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Investigation on Durability and Reactivity of Promising Metal Oxide Sorbents During Sulfidation and Regeneration

Quarterly Report
April - June 1995

K.C. Kwon

July 1995

Work Performed Under Contract No.: DE-FG21-94MC31206

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Tuskegee University
Tuskegee, Alabama

MASTER

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INVESTIGATION ON DURABILITY AND REACTIVITY OF PROMISING METAL OXIDE SORBENTS DURING SULFIDATION AND REGENERATION

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ABSTRACT

Hot-gas desulfurization for the integrated gasification combined cycle (IGCC) process has been investigated by many researchers to remove effectively hydrogen sulfide with various metal oxide sorbents at high pressures and high temperatures. Metal oxides such as zinc titanate oxides, zinc ferrite oxide, copper oxide, manganese oxide and calcium oxide, were found to be promising sorbents in comparison with other removal methods such as membrane separations and reactive membrane separations. Some metal oxide sorbents exhibited the quite favorable performance in terms of attrition resistance and sulfur capacity. Removal reaction of H_2S from coal gas mixtures with ZT-4 or other promising sorbents of fine solid particles, and regeneration reaction of sulfur-loaded sorbents will be carried on in a batch reactor or a continuous differential reactor.

The objectives of this research project are to find intrinsic initial reaction kinetics for the metal oxide-hydrogen sulfide heterogeneous reaction system, to obtain effects of concentrations of coal gas components such as hydrogen, carbon monoxide, carbon dioxide, oxygen, nitrogen and moisture on equilibrium reaction rate constants of the reaction system at various reaction temperatures and pressures, to identify regeneration kinetics of sulfur-loaded metal oxide sorbents, and to formulate promising metal oxide sorbents for the removal of sulfur from coal gas mixtures. Promising durable metal oxide sorbents of high-sulfur-absorbing capacity will be formulated by mixing active metal oxide powders with inert metal oxide powders and calcining these powder mixtures, or impregnating active metal oxide sorbents on supporting metal oxide matrixes.

The Research Triangle Institute, a sub-contractor of this research project, will also prepare promising metal oxide sorbents for this research project, plan experiments on removal of sulfur compounds from coal gases with metal oxide sorbents as well as regeneration of sulfur-loaded metal oxide sorbents, and review experimental results.

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INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more depleted.

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. Coal minerals include primarily pyrites, silicate (quartz, clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur. Sulfur in coal is present as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occurring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. In gasification process, coal is reacted with steam and air or oxygen to produce a medium to high calorific value fuel gas. The fuel gas can be subsequently combusted in a gas/steam turbine combined cycle (IGCC). These IGCC-based power generation options offer much higher thermodynamic cycle efficiencies that promise to reduce all forms of pollutants released from a coal conversion process through a lower fuel consumption and from the use of more energy efficient high pressure and/or temperature unit operations for the removal of environmental pollutants. Among these options, integrated gasification combined cycles (IGCC) are relatively well developed.

Sulfur products in combustion of sulfur present in coal not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. Removal of hydrogen sulfide from hot coal gas produced in integrated gasification combined cycle power generation systems by metal oxide sorbents is required to protect downstream combustion turbines from being corroded with sulfur compounds. Removal of sulfur compound from coal gas products is investigated by using various metal oxide sorbents, and membrane separation methods. Current research results show that removal of sulfur with metal oxide sorbents appears to be the most promising method among others.

Main requirements of these metal oxide sorbents are durability and high sulfur-loading capacity during absorption-regeneration cycles. Spalling of sulfur-loaded fixed-bed metal oxide sorbents occurs during the regeneration of sulfur-loaded metal sorbents. The main causes of spalling of sorbents appear to be temperature rises of sulfur-loaded sorbents due to tremendous exothermic heat of reaction, and sulfate formation during regeneration processes. Sulfate products occupy more space than sulfide products in pores of sorbents, and result in significant structural stresses of metal sorbents.

The main objectives of this research proposal are to formulate durable metal oxide sorbents of high-sulfur-absorbing capacity by a physical mixing method or an impregnation method, to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, and to study kinetics on regeneration of sulfided sorbents, using formulated promising metal oxide solid sorbents.

STATEMENTS OF RESEARCH OBJECTIVES

Experiments will be conducted in an isothermal stirred micro batch reactor or an isothermal continuous differential reactor to obtain kinetic data on both sulfidation of metal oxide sorbents and regeneration of sulfided metal oxide sorbents, and experimental data on mechanical/thermal stabilities of formulated metal oxide sorbents suitable for the design of bench-scale/pilot-scale transport reactors.

(a) Metal-oxide sorbents with high reactivity/capacity and thermal/mechanical stability/durability will be formulated by a physical mixing method or an impregnation method.

(b) Experimental procedures will be developed for both sulfidation and regeneration reactions of formulated metal oxide sorbents at high pressures and high temperatures.

(c) Analytical procedures will be developed for the analysis of concentrations of both sulfur dioxide and hydrogen sulfide in a reaction product gas mixture.

(d) Thermal/mechanical stability of formulated metal oxide sorbents from cyclic sulfidation/regeneration reactions will be investigated in the isothermal stirred batch reactor or the isothermal continuous differential reactor.

Effects of reaction variables on sulfidation/regeneration reaction kinetics will be investigated for formulated promising metal oxide sorbents. The reaction variables include concentrations of coal gas components, total pressures, reaction temperatures, space velocities of gases for continuous differential reactor operations, initial mass ratios of coal gases to sorbents for batch reactor operations, particle sizes of sorbents, and pore volumes of sorbents.

(a) Effects of concentrations of coal gas components such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, and moisture on both sulfidation and regeneration reaction kinetics will be evaluated at various reaction temperatures and pressures, using a stirred batch reactor.

(b) Effects of total pressures and reaction temperatures on sulfidation/regeneration reaction kinetics for formulated metal oxide sorbents will be determined in a stirred batch reactor or a continuous differential reactor.

(c) Roles of initial mass ratios of sorbents to sulfidation/regeneration gas mixtures, particle sizes of sorbents, and pore volumes of sorbents will be found, using a stirred batch reaction system.

(d) Roles of space velocities of regeneration gas mixtures, and particle sizes of sorbents, pore volumes of sorbents will be delineated, using a continuous differential reaction system.

EXPERIMENTAL APPROACH

The main objectives of this project are to investigate reaction kinetics on the removal of sulfur compounds from coal gases at high temperatures and high pressures, using promising solid metal oxide sorbents, to study kinetics on the regeneration of sulfided sorbents, and to formulate promising durable metal oxide sorbents of high-sulfur-absorbing capacity.

Fresh metal oxide sorbent particles with promising formulas and simulated coal gases containing hydrogen sulfide are introduced in a batch reactor. The batch reactor, loaded with the fresh sorbent and the simulated coal gas mixture, is submerged in a fluidized sand bath to maintain the heterogeneous reaction system at a desired reaction temperature. Fine metal oxide sorbents will be used to minimize effects of intraparticle diffusion of hydrogen sulfide through sulfided sorbent particles. The batch reactor, loaded with a mixture of fresh sorbent and simulated coal gas mixtures, is shaken in a constant-temperature fluidized sand bath to reduce effects of mass transfer of hydrogen sulfide to sorbent particles. The sulfidation reaction is terminated at the desired reaction time. Conversions of sorbents are analyzed with an electronic balance and a gas chromatograph.

Experiments on the regeneration of sulfided sorbents will be conducted in the batch reactor. Effects of regeneration temperatures, regeneration pressures, and concentrations of regeneration gases such as oxygen, nitrogen, and moisture on regeneration rate will be investigated in the batch reactor.

Precise laboratory procedures will be developed for H_2S-sorbent heterogeneous reactions in a batch reactor at high pressures and high temperatures. This will involve developing procedures for a proper set-up of a batch reactor and a gas chromatograph for a reaction system. Experiments on intrinsic initial reaction kinetics as well as regeneration kinetics will be performed for metal-oxide sorbents-H_2S heterogeneous reaction systems.

STATUS OF THIS RESEARCH PROJECT

Research activities and efforts of this research project were concentrated on calibrating the recently-purchased gas chromatograph (GC) for the analysis of oxygen as well as hydrogen sulfide, using compressed air as well as 10,000 ppm hydrogen sulfide in nitrogen as the standard gas samples, fabricating a 35 cm^3 316 stainless steel (SS) batch reactor, investigating conversion of hydrogen peroxide into oxygen as a possible source of oxygen in a 13 cm^3 316 SS batch reactor, conducting experiments on reactivity of oxygen with the 316 SS batch reactor wall using air and nitrogen, and carrying out experiments on reactivity of hydrogen sulfide with the 316 SS batch reactor wall.

A 35 cm^3 316 SS batch reactor was fabricated with Swagelok fittings (see Figure 1), which will provide tight sealing for batch reaction experiments. Its suitability for high-temperature cycled batch reactions was tested at 600 °C and 500 psig, using neat nitrogen. The reactor was sent to the Alon Processing, Inc. to be alonized.

A chromatographic calibration curve for the analysis of oxygen was developed with a thermal conductivity detector (TCD), using various gas mixtures of compressed air and neat nitrogen (Table 1 and Figure 2). This calibration curve will be utilized to detect concentrations of oxygen during regeneration of sulfided sorbents, assuming that nitrogen is inert at conditions of regeneration reaction for metal oxide sorbents. The following linear relationship between mole % of oxygen and chromatographic area % of oxygen was developed for oxygen-nitrogen gas mixtures by maintaining a HaySep A GC column at 35 °C.

$$y = 0.6212x - 0.2173 \qquad (1)$$

where x: mole % of oxygen
y: chromatographic area % of oxygen

A chromatographic calibration curve for the analysis of hydrogen sulfide was developed with a flame photometric detector (FPD), using various gas mixtures of 10,000 ppm hydrogen sulfide in nitrogen and neat nitrogen (Table 5 and Figure 4). This calibration curve will be used to analyze concentrations of hydrogen sulfide during sulfidation of fresh/regenerated metal oxide sorbents. The FPD detector detects sulfur compounds only, and does not detect inert nitrogen gas. In this way, there are no inert key compounds for the analysis of hydrogen sulfide. The following linear relationships between concentrations of hydrogen sulfide and chromatographic area % of hydrogen sulfide were developed for H_2S-N_2 gas mixtures, as shown in equations 2 through 4. These relationships will vary with sensitivity of the detector, amounts of injected gas samples, and temperature programmings. Therefore, a relationship should be developed once a day. These relationships were established by injecting 30 μl gas samples into the gas chromatograph, which was maintained at 50 °C. The equation 2 was developed with the Sample A gas mixtures, which were prepared on 7/11/95 (see Table 5), whereas the equation 3 was developed with the Sample B gas mixtures, which were prepared on

7/12/95. The equation 4 was developed with the chromatographic areas from two gas samples such as the 10,000 ppm sample and the 400 ppm sample of the Sample B gas mixtures. The concentrations of H_2S, as shown in the Predicted 1 of Table 5, are predicted with equation 3, whereas the concentrations of H_2S, as shown in the Predicted 2 of Table 5, are predicted with equation 4. The error range of predicted concentrations appears to be 5 %.

$$y = 78.153x^{0.4331} \tag{2}$$

$$y = 74.232x^{0.4367} \tag{3}$$

$$y = 75.154x^{0.4321} \tag{4}$$

Decomposition of hydrogen peroxide into oxygen as a possible source of oxygen was investigated in the 13 cm^3 316 SS batch reactor (see Table 2). No oxygen from this reaction was detected. Reactive atomic oxygen rather than molecular oxygen may be produced from this decomposition reaction, and then be consumed in oxidizing the 316 SS reactor wall.

Oxygen from air instead of hydrogen peroxide as an oxygen source was chosen for the regeneration of sulfided metal oxide sorbents. A method was developed to introduce a desired amount of oxygen into the batch reactor, using air and neat nitrogen (see Table 1). Experiments on reactivity of oxygen with the 316 SS batch reactor wall were conducted with water or without water (see Tables 3 and 4, and Figure 3). Molecular oxygen does not react with the 316 SS batch reactor wall either in the presence or in the absence of water over the temperature range of 300 - 450 °C, whereas molecular oxygen reacts significantly with the 316 SS batch reactor wall above 450 °C. Mole percentages of oxygen, as shown in Table 4, were calculated with the calibration curve for oxygen-nitrogen gas mixtures.

Experiments on reactivity of hydrogen sulfide with the 316 SS batch reactor wall, using 10,000 ppm hydrogen sulfide in nitrogen and neat nitrogen, were carried out in the presence of water (see Tables 6 and 7, and Figure 5). Hydrogen sulfide reacts significantly with the 316 SS batch reactor wall in the presence of water over 300 - 500°C. Conversion percentages of hydrogen sulfide, as shown in Table 7, were calculated with the calibration curve for H_2S-N_2 gas mixtures, as shown in equation 2. Conversions of H_2S were more than 90 % for the reaction time of 20 min at 300°C as well as 500°C.

Spherical metal-oxide-sorbent carriers were ordered from Norton Co. to impregnate active metal oxide sorbents on them, as shown in Table 8. Mr. Tyran Welch, one of our senior chemical engineering student, worked for this project as a research assistant.

PLANS ON FUTURE EXPERIMENTS

Initial reaction kinetics on both sulfidation of sulfur-free sorbents and regeneration of sulfided sorbents will be conducted in the 35 cm^3 Swagelok-fitted alonized 316 SS batch reactor, using sorbents impregnated on the Norton carriers, and the ZT-4 sorbent from the Research Triangle Institute. Instruments and equipment for a continuous differential reactor will be selected and placed on order. Fresh metal oxide sorbents also will be formulated by a physical mixing method.

Table 1. Chromatographic Calibration curve for O_2-N_2 system, using the thermal conductivity detector(TCD).

Oxygen Mole %	Chromatographic Area %
1.87	0.89
1.87	1.05
3.15	1.73
3.15	1.74
3.79	2.01
3.79	2.16
4.42	2.48
4.42	2.61
5.06	2.97
5.06	2.86
5.70	3.36
5.70	3.34

Table 2. Operation conditions for the reaction of hydrogen peroxide with 316 stainless steel in the presence of water and nitrogen at various temperatures.

Reactor Volume, cm^3:	13
Temperature, °C:	300 - 600
Reaction Time, min:	10
Initial Amount of Hydrogen Peroxide, g:	0.002
Initial Amount of Water, g:	0.004
Initial Partial Pressure of Nitrogen at 25°C, psig:	125

Table 3. Operation conditions for the reaction of oxygen with 316 stainless steel in the presence of water and nitrogen at various temperatures.

Reactor Volume, cm^3:	13
Temperature, °C:	300 - 600
Reaction Time, min:	10
Initial Partial Pressure of Oxygen at 25°C, psig:	25 (5 mole % in initial dry gas mixture)
Initial Amount of Water, g:	0.004
Initial Partial Pressure of Nitrogen at 25°C, psig:	125

Table 4. Reactivity of oxygen with 316 SS reactor wall in the presence of nitrogen for 10 min at various temperatures.

Temperatures, °C	Mole % of Dry O_2	Mole % of Wet O_2**
300	5.15	5.87
300	5.47	5.36
350	5.29	5.55
350	5.55	5.57
400	5.26	5.34
400	5.36	5.34
450	4.71	5.23
450	4.68	5.07
500	3.26	2.81
500	3.26	2.59
550	2.62	1.44
550	2.46	1.83
600	3.05	4.63
600	3.18	4.62

**: mole %, excluding water

Table 5. Chromatographic calibration curve for H_2S-N_2 gas mixtures.

H_2S Concentration, ppm			Chromatographic Area	
Actual	Predicted 1	Predicted 2	A(7/11/95)	B(7/12/95)
10000	10384	10031	81753	81961
10000	10309	9960	—	80610
5000	4669	4549	10924	13145
5000	4680	4559	—	13211
2000	2092	2055	1877	2090
2000	2043	2008	1857	1981
1000	—	—	441	—
400	388	388	—	44
400	413	413	39	51

Table 6. Operation conditions for the reaction of H_2S with 316 stainless steel in the presence of water and nitrogen at various temperatures.

Reactor Volume, cm^3:	13
Temperature, °C:	300 - 600
Reaction Time, min:	10
Initial Concentration of H_2S , ppm:	10,000
Initial Amount of Water, g:	0.004
Initial Partial Pressure of Nitrogen at 25°C, psig:	150

Table 7. Reactivity of H_2S with 316 stainless steel in the presence of water and N_2.

	Conversion % at the Temperatures	
Reaction Time, min	300°C	500°C
0	0	0
5	65	79
10	77	90
20	96	98

Table 8. The following spherical catalyst carriers were ordered from Norton Co..

MATERIAL	TYPE	SURFACE AREA m^2/g	MEDIAN PORE DIAMETER, micron
Zirconia	SZ 5*64	0.1-0.5	19
Alumina	XA 25045	4	0.1; 11
Titania	------------	3	0.15
Silica	SS 5*64	0.1 - 0.4	1.7

Figure 1. Batch Reactor Assembly

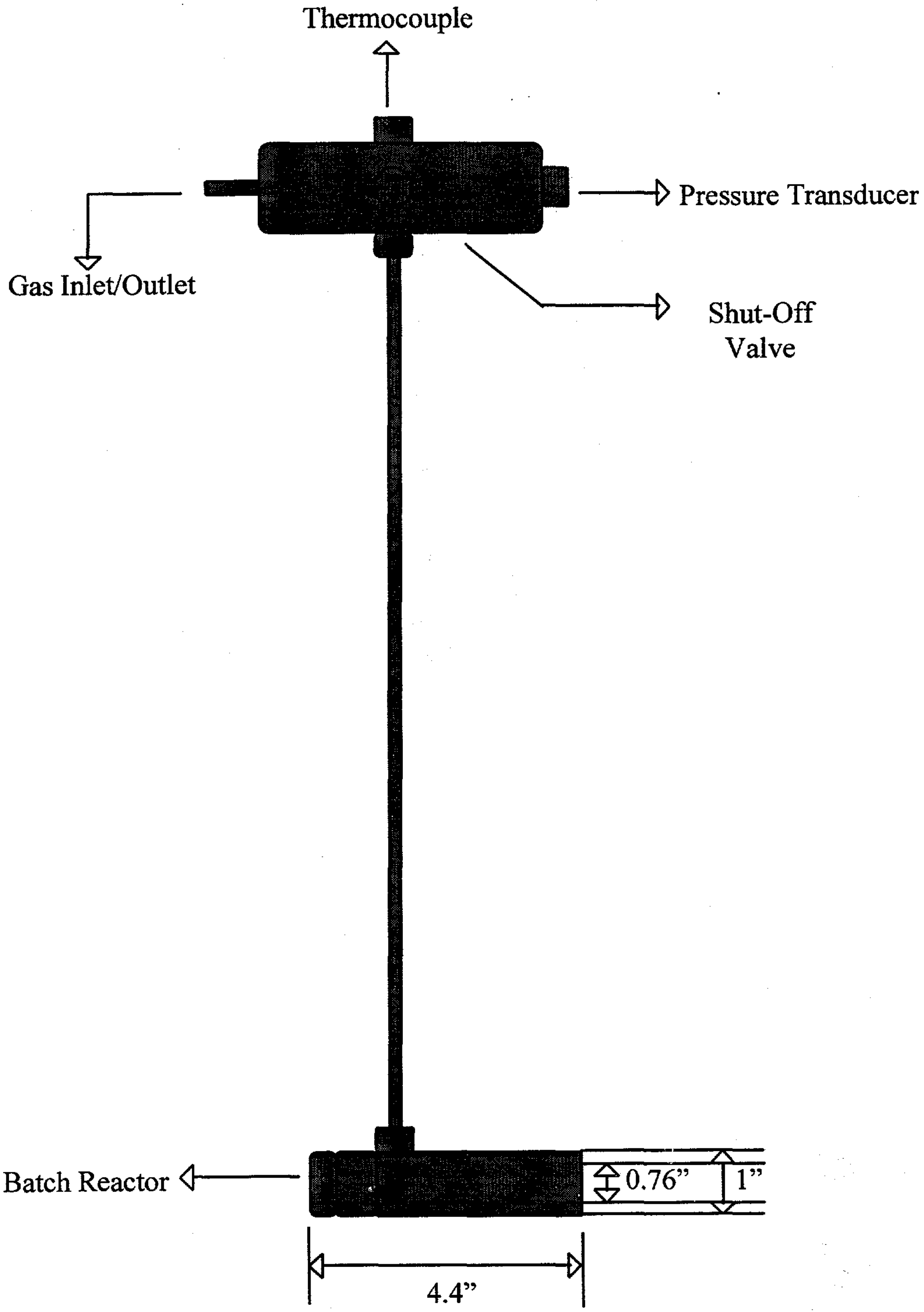

Figure 2. Chromatographic cailbration curve for O_2-N_2 gas mixtures, using a TCD dectector at 35°C.

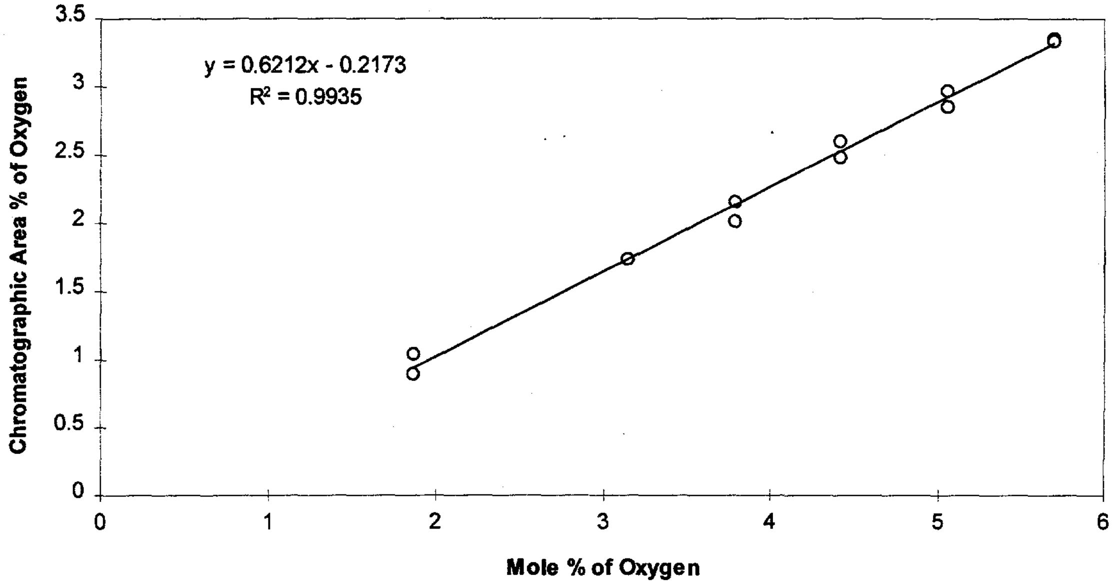

Figure 3. Reactivity of oxygen with 316 stainless steel at various temperatures.

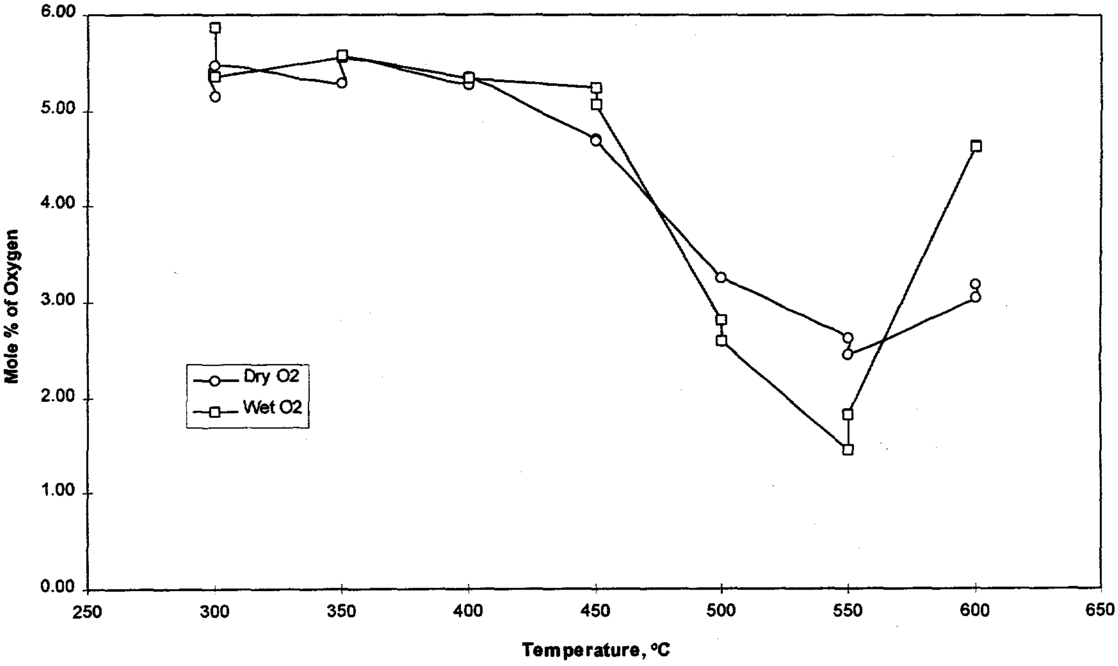

Figure 4. Chromatographic calibration curve for H_2S-N_2 gas mixtures.

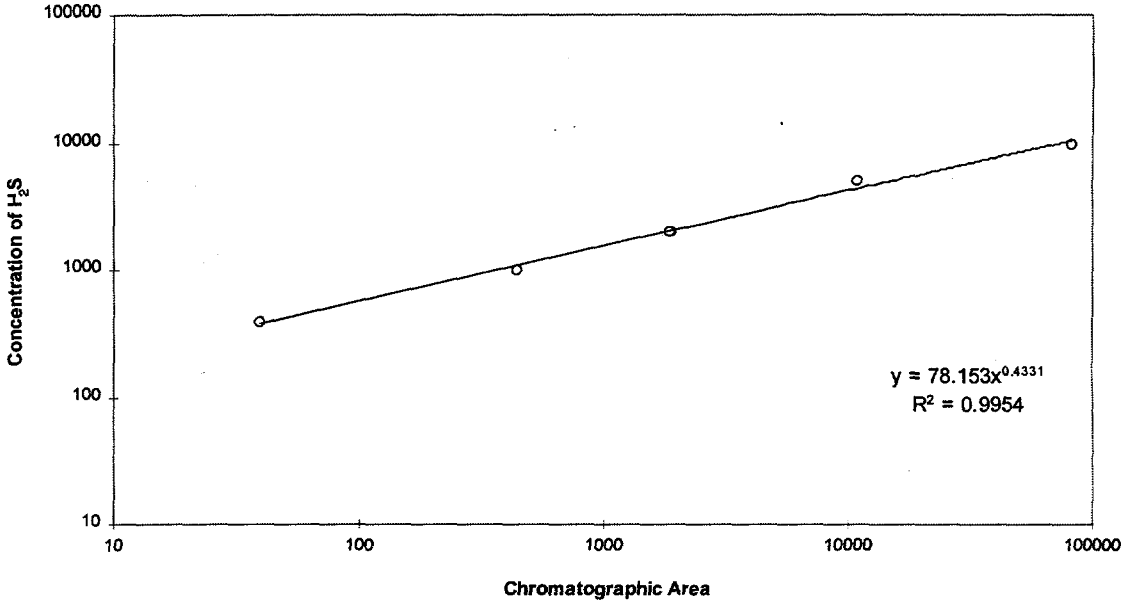

Figure 5. Reactivity of H_2S with 316 stainless steel in the presence of nitrogen and water.