically into a high energy oxidizing jet located in the combustion zone. The coal is rapidly devolatilized and caked, and the residual char is gasified by steam in the upper region of the fluidized bed. The jet induces a vigorous toroidal motion of solids between the lower heat producing combustion region and the upper heat consuming gasification region. The coal ash undergoes partial melting and sintering in the hotter combustion jet, and the resulting 'glue' action causes fine ash particles to agglomerate. These ash agglomerates are separated from the char in a fluidized bed

separator located in the bottom section of the gasifier, are cooled with recycle gas, and are extracted by means of a rotary feeder and depressurizing lockhoppers. Fines elutriated from the gasifier are captured in an external cyclone and recycled directly to the gasifier by means of a nonmechanical valve. Fines escaping the cyclone are captured in a full-flow sintered metal filter. This filter is capable of operation up to 1200°F and removing all fines one micron or greater in size. The gasifier may be operated either in the air-blown mode for low-Btu gas (100-160 Btu/scf) or in the oxygen-blown mode for medium-Btu fuel or synthesis gas (200-300 Btu/scf).

The process has been demonstrated for a wide range of feedstocks and conditions at the Waltz Hill 15-30 tons/day Process Development Unit (PDU) under funding by the DOE and its predecessor agencies. In addition to its ability to process a variety of feedstocks, the process has also demonstrated effective utilization of coal fines, high overall carbon conversion efficiency, and virtual elimination of tar and oil in the product gas.

### 3.2 In-Bed Desulfurization

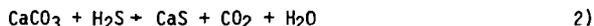
In-bed desulfurization has been identified as a potential hot gas cleanup concept for meeting environmental regulations on sulfur emissions from the KRW gasifier. Such a system would have economic advantages over cold gas clean-up in a coal gasification combined cycle power generation application. KRW has conducted four in-bed PDU tests in 1984 and 1985 to demonstrate the feasibility of this concept. In addition to achieving over 90% desulfurization to meet the New Source Performance Standards for sulfur emissions, the process cold gas efficiency improved by 20% over conventional PDU gasifier operation.

Hot gas clean-up via the in-bed concept involves the removal of sulfur bearing gases, H<sub>2</sub>S and COS, by reacting them with dolomite (CaCO<sub>3</sub>.MgCO<sub>3</sub>) or limestone (CaCO<sub>3</sub>) to form sulfided or spent sorbent (CaSMgO or CaS). Sorbent is fed into the gasifier freeboard to mix with the the bed char and remove H<sub>2</sub>S and COS from the product gas. The spent sorbent is eventually withdrawn through the gasifier annulus along with ash agglomerates.

The overall reaction occurring in the gasifier bed is:



for the dolomite/hydrogen sulfide reaction, or similarly:



for the limestone/hydrogen sulfide reaction. Calcium sulfide (CaS) is a reactive waste which can recombine with acidic water to release toxic H<sub>2</sub>S gas. Further treatment is necessary to convert the CaS to the environmentally acceptable sulfate:



The primary goal of oxidation is to reduce the activity of the sulfide with the environment and render the waste non-hazardous. The waste could then be disposed of in conventional solid waste landfills.

#### 4.0 DESULFURIZATION PERFORMANCE

The development program has comprised a series of PDU tests to first demonstrate gasifier operability and, thereafter, to optimize the desulfurization process. During tests TP-036-1 and TP-036-2, the gasifier was successfully operated with dolomite injection in a controlled and balanced manner. The subsequent tests, TP-036-3 and TP-036-4, demonstrated that high levels of desulfurization could be achieved with both dolomite and limestone sorbents. Table 1 summarizes the significant achievements of the in-bed desulfurization program.

TABLE 1. SUMMARY OF KRW IN-BED DESULFURIZATION RESULTS\*

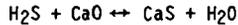
Coal Type	Coal Sulfur Content (%)	Sorbent Type	H <sub>2</sub> S (ppm)	COS (ppm)	Ca/S Molar Feed Ratio	Steady State Desulfurization Achieved (%)
Pgh. #8	2.3	Glass Dolomite	550	263	1.67	86
Pgh. #8	4.5	Glass Dolomite	679	216	1.55	92
Pgh. #8	4.5	Greer Limestone	651	258	1.84	90
Wyoming	2.0	Glass Dolomite	484	167	2.0	91

\*preliminary

The equivalent desulfurization for limestone injection into conventional furnaces and atmospheric fluidized bed combustors (AFBC) require Ca/S molar feed ratios of 3 to 6 (2, 3) compared to the ratios of 1.5 to 2.0 demonstrated by the KRW process. The advantages of desulfurization in the reducing gasifier environment are attributed to the faster rate of hydrogen sulfide/calcium oxide reaction compared to the sulfur dioxide/calcium reaction and the absence of sintering. Sintering is indicated by low BET surface areas (4). Sorbent surface area measurements of the bed material were relatively high at 10-40 m<sup>2</sup>/g compared to typical calcine surface areas which range from 0.5 to 40. m<sup>2</sup>/g for calcined carbonates (5). The reducing environment apparently does not increase sintering.

PDU results indicate desulfurization is a function of the sulfur input rate and output rate. The sulfur species concentrations in the product gas were characteristically in the range of 500-650 ppm for H<sub>2</sub>S and 160-270 ppm for COS for large variations in feedstock sulfur content. Since the sulfur output rate is limited, the degree of desulfurization increases as the sulfur input rate (coal sulfur content) increases.

Desulfurization varies inversely with product gas steam concentration based on recent PDU tests. A negative correlation coefficient of 0.8 was found linking steam and hydrogen sulfide concentrations for the KRW Data Base. Equilibrium effects via the reaction



4)

are probably negligible because the value of the equilibrium constant is so large for gasifier temperatures in the range of 1600 to 1900°F (6). In fact, H<sub>2</sub>S concentrations were generally on the order of 200-400 ppm higher than equilibrium levels, so it seems improbable that equilibrium limits desulfurization. (If, however, gas phase diffusion of H<sub>2</sub>O from the reacting core is the limiting rate the equilibrium concentrations of H<sub>2</sub>S in the particle core may limit desulfurization). KRW investigations of the mechanism by which H<sub>2</sub>O limits desulfurization are currently underway.

Small incremental increases in desulfurization were also achieved with large increases in the calcium/sulfur feed ratio as shown in Table 2.

Table 2  
Incremental Increase in Desulfurization as a  
Function of Ca/S Ratio for Pgh. 4.5% Sulfur Coal

<u>Ca/S Feed Ratio</u>	<u>Observed % Desulfurization</u>	<u>Observed H<sub>2</sub>S ppm</u>	<u>Equilibrium H<sub>2</sub>S ppm</u>
1.84	91	651	180
3.41	94	424	242

These results differ significantly from fluidized bed combustor experience where desulfurization is directly proportional to and highly dependent on the Ca/S feed ratio.

## 5.0 WASTE CHARACTERIZATION

Because of the complexity of environmental regulations, an investigation of waste characterization testing and disposal laws' was conducted. Section 3001 of the RCRA directs the EPA to promulgate criteria for identifying and listing hazardous waste. In a large number of cases, it is possible to determine a wastes classification by its specific exclusion or identification as a hazardous waste. For other wastes, the EPA has prescribed tests to determine whether it possesses one of four hazardous characteristics - corrosivity, ignitability, reactivity, and extraction procedure (EP) toxicity. Since coal gasification wastes are not on any of the promulgated hazardous wastes lists by specific and nonspecific sources, it is the responsibility of the generator to determine if the released waste possesses any of the four hazardous characteristics.

Reactivity and EP toxicity are the most critical characteristic for in-bed waste disposal. Presently, the EPA has not yet promulgated a test procedure or a quantitative threshold for toxic gas generation reactivity. During the interim they have recommended a draft test method and interim reactivity thresholds

(7, 8). The quantitative threshold for the total available sulfide measured via the draft test method is 500 mg evolved H<sub>2</sub>S/Kg waste when subjected to an acid leach (ph = 2.0) for 30 minutes. Wastes releasing more than that level may be regulated as hazardous.

Unsulphated in-bed solid waste samples from the fines loss, separator pit sludge and gasifier discharge were analyzed for reactive sulfide levels and EP toxicity. Table 3 contains typical EP toxicity test results.

TABLE 3. TYPICAL RCRA EP TOXICITY TEST RESULTS OF KRW IN-BED DESULFURIZATION SOLIDS WASTES (mg/L)

Metal	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Maximum Allowable Concentration	5	5	100	1.0	5.0	0.2	5.0	1.0
Gasifier Discharge	0.03	0.048	<0.1	<0.005	0.03	<0.03	<0.002	<0.004
Fines Loss	0.01	0.068	0.4	<0.005	<0.01	<0.03	0.012	0.009
Separator Pit Sludge	0.01	0.002	0.6	<0.005	<0.01	<0.03	<0.002	<0.004

The level of EP toxic metals in samples taken during TP-036-3 and TP-036-4 were all significantly below the RCRA toxic levels.

Typical reactive sulfide levels for the in-bed process are shown in Table 4.

TABLE 4. REACTIVE SULFIDE TEST RESULTS FOR KRW IN-BED DESULFURIZATION SOLID WASTES FROM TP-036-3

Sample	Sulfide Wt %	Reactive Sulfide (mg/kg)
Untreated Gasifier Discharge	8.6	>1200
Fine Loss	1.3	<5
Separator Pit Sludge	0.9	<5

The fines loss samples from the process had extremely low reactive sulfide levels of less than 5 ppm. Separator pit sludge, which consists of wet fines carryover from the quench/cooling system, also had less than 5 ppm reactive sulfide. However, all untreated PDU withdrawal wastes generated during TP-036-3 sorbent injection may be potentially hazardous when subjected to the interim EPA reactivity test.

As part of an extensive study of the characteristics of in-bed wastes, the gasifier discharge material was sulfated in laboratory scale reactors under a variety of experimental conditions. Table 5 summarizes the reactor conditions, reactive sulfide levels, and sulfur analysis of several samples.

TABLE 5. EXPERIMENTAL CONDITIONS, SULFUR ANALYSIS AND REACTIVE SULFIDE LEVELS OF SULFATED GASIFIER DISCHARGE

Reactor Type	Furnace Temp. (°F)	Oxygen Concn. (Vol %)	Gas Flow Rate (liters/min)	Contact Time (hrs)	Reactive Sulfide (mg/kg)	Total Sulfur (Wt%)	Percent Sulfation (mole %)
Packed Bed	1500°F	21	5	1	5	5.00	80.7
Fluidized Bed	1500°F	5	>10	1	<5	NM	NM
Open Dish	1500°F	21	0	1	<5	7.48	63.4
Open Dish	1500°F	21	0	3	<5	8.02	74.0

NM - Not Measured

The configuration and experimental conditions tested were adequate for reducing the reactive sulfide levels of the withdrawal sample to less than 500 mg/kg. These results are encouraging for the in-bed program because sulfation is the simplest and most direct method of treating in-bed wastes. Further studies of reaction kinetics are necessary to determine the optimal conditions for sulfation of the in-bed wastes to meet RCRA requirements. Tests are underway at the PDU to evaluate the technical feasibility of a continuous waste treatment process.

#### 6.0 GASIFIER PERFORMANCE

Gasifier performance was observed to improve during in-bed testing. The results of those set points in which gasifier performance was significantly enhanced due to sorbent injection are shown for tests TP-036-3 and TP-036-4 in Table 6.

TABLE 6. PILOT PLANT PERFORMANCE WITH IN-BED DESULFURIZATION

Coal	Sorbent	Air/Coal (lb/lb)	Gasifier Bed Temp. (°F)	Carbon Conversion Efficiency (%)	Cold Gas Efficiency (%)
Pittsburgh	--	4.28	1846	90	50
Pittsburgh	Dolomite	3.39	1950	90	73
Pittsburgh	Dolomite	3.37	1970	91	72
Pittsburgh	Limestone	3.27	1830	92	70
Wyoming	Dolomite	3.03	1820	91	65

Results from set points without sorbent injection are also shown for comparison. The benefits of sorbent injection are an increase in the cold gas efficiency and a decrease in the apparent fines elutriation rate.

Cold gas efficiencies increased dramatically during in-bed desulfurization from 50 to 70%. The increase in cold gas efficiency and corresponding drop in air/coal ratio may indicate improved gasification.

The catalytic effect of calcium on gasification rates has been documented by Walker (9), Freund (10), and Van Heek and Muhlen (11). Freund (9) found calcium catalyzed carbon reacted at a rate 100 times the rate of uncatalyzed carbon for the gasification of CO<sub>2</sub>. Catalytic effects are one of several potential contributing factors being investigated by KRW.

Fines loss rates and elutriation decreased dramatically with the bed weight of the gasifier/desulfurizer as shown in Figure 2. Increasing bed weight reflects the replacement of low density char (25 lb/ft<sup>3</sup>) by high density sorbent (80 lb/ft<sup>3</sup>) and the reduction of bed voidage. Reduced fines loss and elutriation rates are primarily the result of increased gasification rates and longer fines residence times. Improved gasification is attributed to the presence of the calcium based sorbents in the bed. Low bed voidage indicates low gas bypassing as bubbles. Fluidized bed filtering of fine material increases with decreased gas bypassing (12). The filter mechanism increases the fines residence time in the bed so that a larger portion is consumed before escaping the bed surface.

## 7.0 CONCLUSIONS

In-bed desulfurization integrated with hot particulate removal is potentially the most economical fossil energy process for converting all types of U.S. coals to electricity while complying with New Source Performance Standards (NSPS) for sulfur removal.

The in-bed program for direct injection of calcium-based sorbents into the KRW gasifier has demonstrated

- o desulfurization exceeding 90% for a 4.5% sulfur coal
- o cold gas efficiencies over 70%
- o feasible waste treatment by sulfation

Future development work at KRW includes pilot-scale sulfation of the gasifier discharge and demonstration of through put improvements. Laboratory scale investigations of desulfurization and the effect of calcium-based sorbents on char gasification will be conducted in parallel with the pilot plant testing to determine the controlling mechanisms for the relevant reactions.

KRW is also developing an external bed desulfurization system using zinc ferrite sorbent which is capable of removing sulfur compounds in a hot (1100°F) coal gas stream to a level of 10ppm. Installation and testing of the external bed desulfurization system is currently underway at the KRW Process Development Unit.

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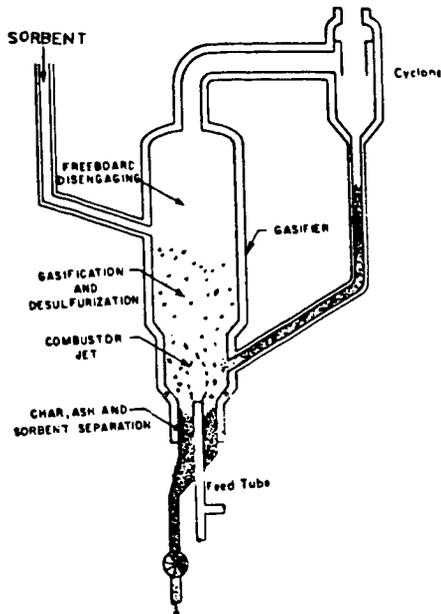


Figure 1. KRW Gasifier/Desulfurizer

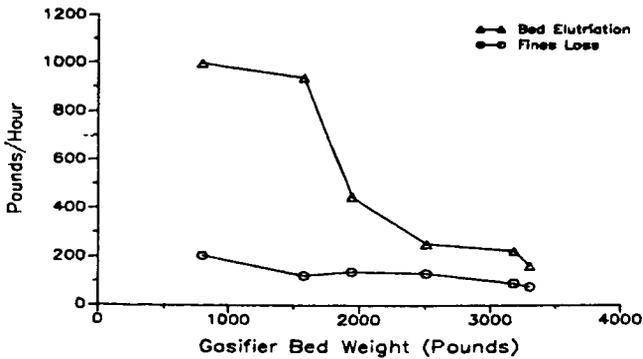


Figure 2. Variation of Fines Elutriation and Loss with Bed Weight in Gasifier/Desulfurizer