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STUDIES INVOLVING HIGH TEMPERATURE DESULFURIZATION/REGENERATION REACTIONS OF METAL OXIDES FOR FUEL CELL DEVELOPMENT

Final Report

By
Vinod Jalan

October 1983

Work Performed Under Contract No.: DE-AC21-81MC16021

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

By
Giner, Inc.
Waltham, Massachusetts

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ABSTRACT

Research conducted at Giner, Inc. during 1981-83 under the present contract has been a continuation of the investigation of a high temperature regenerable desulfurization process capable of reducing the sulfur content in coal gases from 200 ppm to 1 ppm. The overall objective has been the integration of a coal gasifier with a molten carbonate fuel cell, which requires that the sulfur content be below 1 ppm. Commercially available low temperature processes incur an excessive energy penalty. Results obtained with packed-bed and fluidized bed reactors have demonstrated that a CuO/ZnO mixed oxide sorbent is regenerable and capable of lowering the sulfur content (as H_2S and COS) from 200 ppm in simulated hot coal-derived gases to below 1 ppm level at 600-650°C.

Four potential sorbents (copper, tungsten oxide, vanadium oxide and zinc oxide) were initially selected for experimental use in hot regenerable desulfurization in the temperature range 500-650°C. These choices were based on consideration of low attainable equilibrium concentration, favorable sulfidation and regeneration reaction chemistry, and the prospect of acceptable thermal stability. Experimental bench scale evaluations of the desulfurization and regeneration performance in fixed bed and fluidized-bed reactor configurations were conducted for three of the four sorbents: copper, zinc oxide, and vanadium oxide.

Results of further studies conducted at Giner, Inc. identified Cu and CuO/ZnO to be especially attractive sorbents and the use of steam-air to be efficient for regeneration of the spent sorbent. Further optimization has established highly dispersed CuO on zeolite, highly dispersed [CuO + ZnO] on zeolite, and a coprecipitated CuO/ZnO as the three most promising sorbents for efficient utilization of the theoretical desulfurization capacity. Based on engineering considerations, such as desulfurization capacity in per weight or volume of sorbents, a coprecipitated CuO/ZnO was selected for further study. A structural reorganization mechanism, unique to mixed oxides, was identified: the creation of relatively fine crystallites of the sulfided components (Cu_2S and ZnS) to counteract the loss of surface area due to sintering during regeneration. Studies with 9 to 26% water vapor in simulated coal gases show that sulfur levels below 1 ppm can be achieved in the temperature range of 500^o to 650^oC. The ability of CuO/ZnO to remove COS, CS_2 and CH_3SH at these conditions has been demonstrated in this study. Also a previously proposed pore-plugging model was further developed with good success for data treatment of both packed bed and fluidized-bed reactors.

ACKNOWLEDGEMENT

This report summarizes the technical results of a two year study conducted at Giner, Inc. for the Morgantown Energy Technology Center (METC) of the United States Department of Energy (DOE) under Contract No. DE-AC-21-81MC16021. Work was accomplished under the direction of Dr. Vinod Jalan, Principal Investigator. Those who contributed to this study were Dr. Jose Giner and Messrs. Clyde Brooks, Mahesh Desai and Robert Waterhouse, of Giner, Inc. Professor Christos Georgakis and Mr. Donald Koch of Massachusetts Institute of Technology, and Dr. M. S. Ananth of Indian Institute of Technology, Madras (Visiting Professor at Princeton University) provided expert guidance in mathematical modeling.

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EXECUTIVE SUMMARY

Giner, Inc., under the support of Morgantown Energy Technology Center (METC) has carried out a program to develop a high temperature desulfurization system to facilitate the integration of a coal gasifier with molten carbonate fuel cell or combined cycle gas turbine power plants. The program began with systematic, fundamental investigations based on thermodynamic feasibility of sulfur removal and regeneration, effects of water gas shift reaction, and carbon deposition. The selection criteria included practical considerations of cost, sulfur uptake capacity, regeneration efficiency and cycle life. The developmental phase consisted of preparation of high activity sorbent structures, determination of operating parameters and evaluation in fluidized and packed bed reactors.

The original program was based on the premise that a two-stage sulfur removal would be utilized -- the first stage would be the reduction of hydrogen sulfide from 6000 to 200 ppm by the regenerable iron oxide process developed at Morgantown and the second stage to be developed in this program to further reduce hydrogen sulfide levels to less than one ppm. Since then, the emphasis at METC has shifted to regenerable ZnO and $ZnFe_2O_4$. The zinc ferrite process has improved sulfur capacity over ZnO, but at a cost of exit stream purity -- ZnO can bring the H_2S level down to 2 ppm but $ZnFe_2O_4$ at the same conditions (538°C with 27% H_2O vapor) cannot reduce H_2S levels below 5 ppm, which is far from being acceptable for the molten carbonate fuel cells. Therefore, the necessity of a secondary high temperature desulfurization process to reduce H_2S levels <u>below</u> 1 ppm still remains.

During the course of this program, it was shown that: (1) CuO/ZnO is a regenerable sulfur sorbent capable of reducing H_2S levels below 1 ppm, (2) the use of a steam-air mixture was efficient for regeneration of spent sorbents, and (3) the reverse flow approach was useful for regeneration to minimize sulfate formation, i.e., desulfurization is carried out by passing the coal gases from bottom to top and the regeneration is carried out by passing the steam-air mixture from top to bottom. The latter two approaches were successfully incorporated into the zinc ferrite studies at METC.

Further optimization has established highly dispersed CuO on zeolite, highly dispersed [CuO + ZnO] on zeolite, and a coprecipitated CuO/ZnO as the three most promising sorbents. Based on engineering considerations, CuO/ZnO was selected for further study. A structural reorganization mechanism, unique to mixed oxides, was identified: the creation of relatively fine crystallites of the sulfided components (Cu_2S and ZnS) which counteracts the loss of surface area due to sintering during regeneration. Studies with 9 to 26% water vapor in simulated coal gases show that sulfur levels below 1 ppm can be achieved in the temperature range of 500^{o} to $650^{o}C$. Although adequate for the performance of this program, the detection tube technique could not provide quantitative measurement of H_2S below the 1 ppm level. The ability of CuO/ZnO to remove COS, CS_2, and mercaptans at these conditions was also demonstrated. This study has finally shown the feasibility of regeneration of spent sorbents by the simulated MCFC cathode exit gases, e.g., 5% O_2, 10% CO_2, 10% H_2O and 75% N_2.

The program has met the overall objective towards the development of a high temperature ($550-650^{o}C$) desulfurization process by identifying CuO/ZnO as an efficient regenerable sorbent that can reduce H_2S concentrations to below 1 ppm. Among other major accomplishments are: the invention of steam-air mixture for regeneration, elucidation of structural reorganization of CuO/ZnO sorbent, and the development of a pore-plugging model for data analysis. During the performance of the program, there were three unexpected findings which required special attention. Further work is recommended to take advantage of these findings, which are:

(1) A possible formation of $V(HS)_3$ or a sulfided compound of vanadium eutectic with some impurity or support material.

(2) Interaction of CuO with Stainless Steel Reactor giving a real synergistic effect between CuO and Fe suggesting CuO/FeO_x and $CuO/ZnO/FeO_x$ as potential desulfurization sorbents.

(3) Higher than anticipated sulfur uptake capacity of CuO/ZnO in the fluidized-bed reactor.

Based on the results obtained here and these unexpected finding recommendations are made to further this program to provide a complete process integration with coal gasifier and fuel cell or other applications such as combined cycle power plants.

OBJECTIVE

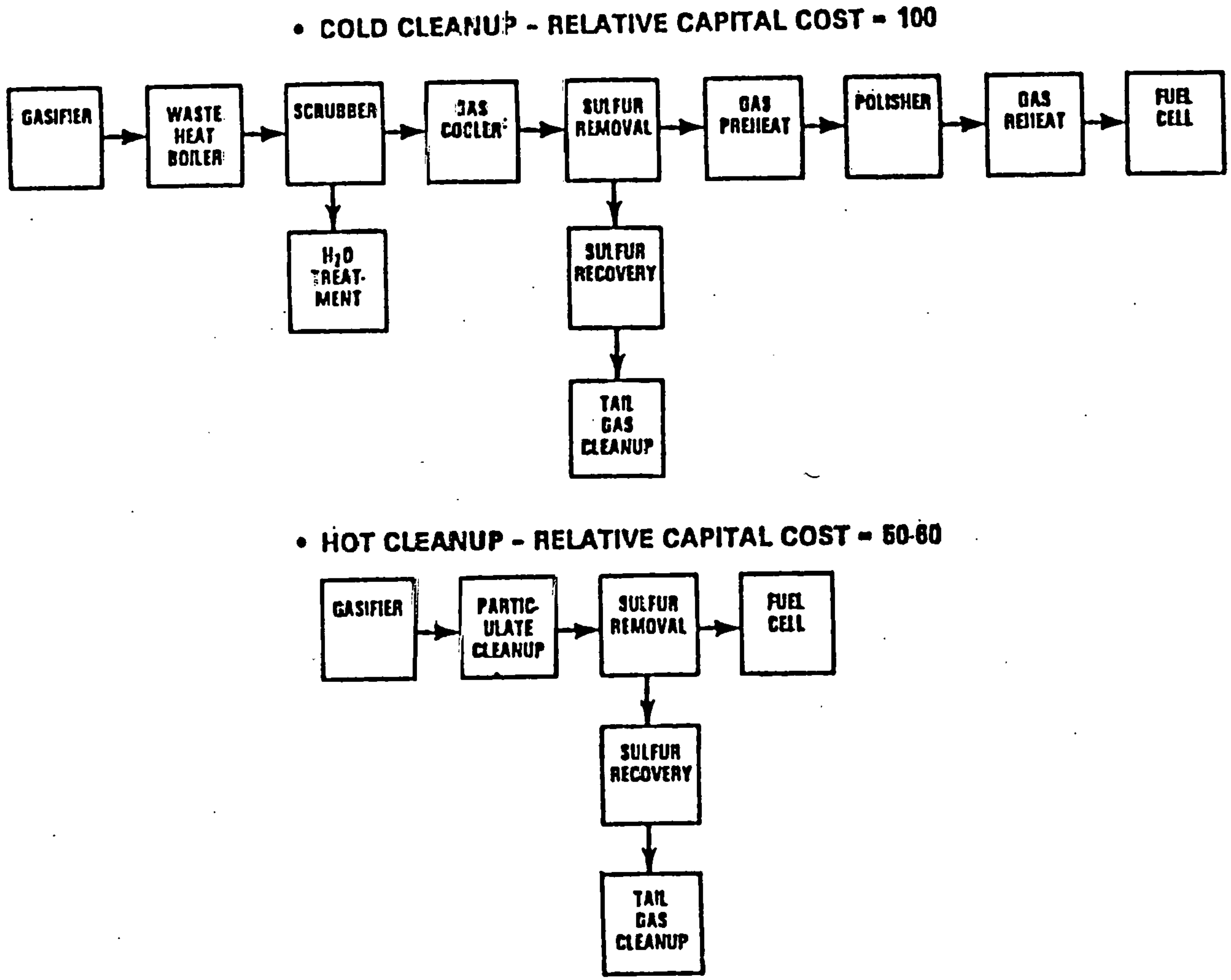
The overall objective of this program was to develop a low cost, commercially feasible desulfurization system which could be integrated into a molten carbonate fuel cell powerplant. The immediate objectives were to prepare, characterize and optimize promising desulfurization agents which could remove H_2S to below 1 ppm at intermediate to high temperatures (500 - 700°C), and which could be regenerated efficiently. The cost and operation of the desulfurization system had to be consistent with the cost and heat rate objectives of the powerplant.

I. INTRODUCTION

Molten carbonate fuel cell powerplants appear to provide the most attractive way to convert coal or other fossil fuels to electricity. Recent design studies show that a baseload electric plant operating on coal can provide an alternative technology with higher efficiency and lower gaseous emissions. However, the successful development of molten carbonate cells, especially their integration with a coal gasifier, requires that H_2S be removed from fuel gases down to one ppm or lower levels.

Sulfur removal is an essential requirement in the clean up of the gases from coal gasification for many applications, but it is particularly exacting for the molten carbonate fuel cell. There are a large number of commercial sulfur removal processes available. The limitations that restrict their applicability to clean up molten carbonate fuel cell feed-stock consist of disadvantages such as: relatively low operating temperatures of about 150°C or less; scrubbing agents that are incompatible with some of the more reactive fuel gas components such as CO_2; failure to remove sulfur to acceptable levels for the fuel cell; excessive plant capital cost; and creation of secondary pollution problems in disposal of the recovered sulfur and regeneration of the scrubbing liquids.

There are distinct technical and economic advantages in using high temperature desulfurization processes for sulfur removal from coal gases (Figure 1). The energy penalty (TRW, 1979) associated with cooling the gases from the gasifier for the low temperature commercial desulfurization processes such as Selexol, Rectisol, etc., is high (Table 1). There are also significant plant cost advantages to high temperature desulfurization processes in regard to fuel processing costs (Table 2). Additional advantages of a hot regenerable sorbent are: (1) loss of fuel gas components due to retention in the desulfurization solvents is avoided, (2)



<u>Figure 1</u> Sulfur Removal Options for Molten Carbonate Fuel Cells (Neal,1982)

TABLE 1

ENERGY ADVANTAGES OF HIGH TEMPERATURE GAS CLEANUP

(Ref. TRW, 1979)

Case	Energy Penalty %
1 - Raw gas from fixed-bed gasifier containing tar, oils, organic S and N compounds. - Low temperature cleanup with state of the art technology.	25.0
2 - Product gas from fluid-bed gasifier containing no tar or oils. - Low temperature cleanup with state of the art technology	13.2
3 - Product gas from fluid-bed gasifier containing no tar or oils. - High temperature cleanup with developmental stage processing system.	1.3

TABLE 2

COST COMPARISON OF LOW AND HIGH TEMPERATURE GAS CLEANUP

(Ref. Blecher, 1980)

GASIFIER	UNIT COST ($/Installed KW) Low Temperature (Selexol)	High Temperature (Conoco)
Two Stage: Entrapped Bed		
Air-Blown	253	220
O_2-Blown	307	299
Fluid Bed: U-Gas		
Low Steam Rate	243	182

secondary waste disposal problems associated with liquid scrubbers are minimized, and (3) compatability with dispersed power plants of small or intermediate size is provided. Consequently, these economic considerations dictated that the desulfurization system operate in the 500 to 650°C temperature range.

The original program was based on the premise that a two-stage sulfur removal would be utilized, the first stage being the reduction of H_2S from 6000 to 200ppm by the regenerable iron oxide process developed at METC. Since then, the emphasis at METC has shifted to regenerable ZnO and $ZnFe_2O_4$. The zinc ferrite process has improved sulfur capacity relative to ZnO, but at the cost of exit stream purity; ZnO can bring the H_2S level down to 2 ppm but $ZnFe_2O_4$ at the same conditions (538°C with 27% H_2O vapor) cannot reduce H_2S levels below 5 ppm, which is not acceptable for molten carbonate fuel cell applications. Therefore, the necessity of a secondary high temperature desulfurization process to reduce H_2S levels below 1 ppm still remains.

During the past year, Giner, Inc. has continued a program under support of Morgantown Energy Technology Center (METC) with the objective of developing a high temperature desulfurization system to facilitate the integration of coal gasifier with molten carbonate fuel cells (MCFC) or combined cycle gas turbine power plants. The particular incentive to undertake the present study was the potential advantage provided by a satisfactory second stage compatible with selection of any of the above systems for use in sulfur removal from molten carbonate fuel cell feed-stock. The commercial use of intermediate temperatures of 200-450°C for non-regenerable ZnO guard-beds for protection of sulfur sensitive catalysts such as those used for steam reform of hydrocarbons, methanation of H_2/CO gases, synthetic ammonia catalysts, etc. is well established.

This type of non-regenerable guard-bed is not economically attractive for use for removal of sulfur above the trace level for gas production systems with the large volumes anticipated for coal gasifier-integrated molten carbonate fuel cell power plants. There are other adsorbent systems such as activated carbon and sponge iron which have received attention as second stage sulfur removal guard-bed type applications, but they have not yet been developed sufficiently to solve the problem.

The performance criteria considered in identification of promising sorbent candidates consist of:

- rapid sulfidation kinetics
- low equilibrium H_2S concentrations
- high conversions of the removal agent to the sulfided state,
- rapid regeneration kinetics,
- thermal and mechanical stability for the removal agent under both conditions of sulfidation and regeneration, and
- compatibility of the removal agent with other more reactive gas components.

The Giner, Inc. program began with a systematic screening of potential sorbents based on thermodynamic feasibility of high temperature sulfur removal and regeneration, effects of water gas shift reaction, and carbon deposition. The selection criteria included practical considerations of cost, sulfur uptake capacity, regeneration efficiency, and cycle life. The developmental phase consisted of preparation of high activity sorbent structures, determination of operating parameters and evaluation in fluidized and packed-bed reactors.

During the prior phase of the program, we had identified the following: 1) CuO/ZnO as a regenerable sulfur sorbent capable of reducing H_2S levels below 1 ppm, 2) use of steam-air mixture for efficient regeneration of spent sorbents, and 3) reverse flow approach for regeneration to minimize sulfate formation, i.e., desulfurization is carried out by passing the coal gases from bottom to top and the regeneration is carried out by passing steam-air mixture from top to bottom. The latter two approaches have been successfully incorporated into the zinc ferrite studies at METC (Grindley, 1981). Further optimization established highly dispersed CuO on zeolite, highly dispersed [CuO + ZnO] on zeolite, and coprecipitated CuO/ZnO as the three most promising sorbents. A question has been raised about the danger of poisoning due to copper pickup on the Ni anode when CuO/ZnO is used at high temperature (Personal Communication, METC). Although Cu is a poison for some gas phase reactions over Ni catalyst, this is not a case at the anode of MCFC as evidenced by recent efforts to utilize Cu based MCFC anodes (Camara and Ong,1983). Although the effects of H_2S on Cu anodes is not known, due to its high affinity for sulfur, it is believed that the requirements of low sulfur containing gases would still exist. Under the current program, the desulfurization capacity of the most promising sorbent systems was studied in supported and unsupported form using both fixed-bed and fluidized-bed reactor configurations. The test parameters considered involved: 1) preparation procedure, 2) nature of support, 3) sorbent particle size, 4) water partial pressure, 5) desulfurization temperature, 6) regeneration mode, 7) ability to remove organic sulfur (COS, CS_2, CH_3SH), 8) reactor wall effects, 9) prereduction in H_2S-free fuel gas versus H_2-N_2 mixtures, and 10) maintenance of desulfurization capacity after several regenerations.

The sorbents were characterized by scanning electron microscopy (SEM), energy dispersive analysis by x-ray (EDAX), x-ray diffraction (XRD), chemical analysis, Hg porosimetry, and BET surface area. Modeling of the fixed-bed and fluidized-bed reactors was continued to aid in the data treatment.

II. DESULFURIZATION TECHNOLOGIES RELEVANT TO MCFC

A. Low Temperature Processes

There are a number of desulfurization processes available for sulfur removal, primarily of H_2S, from coal gases. These can be classified into two principal categories,low and high temperature processes. The low temperature processes can be defined, somewhat arbitrarily as those operating below about 120°C. The low temperature processes (Table 3) fall into four categories: chemical solvent types, physical solvent types, direct conversion and dry bed types.

The chemical solvent types that are commercial processes consist of MEA (monoethanolamine), DEA (diethanolamine),TEA (triethanolamine), Akazid (potassium dimethylaminoacetate), Benfield (potassium carbonate solution and amine), and Catacarb (activated potassium carbonate solution). These processes operate in the range of about 80 for MEA up to about 250°C for Benfield and Catacarb and are capable of removing H_2S and varying amounts of COS at an efficiency of about 99 percent. Sulfur vapor pressures are not usually reduced below 100 ppm as H_2S without process modification, however.

The physical solvent type processes consist of sulfinol (sulfolane + Diisopropanol amine), Selexol (polyethylene glycol) and Rectisol (methanol). These processes operate at lower temperatures than the chemical solvent type processes ranging from about 50°C for Sulfinol to less than -18°C for Rectisol. Sulfur removal efficiencies of 99 percent can be obtained for these processes, but once again, sulfur levels below 100 ppm are not readily attained. All three of these are commercial processes.

The two direct conversion processes consist of the Stretford (Na_2CO_3 + anthraquinone sulfonic acid) which is a commercial process and Townsend (triethylene glycol). Sulfur removal efficiencies of 99.9

TABLE 3

LOW TEMPERATURE CLEANUP PROCESSES

Process	Absorbent	Type of Absorbent	Temp. °C	Efficiency of S. Removal		Absorbent Characteristics		Form of Sulfur Recovery
				% H_2S Influent	Effluent H_2S ppm	Regeneration	Selectivity Toward	
CHEMICAL SOLVENT TYPE								
1. MEA	Monoethanolamine	Aqueous solution	25 to 50	99	~100	Thermal	Forms non-regen.comp. CS_2	As H_2S gas
2. DEA	Diethanol amine	Aqueous solution	40 to 55	99	~100	Thermal	Absorbs CO_2 Does not absorb COS, CS_2	As H_2S gas
3. TEA	Triethanolamine	Aqueous solution	40 to 65	99	~100	Thermal	H_2S	As H_2S gas
4. Alkazid	Potassium dimethyl amino acetate	Aqueous solution	20 to 50	99	~100	With Steam	H_2S	As H_2S gas
5. Benfield	Activated potassium carbonate	Aqueous solution	65 to 120	99	H_2S + COS ~100	With Steam	H_2S is high	As H_2S gas
6. Catacarb	Activated potassium carbonate	Aqueous solution	65 to 120	99	H_2S + COS ~100	With Steam	H_2S partial also absorbs COS, CS_2	As H_2S gas

TABLE 3 (cont.)

<u>PHYSICAL SOLVENT TYPE</u>								
7. Sulfinol	Sulfolane + Diisopropanoamine	Organic solvent	25 to 50	99	H_2S + COS ~100	Low Pressure or With Steam	H_2S Also absorbs COS, SC_2 and mercaptans	As H_2S gas
8. Selexol	Polyethylene Glycol ether	Organic solvent	-7 to 27	99	H_2S + COS ~100		H_2S also absorbs COS	As H_2S gas
9. Rectisol	Methanol	Organic solvent	< -18	99	~100		H_2S	
<u>DIRECT CONVERSION</u>								
10. Stretford	Na_2CO_3 + anthraquin	Alkaline solution	-	99.9	~10		H_2S	Elemental Sulfur
11. Townsend	Triethylene glycol	Aqueous solution	65 to 120	99.9	~10		H_2S	Elemental Sulfur
<u>DRYBED TYPE</u>								
12. Iron Sponge	Hydrated Fe_2O_3	Fixed bed	20 to 40	99	H_2S + COS ~100		H_2S and also towards COS, and mercaptans	Elemental Sulfur

---

All processes are commercial.

percent can be achieved, but at temperatures well below 120°C for the Townsend and approaching ambient for the Stretford. The particular merits of these processes are the low sulfur levels attainable, 10 ppm as H_2S, and the recovery of the sulfur in elemental form. A dry bed process is the commercial iron sponge (hydrated Fe_3O_4) process which is operable below 40°C and achieves about 99 percent sulfur removal, but attaining only about 100 ppm H_2S. Sulfur recovery in the elemental form is claimed but not commonly practical.

The <u>Dry Bed</u> process at low temperature consists primarily of an iron sponge used at 20 to 40°C to remove H_2S and COS. This sorbent is not capable of reduction of sulfur levels much below 100ppm and is not regenerable.

Lorton (1980) recently evaluated sulfur removal processes for advanced fuel cell systems and selected the Selexol, Benfield, Sulfinol and Rectisol processes for detailed technical and economic comparison. In this study, two raw gas compositions based on oxygen-blown and air-blown Texaco gasification were used. The bulk of the sulfur was removed, leaving small amounts (1 or 25 ppm as H_2S) in the gas. The visualized process consisted of the sulfur removal unit, sulfur polishing unit (zinc oxide bed), sulfur recovery/tail gas cleanup unit and, where applicable, a catalytic COS hydrolysis pretreatment unit. Permissible environmental emissions corresponding to a range of 0.01 to 0.05 lb. SO_2 per MBTU were achieved and the Selexol process with COS prehydrolysis at 480°C and the Rectisol-II process (under development) were found to be the most promising of the four processes considered.

B. High Temperature Processes

The cleanup of sulfur from fossil fuel gases and flue gases using dry scrubbing over solid sorbents has been studied extensively. In fuel gas desulfurization, principal attention has been given to mid-temperature (>200^{o}C) physical adsorption of H_2S, COS and organic sulfur compounds, such as mercaptans and thiophenes, on carbon (Dietz, 1948) and on zeolites (Milton 1959; Breck 1964; Haynes, 1964; Turnock, 1971, 1973; Collins, 1972; Rosynek, 1976). Higher temperature adsorption processes on various metal loaded sorbents for fuel gas desulfurization have also been studied (Grindley, 1982; Meissner, 1976; Reeve, 1958; Bureau, 1967; Schultz, 1970; Oldaker, 1975, 1976; Joshi, 1977; Agrawal, 1980; Steiner, 1977; Wheelock, 1976, 1977; Gutman, 1969; Onursal, 1979; Huff, 1936; Nachod, 1948) but to a lesser degree of understanding. Adsorption processes attaining commercial scale development for fuel desulfurization consist of the Calgon process employing metal oxide impregnated carbon (Calgon, 1978) and the processes of Haynes (1961, 1964) and Linde (Milton, 1939, 1964; Breck, 1964; Collins, 1972; Turnock, 1971, 1973) using zeolites. These processes primarily involved physical adsorption of the sulfur component as opposed to a chemical sulfiding reaction.

The technology for the hot desulfurization of coal fuel gases (>500^{o}C) is less advanced than for flue gas cleanup applications, but there are several useful recent contract reports (TRW, 1979; Onursal, 1979; Curran, 1977; Blecher, 1980; Lorton, 1980; Vidt, 1981) of which one (Onursal, 1979) gives a general discussion of hot fuel gas desulfurization processes. Two other studies (Curran, 1977; Blecher, 1980) cover hot coal gas cleanup technology (TRW, 1979; Vidt, 1981) applicable to powerplants in general. Three studies (Moore,1977; TRW, 1979; Vidt, 1981) specifically address sulfur removal from coal gases for integration with advanced fuel cell systems. A summary, collected from the contract and patent literature, of the state of the art of process technology on the hot desulfurization of coal gases relevant to cleanup of low and intermediate BTU gases is presented in Tables 4 and 5. The summary covers the type of sulfur removal agent, applicable temperature range for desulfurization, mode of regeneration, state of development of the process, principal known disadvantages, sponsor of research, and literature source.

The three general types of desulfurization agents consist of dolomites, molten salts, and metal/metal oxide. Physical configurations consist of fixed bed, fluidized bed and melt. The examples cited in Tables 4 and 5 are representative of the principal types of systems studied.

1. Dolomite Processes

There are several dolomite processes which have been evaluated: the OCR/Air Products and Chemicals/Morgantown Energy Research Center (MERC) (O'Brien, 1976), Conoco (Curran, 1977), Westinghouse (Lemezis, 1975), and United States Steel (Feinman, 1980). Among these systems, the Conoco process appears to have reached the most advanced stage of development, i.e., pilot plant scale. The other processes do not appear to be under investigation at the present time. In the Conoco process effluent sulfur levels of the order of 200-300 ppm H_2S are achieved at 900°C in fluidized bed configuration of half calcined dolomite ($CaCO_3/MgO$). Regeneration of the sulfide sorbent is conducted with carbon dioxide/steam mixtures around 700°C. Disadvantages of the dolomite system include the need for very high temperatures, insufficient sulfur removal, relatively poor sulfidation and regeneration kinetics inferior to iron oxides, sorbent attrition in the fluidized-bed, and accumulation of unregenerated ash ($CaSO_4$).

Table 4. Hot Gas Desulfurization of Coal Syn Gas -- Status Summary

Process	Agent	Desulfurization		Regeneration		State of Development	Disadvantages	R&D Sponsor	References
		Temp. °C	Attainable H_2S Conc. ppm	Temp. °C	Agent				
Dolomite									
Calcined dolomite	CaO-MgO	870-930	600	600-650	CO_2/steam	Bench scale; no current work	Rapid coking; sorbent degradation; reactor corrosion	OCR, Air Products & Chemicals and MERC (MERT)	OBrien, 1976
Conoco half calcined dolomite	$CaCO_3$-MgO	900	200-300	700	CO_2/steam	Bench scale; pilot plant; no current work?	Sulfidation kinetics inferior to FeO_x; poor regenerability	Conoco	Onursal, 1979
Westinghouse dolomite	$CaCO_3$-MgO	815-925	<600	800	Air	Bench scale; pilot plant; no current work	Creates excessive non-regenerated ash ($CaSO_4$/MgO)	Westinghouse R&D	Lemezis 1975
U.S. Steel dolomite	CaO-MgO	1000	<65	Proprietary; produces H_2S		Bench scale Current work?	Produces hydrated unregenerated dolomite ash	U.S. Steel R&D	Feinman, 1980
Molten Metals/Salts									
Battelle molten salt	Li, Na, K, Ca, Carbonate	850-1000	<40	Complex aq. chem. via carbonation with H_2S to Claus		Bench scale?	Complex regen., salt carry over and corrosion	Battelle-Northwest	Moore, 1975,1977 Cover,1973
IGT Meissner	Pb	330-1200	---	>330	Electrolysis	Bench scale expts; current work	Corrosion; Pb volatilization	IGT Meissner	Meissner 1976

Table 5. Hot Gas Desulfurization of Coal Syn Gas -- Status Summary   Metal/Metal Oxides

Process	Agent	Desulfurization		Regeneration		State of Development	Disadvantages	R&D Sponsor	References
		Temp. °C	Attainable H_2S Conc. ppm	Temp. °C	Agent				
Appleby-Frodingham	Iron oxide granules	355-420	150	600-800	Air	Prototype tests? abandoned	Sorbent attrition and pipe corrosion	Appleby-Frodingham Steel Company	Reeve, 1953 Bureen, 1967
METC	Iron oxide silica	400-750	200-800	950	Air/steam	Bench scale; pilot plant; commercial design	High effluent S; sorbent vulnerable to degradation	METC and Air Products	Shultz, 1970 Oldaiget, 1975, 1976 Soshi, 1977
Catalysts and Chemicals	ZnO	150-650	---	Not evaluated		Bench scale expts. terminated	Not effective above 650°C	Catalysts and Chemicals	Gutmen, 1969
IFP ZnO	ZnO on support	400-600	10	600-900	Air?	Bench scale current work?	Information unavailable	Institut Francais du Petrole	Onursal, 1979
METC Zinc ferrite-ZnO	Zn ferrite-ZnO-binder carrier	400-650	10	to 650	Air/steam	Bench scale current work	Requires good regen. temp. control -sorbent life undetermined	METC/DOE	Grindley, 1982 1983
Exxon	$La_2O_3-Al_2O_3$	150-930	---	150-930	Air/steam	Bench scale expts. terminated	Proprietary	Exxon	Wheelock, 1976 Wheelock, 1977
Foster-Wheeler	Ni support	540-790	---	540-790	Air	Bench scale expts. terminated	Not published	Foster-Wheeler	Steiner, 1977
Johns Hopkins	Cu/Cr/V	350-820	---	---	Air	Bench scale expts. terminated	Failure to sustain sulfur removal capacity	Johns Hopkins U. and gas companies	Huff, 1936
Atlantic Refining	Cu/Pb/Zn aluminosilicate	90-540	---	370-540	Air/steam	Bench scale expts. terminated	Low removal efficiency	Atlantic Refining	Nachod, 1948
Kennecott	Cu/CuO/$Cu(OH)_2$	480-500	---	820	Air	Terminated	Difficult regeneration	Kennecott	Meyer, 1978 Agrawal, 1980
Esso	Cu/SiO_2	300-980	---	400-740	Cu_2O	Bench scale expts. terminated	Temp. control requires circulation	Esso	Lewis, 1963

2. Molten Salt Processes

The principal molten salt process that has been evaluated for hot fuel gas desulfurization is the molten carbonate eutectic of lithium, sodium and potassium (Moore, 1975, 1977) with about 17 weight percent $CaCO_3$ added. Effluent sulfur levels of 40 ppm H_2S are attained in the operating range of 850 to 1000^oC. Regeneration is achieved via a complex aqueous chemical route involving carbonation and displacement of the sulfur as H_2S. Problems with this process, in addition to the complex regeneration route, are ash accumulation in the melt, carry-over of melt components into the piping, and severe materials corrosion. Battelle Northwest Research Laboratories (Moore, 1975, 1976) have carried out the most recent work on this process, whereas workers at M. W. Kellogg (Cover, 1973) and Rockwell (Botts, 1976) have made early contributions to the technology. An additional melt system examined for coal desulfurization involves molten lead at 327-1000^oC (Meissner, 1976).

3. Metal/Metal Oxide Processes

The principal metal/metal oxide hot gas desulfurization sorbents considered for coal gas cleanup have been iron oxides (Reeve, 1958; Bureau, 1967; Schultz, 1970; Oldaker, 1973, 1976; Joshi, 1977), copper/copper oxides (Huff, 1936; Nachod, 1948;Lewis 1963; Meyer, 1978; Agrawal, 1980), supported nickel (Steiner, 1977; Setzer, 1969), a supported copper/chromium/vanadium sorbent (Huff, 1936), supported copper/lead/zinc (Nachod, 1948), supported La_2O_3 (Wheelock, 1976, 1977), zinc oxide (Gutman, 1969) and a zinc ferrite/zinc oxide sorbent (Grindley, 1982) shown in Table 5. Among these iron oxide, zinc oxide, and copper based systems have been of most interest.

a. Iron Oxide Processes

An iron oxide process, the Appleby-Frodingham (Reeve, 1958;

Bureau, 1967), demonstrated excessive sorbent degradation and has been abandoned for economic reasons. The METC iron oxide/silica (fly ash) sorbent (Schultz, 1970; Joshi, 1977) is the most advanced of the regenerable fixed bed systems. This process will achieve 200-800 ppm H_2S in the effluent coal gases at temperatures in the range of 400 to 750^{o}C. Regeneration is achieved at 950^{o}C in air or air/steam. This process has been evaluated up through pilot plant stage and commercial process design.

b. Zinc Oxide Based Processes

Two sorbents used in this category are supported ZnO (Onursal, 1979) and a mixed oxide --iron oxide and zinc oxide reacted to form zinc ferrite (Grindley, 1982). The supported zinc oxide is under investigation by the Institut Francais du Petrole (IFP), where low effluent H_2S concentration has been claimed. However, according to the best available information (unpublished), the development to date, has not advanced past bench scale. Evaluations of the IFP zinc oxide at METC (Steinfeld, 1982) show that it was capable of removing H_2S to about 10 ppm but with low sulfur capacity relative to Harshaw zinc oxide. Its regenerability was determined to be good, and no loss of surface area was detected after three sulfidation/regeneration cycles. The second sorbent, an extrudate of zinc ferrite with a binder, is currently undergoing bench scale evaluation at METC (Grindley, 1982). They report sulfur removal to levels of about 5 ppm H_2S. Since iron oxide is not capable of sulfur removal to this level, the zinc oxide is believed to be the dominant desulfurization agent. The zinc ferrite process has been shown to have improved sulfur capacity over zinc oxide, but with the penalty of exit stream purity. This can be explained by postulating that under the desulfurizing conditions zinc ferrite merely acts as a physical mixture of zinc oxide and iron oxide with the latter acting as a high sulfur capacity constituent but a diluent for low level sulfur removal by ZnO. The effect of zinc oxide concentration on sulfur removal ability is shown in Figure 2 (taken from Steinfeld, 1982). As shown in Figure 3 (also taken from Steinfeld, 1982), zinc oxide can reduce the H_2S concentration to 2 ppm but zinc ferrite at the same conditions (1000°F with 27.66 percent steam) cannot reduce H_2S levels below 5 ppm which is above the acceptable concentration for the molten carbonate fuel cells. Furthermore, judging from Figures 2-18, 2-19 and 2-20 of the Steinfeld, 1982 reference, regenerability of zinc ferrite at 1000-1200°F (538-649°C) is poor.

c. Copper Based Processes

The earlier studies involving copper sorbents (Huff, 1936; Nachod, 1948; Lewis 1963; Meyer, 1978; Agrawal, 1980) are of interest because of their relevance to the current work reported in this paper. Desulfurization was examined for the copper sorbents in question (Table 5) at temperatures up to 980°C. The most effective regeneration was conducted by solid-solid reaction between Cu_2S and CuO. The principal disadvantages of these copper sorbents were difficult regeneration and failure to sustain desulfurization capacity after regeneration. These studies have been terminated. Results of these studies are examined in some detail below.

About the earliest significant effort to evaluate copper sorbents for hot gas desulfurization was that conducted at Johns Hopkins University (Huff, 1936). The sorbents prepared were mixed oxides of copper with iron, uranium, chromium, tin, manganese, vanadium, molybdenum, antimony and bismuth as binary and ternary combinations with various binder components such as clay, pumice, alundum and lime. Bench scale desulfurization experiments were conducted with "blue gas" and carbureted water gas containing 1600 ppm H_2S and 100 ppm organic sulfur compounds over the temperature range of 350 to 816°C.

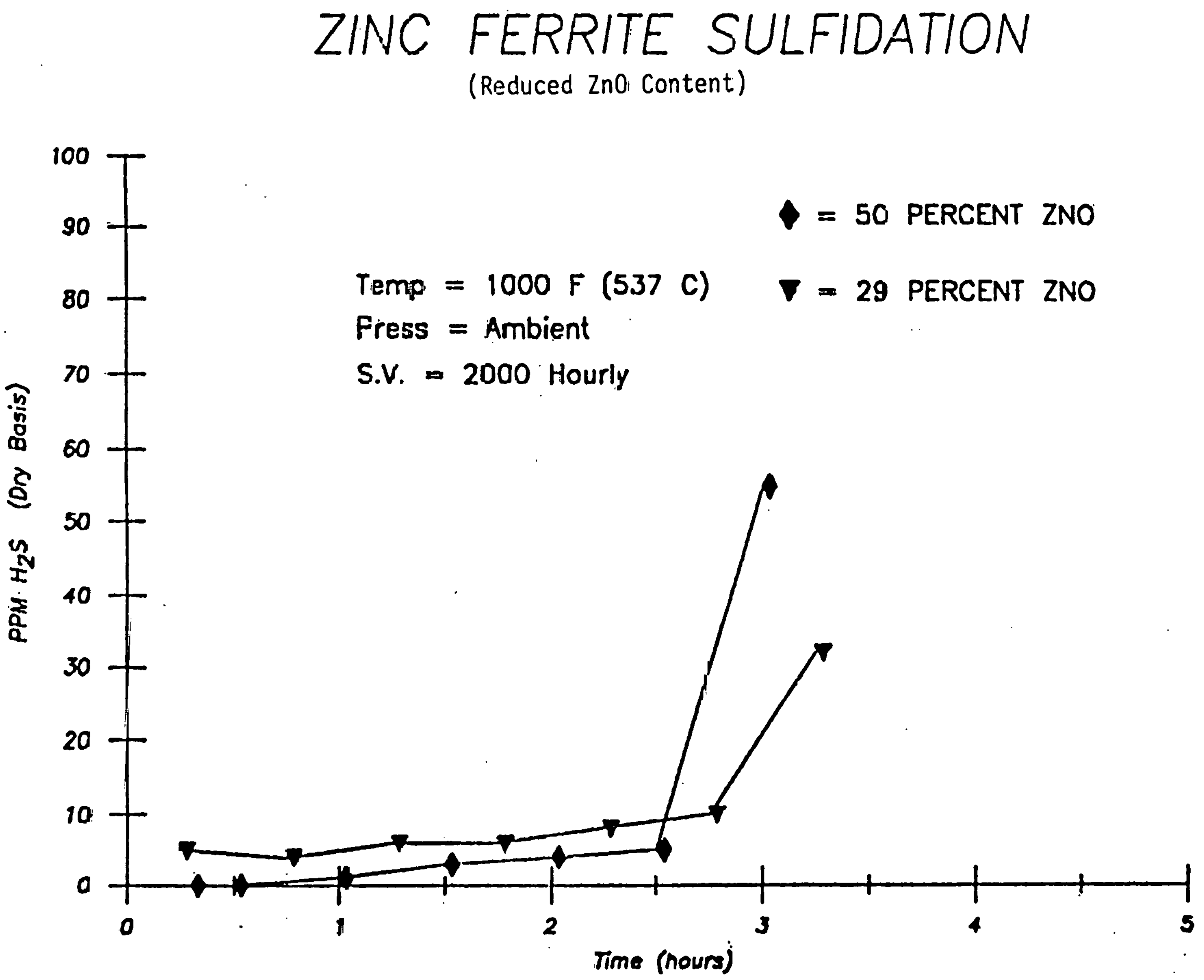

ZINC FERRITE SULFIDATION
(Reduced ZnO Content)
♦ = 50 PERCENT ZNO
▼ = 29 PERCENT ZNO
Temp = 1000 F (537 C)
Press = Ambient
S.V. = 2000 Hourly
PPM H_2S (Dry Basis)
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
Time (hours)

Figure 2

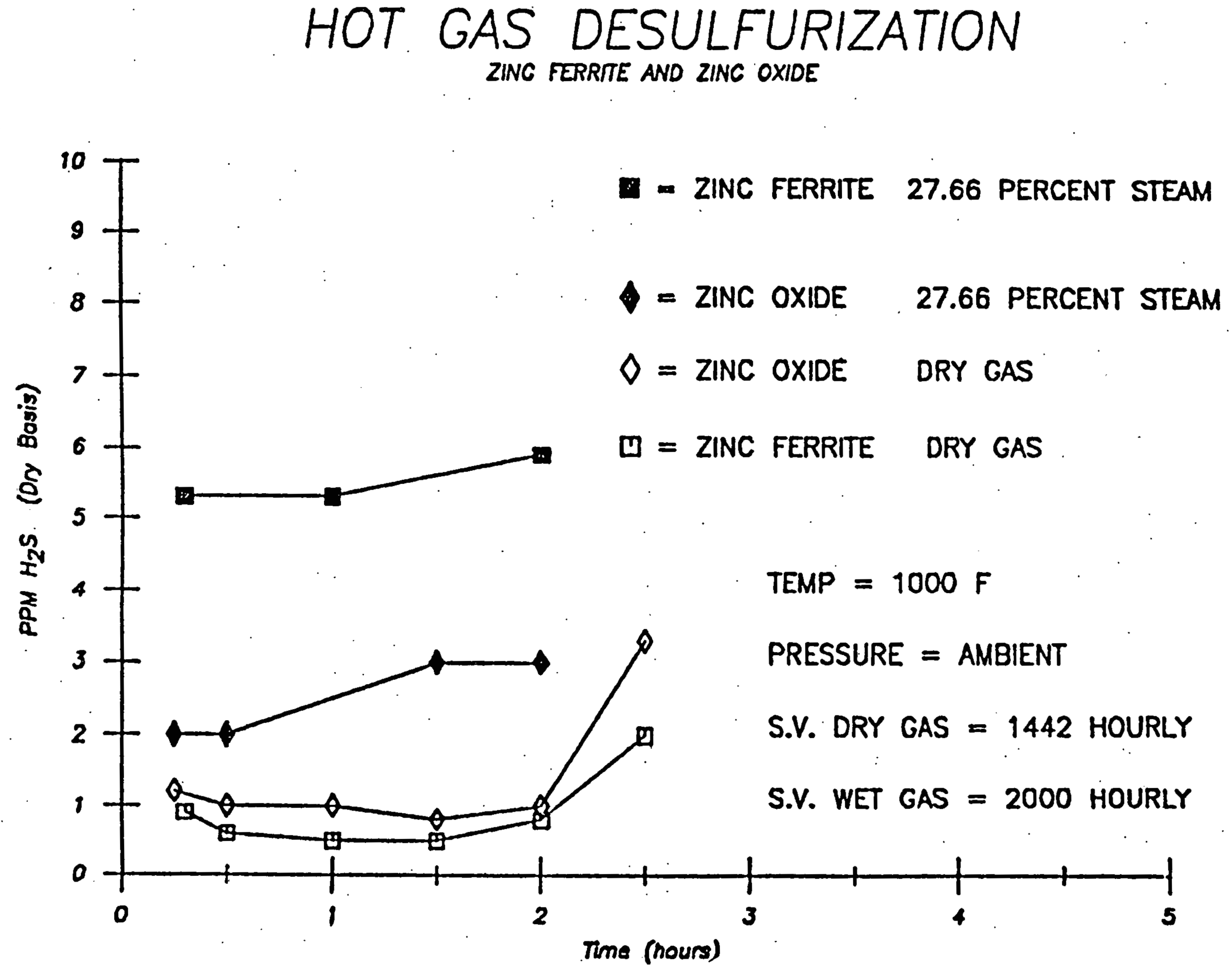

HOT GAS DESULFURIZATION
ZINC FERRITE AND ZINC OXIDE
■ = ZINC FERRITE 27.66 PERCENT STEAM
◆ = ZINC OXIDE 27.66 PERCENT STEAM
◇ = ZINC OXIDE DRY GAS
□ = ZINC FERRITE DRY GAS
TEMP = 1000 F
PRESSURE = AMBIENT
S.V. DRY GAS = 1442 HOURLY
S.V. WET GAS = 2000 HOURLY
PPM H_2S (Dry Basis)
0
1
2
3
4
5
6
7
8
9
10
Time (hours)
0
1
2
3
4
5

Figure 3

Copper was considered the most efficient agent for H_2S removal, with chromium and uranium largely responsible for removal of organic sulfur compounds. Addition of steam was considered to enhance the removal efficiency of organic sulfur compounds. The most effective desulfurization temperature range was 450 - 550°C. One of the most promising mixed oxide sorbents had a composition of 24 wt% copper and 6 wt% vanadium as metals with the remainder a clay binder. Regeneration of the sulfided sorbents was conducted with air oxidation. Some large scale plant tests were also conducted with these sorbents. High initial sulfur removals in excess of 97% were obtained with some of these sorbents, but removal efficiency declined with repeated desulfurization/regeneration duty cycles. This degradation of desulfurization capacity was attributed to deactivation of the copper by reaction with the binders.

The next significant use of copper in hot sulfur removal sorbents was that of Nachod, et al. (1948) in which heavy metals, such as copper, zinc and lead, supported on aluminosilicates were used to remove sulfur from petroleum distillates and gases containing inorganic (H_2S) and organic sulfur compounds in the temperature range 90 to 540°C. Sulfided sorbents were regenerated with air/steam mixtures at 370 - 540°C. The active metals (Cu, Zn, and Pb) introduced as acetate salts were considered to be bound to the aluminosilicate supports as exchange cations replacing the sodium and potassium initially present on the aluminate and silicate support precursors. Unfortunately, the aluminosilicates formulated were very inferior to the hydrothermally stable zeolites currently available. The maximum sulfur removal efficiencies reported were of the order of 43%. Publication of results was limited to a patent (Nachod, 1948).

A subsequent study of copper sorbents is that of Lewis (1963) who used copper supported on silica to desulfurize H_2S/H_2 gas mixtures over the temperature range 300 - 1000°C. Ultimate application was intended for coke oven gas, producer gas, water gas and hydrocarbon gases. The Cu/SiO_2 sorbents containing 2-20 wt% Cu were prepared by solution impregnation. The desulfurization evaluation tests were conducted with concentrations of H_2S of 1-1.5% in hydrogen with the sorbent in fluidized bed or stirred gas/solid reactors. Sulfided sorbents were regenerated by oxidation with air or Cu_2O in the temperature range 400 - 700°C. Metallic copper was considered the preferred sulfur removal agent and efforts were made during regeneration to limit the oxygen concentration so that the regeneration of the sulfided copper produced primarily metallic copper and SO_2. This regeneration mode led to production of high purity SO_2 and a sorbent consisting of 90 wt% Cu and 10 wt% Cu_2S with negligible Cu_2O. Sulfur removal efficiencies of 98.5% (from 1.5 percent to 225 ppm) were realized in bench scale tests in what was considered the optimum desulfurization temperature range (350 to 600°C), with removal efficiencies declining to 80-95% in the higher temperature range of 600 - 930°C. Information about that process is available only from the patent literature, and the reasons for termination of the work are not known.

The most recent study since that of Lewis (1963) is the Kennecott copper process (Meyer, 1978; Agrawal, 1980) in 1978-80. Bench scale desulfurization tests were conducted with simulated Lurgi fuel gas containing H_2, CO and 1-1.5% H_2S over the temperature range 480 to 510°C. Four copper sorbents were evaluated. These consisted of copper metal, $Cu(OH)_2$, CuO and a copper chalcopyrite concentrate containing 24 wt% Cu, 21.5 wt% Fe and 26 wt% S in a fixed bed configuration with sand diluent. Sulfur removal efficiencies in excess of 90% (1.5% to 1500 ppm) were obtained. Sorbents were regenerated at 816°C in air to minimize copper sulfate formation. Although the high temperature yielded 99% regeneration, there was considerable sorbent degradation which diminished the efficiency of H_2S removal at the start of the next sulfur removal cycle. Work on this process was terminated in 1976 and available information is contained primarily from a contract report (Meyer, 1978) and in a preprint from a recent meeting (Agrawal, 1980) where a major problem identified was the hot-solid-transport for a solid-solid regeneration scheme.

III. DESULFURIZATION/REGENERATION REACTIONS

A. Desulfurization

The desulfurization reaction for hydrogen sulfide removal in a reducing atmosphere at temperatures much in excess of 400°C over metals and metal oxides is primarily sulfidation. For a metal oxide with invariant valence such as zinc the sulfidation reaction is: $ZnO + H_2S \longrightarrow ZnS + H_2O$. For metal oxides such as V_2O_5 or WO_3 which undergo reduction to a lower oxide, typical reactions consist of:

$$V_2O_3 + 3H_2S \rightarrow V_2S_3 + 3H_2O$$

and $$WO_2 + 2H_2S \rightarrow WS_2 + 2H_2O$$

The sulfides formed can be expected to vary substantially from the stoichiometry indicated by the above equations, notably for vanadium systems. Idealized stoichiometry has been assumed in the present work in the calculation of the reported mole percent conversions.

For the metal oxides of copper the expected sulfidation reactions are:

$$CuO + H_2S \rightarrow CuS + H_2O$$

or $$Cu_2O + H_2S \rightarrow Cu_2S + H_2O$$

and, since the oxides are readily reduced to the metallic state at temperature above 200°C:

$$2Cu + H_2S \rightarrow Cu_2S + H_2$$

At temperatures above 400°C, only Cu_2S is stable (Evans, 1959). The highest desulfurization capacity for the copper oxides result from conversion to metallic copper by reduction in hydrogen or in simulated coal gas prior to the sulfidation reaction with H_2S. Oxidized copper, if not prereduced, will be quickly reduced upon contact with the fuel gas.

B. Regeneration

Regeneration of the sulfided metals is most directly accomplished by direct oxidation with air to form the metal oxide with the conversion of the sulfur as sulfur dioxide. Typical reactions are:

$$ZnS + 1.5\ O_2 \rightarrow ZnO + SO_2$$

$$V_2S_3 + 5.5\ O_2 \rightarrow V_2O_5 + 3SO_2$$

$$Cu_2S + 2\ O_2 \rightarrow 2\ CuO + SO_2$$

Intermediate sulfur products from oxidation can be elemental sulfur or metal sulfates such as $ZnSO_4$, $ZnO \cdot 2\ ZnSO_4$, $CuO \cdot CuSO_4$ and $CuSO_4$. The production of elemental sulfur is minimal at temperatures above about 500°C in the presence of excess oxygen. The formation of the metal sulfate intermediate is negligible in the case of the vanadium for which the sulfates are unstable above about 400°C. The zinc and copper sulfates have relatively high decomposition temperatures and require low ambient SO_2 partial pressures to minimize the amount of the metal sulfates at temperatures in the range of 500-650°C. Zinc sulfate is reported to decompose thermally in the range of 600-750°C and requires an ambient SO_2 partial pressure below 10 ppm at 650°C to avoid persistence of $ZnSO_4$ (Mu, 1981). Based on our past work (Jalan, 1981) the regeneration process was found to be enhanced by using a combination of air and steam. The steam apparently facilitates the decomposition of metal sulfate formed during the oxidation of the sulfide by an intermediate hydrolysis. The postulated reactions, in the presence of oxygen, are:

$$ZnSO_4 + H_2O \rightarrow Zn(OH)_2 + SO_3$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

Copper sulfate is reported to decompose thermally in a range of 570-705°C and requires similar low ambient SO_2 partial pressure to avoid persistence of $CuSO_4$ (Mu, 1981). For copper oxide on alumina system, copper sulfate is observed to form even at low SO_2 partial pressures and at low temperatures such as 450°C (McCrea, 1971). One regeneration alternative for facilitating sulfate decomposition if formed, is to complete the process in an inert gas such as nitrogen at 750°C after the bulk of the sulfur has been removed as SO_2 by air oxidation. Another regeneration alternative for copper sorbents is the use of low oxygen partial pressure in the initial regeneration of CU_2S by the reaction:

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

Another regeneration mode is reduction of the residual metal sulfates

$$CuSO_4 + 2H_2 \rightarrow Cu + SO_2 + 2H_2O$$

This type of regeneration mode has been proposed for the regeneration of supported copper sorbents used for SO_2 removal from flue gases (McCrea, 1971). Direct hydrogen reduction of metal sulfides, such as Cu_2S, as a regeneration mode is:

$$Cu_2S + H_2 \rightarrow 2Cu + H_2S$$

This would be an attractive mode since hydrogen sulfide can be thermally dissociated to yield elemental sulfur at temperatures above 400°C and has been studied over copper and other transition metals (Wilson, 1974; Chivers, 1980). While the bulk of the sulfur can be displaced as H_2S by hot reduction, the formation of metal subsulfides can be expected to persist down to extremely low H_2S partial pressures.

IV. CURRENT PROGRAM-GINER, INC.-1981-1983

Work has been conducted during the past two years to identify and evaluate which metal/metal oxide systems are most appropriate as hot regenerable sorbents for advanced fuel cell systems capable of reducing the sulfur content of coal gases to 1 ppm. This program was undertaken in as much as certain metal/metal oxide sorbents provide promising potential for the molten carbonate fuel cell, owing to: (1) the low levels of sulfur attainable, (2) the high capacity for sulfur removal, (3) regenerability, (4) maintenance of sulfur removal capacity during desulfurization/regeneration duty cycles, (5) capacity for removal of organic as well as inorganic sulfur compounds, (6) compatibility with fuel gas components, (7) economic utilization of fuel gas heat content, and (8) economies in plant capital and operating costs.

Desulfurization sorbents evaluated under the Giner, Inc. program have consisted of: unsupported ZnO and CuO; CuO, ZnO, and CuO/ZnO on supports (silica, alumina and zeolite); mixed CuO/ZnO and V_2O_5 (unsupported and on alumina); and a proprietary sorbent (United Catalyst C125, which subsequently was found to contain calcium oxide and was dropped from further study). Both fixed-bed and fluidized-bed reactor configurations have been used in these studies. The parameters evaluated were: (1) the nature of the support, (2) sorbent particle size, (3) water partial pressure, (4) desulfurization temperature, (5) regeneration mode, desulfurization of inorganic (H_2S) and, (6) organic (COS, CS_2 and CH_3SH) sulfur compounds and (7) interferences from reactor materials (stainless steel vs. quartz).

Sorbent characterization has been conducted for CuO/ZnO and supported CuO sorbents with EDAX, SEM, XRD, and gas adsorption, mercury porosimetry and chemical analysis to evaluate surface structural changes accompanying prereduction, desulfurization and regeneration. Data treatments consisted of modeling for fixed-bed reactors and fluidized-bed reactor parameter evaluation, notably particle size effects.

The evaluation program at Giner, Inc. for the period preceding 1981 (Jalan, 1981) demonstrated that the desulfurization agents such as CuO (reduced to Cu), V_2O_5 (reduced to V_2O_3) and mixed oxide CuO/ZnO initially selected based on thermodynamic criteria merited further investigation as hot regenerable sorbents for second stage sulfur removal from coal gas feed stock for advanced fuel cells. In addition, it was established that desulfurization over supported sorbents offered significant improvements in the efficiency of sorbent utilization. Further evidence was obtained for the advantages of using air-steam gas mixtures in regeneration of sulfided sorbents.

A. Apparatus

All the experiments were carried out with a simulated coal gas mixture (25.8% H_2, 47.2% N_2, 15.5%CO_2, and 11.5%CO on dry basis) containing 200 ppm H_2S and varying amounts of water vapors unless otherwise specified. Although the aim was to reduce the H_2S levels to less than one ppm, the desulfurization runs were carried out until the exit H_2S concentration was measured to be above 10 ppm. The experiments were carried out in a fixed-bed and a fluidized-bed reactor as described below.

1. Fixed-Bed Reactor: The fixed-bed reactor (Fig. 4) used in the desulfurization performance tests has been described in the preceding contract reports (Jalan, 1981a,1981b). The only significant modification used with this reactor consisted of introduction of a quartz liner for certain tests to evaluate wall effects.

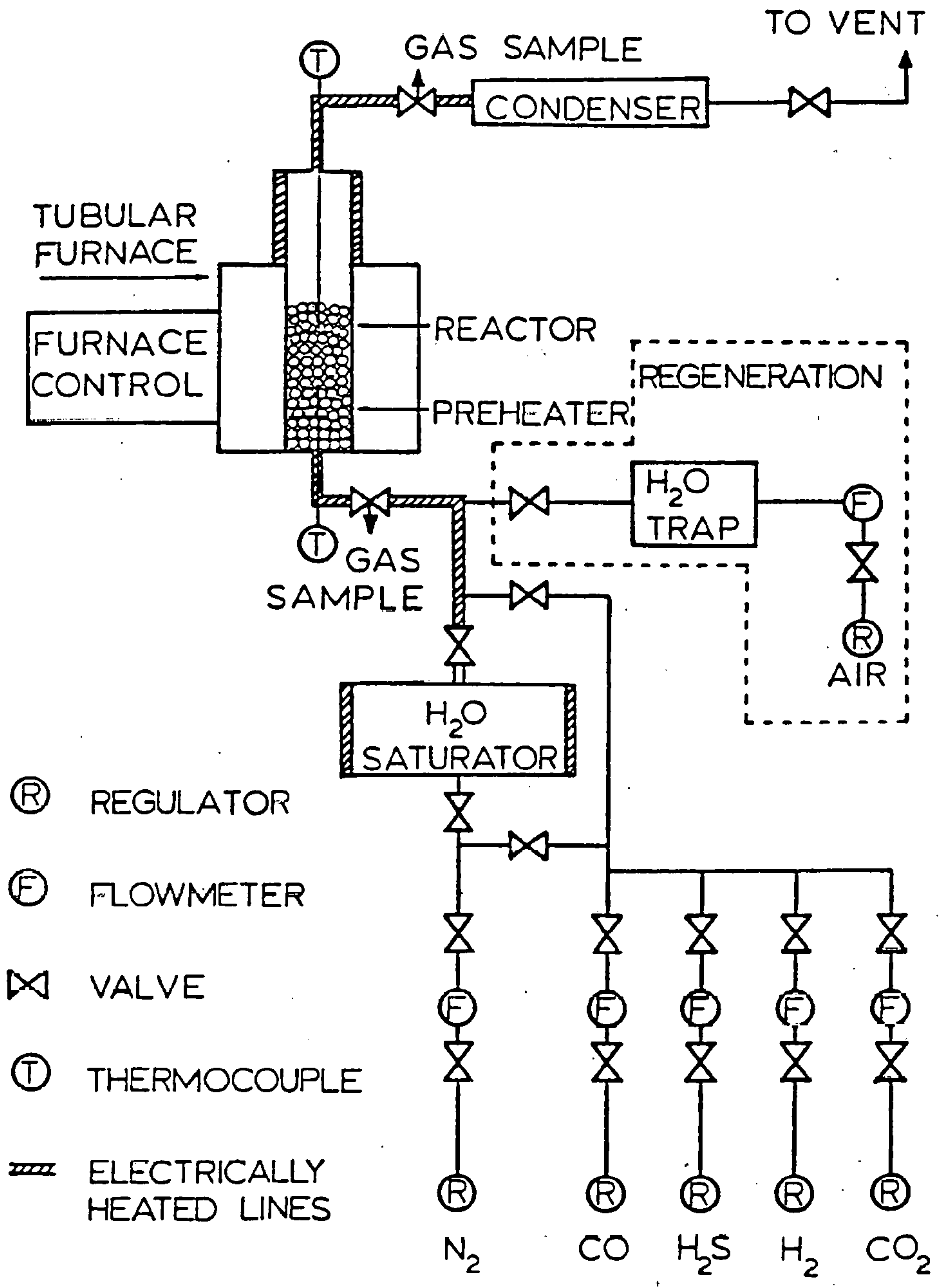


Figure 4. Experimental Fixed Bed Reactor for Desulfurization Studies

2. Fluidized Bed-Reactor: The fluidized-bed reactor used is shown in Figs. 5-7 and the design and initial evaluation tests are discussed below.

The design of the experimental fluidized-bed reactor and the envelope of operating conditions to be applied to it are motivated by several practical requirements:

- The reactor must be large enough to yield meaningful results in terms of scale-up and applicability to other systems, to the data produced from it and to the model developed to match that data.
- The total time required to perform each experiment should be limited to a single working day or at most overnight, a maximum of 20 hours.
- The conversion attained in the reactor should be greater than 99.5% in order to reduce the H_2S concentration from an inlet concentration of 200 ppm to 1 ppm.

Of these requirements, the first is the most difficult to quantify. A brief survey of the literature combined with past experience led us to define a minimum diameter of 3 cm for the reactor. Then, considering the scale of the present laboratory facility, and the costs of furnaces, a maximum diameter of 5 cm was chosen. On the basis of the first requirement listed above, the 5 cm diameter reactor was chosen as the foundation for our initial design calculations. This choice was later re-evaluated against the results of these calculations. Another factor on which the initial design study was based was to limit the L/D (length to diameter) ratio for the resting bed to no less than one. The effect of this choice was then evaluated in the design calculations. With these two dimensions of bed diameter and rest height established, the two parameters against which the second two requirements were applied were particle size and gas flow rate.

The fluidized-bed experiments were performed at minimum fluidizing

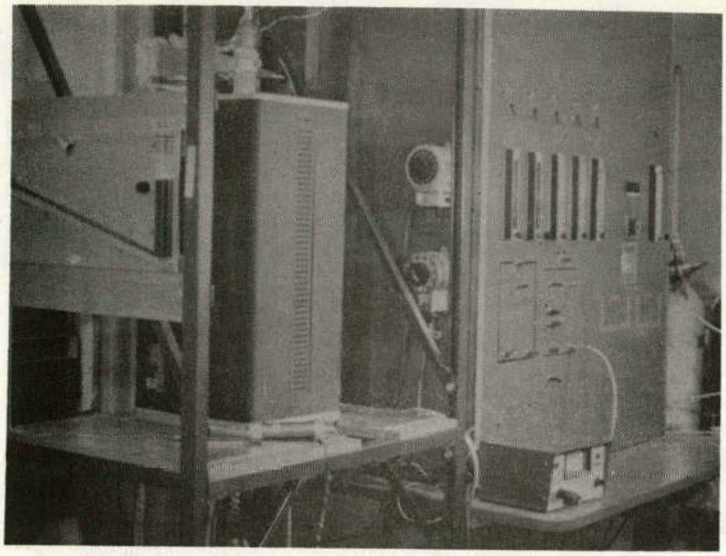


Figure 5. The Fluidized-bed Desulfurization Apparatus: Reactor (left) and Gas Mixing System (right)

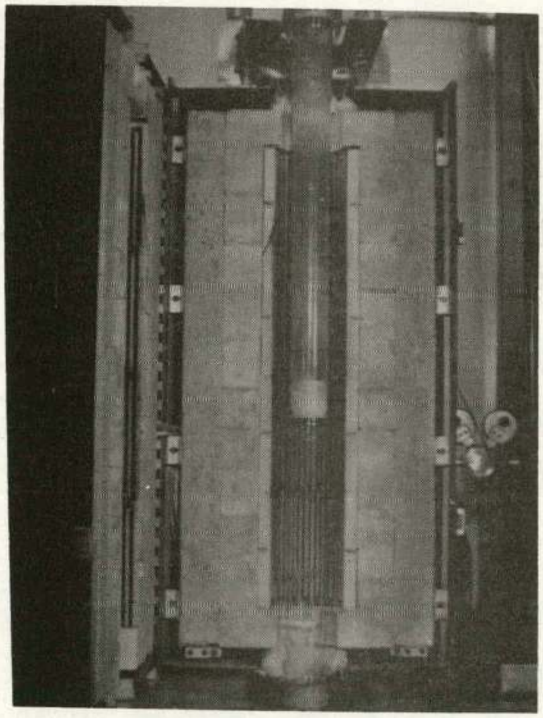


Figure 6. Close-up of the Quartz Reactor and Tube Furnace

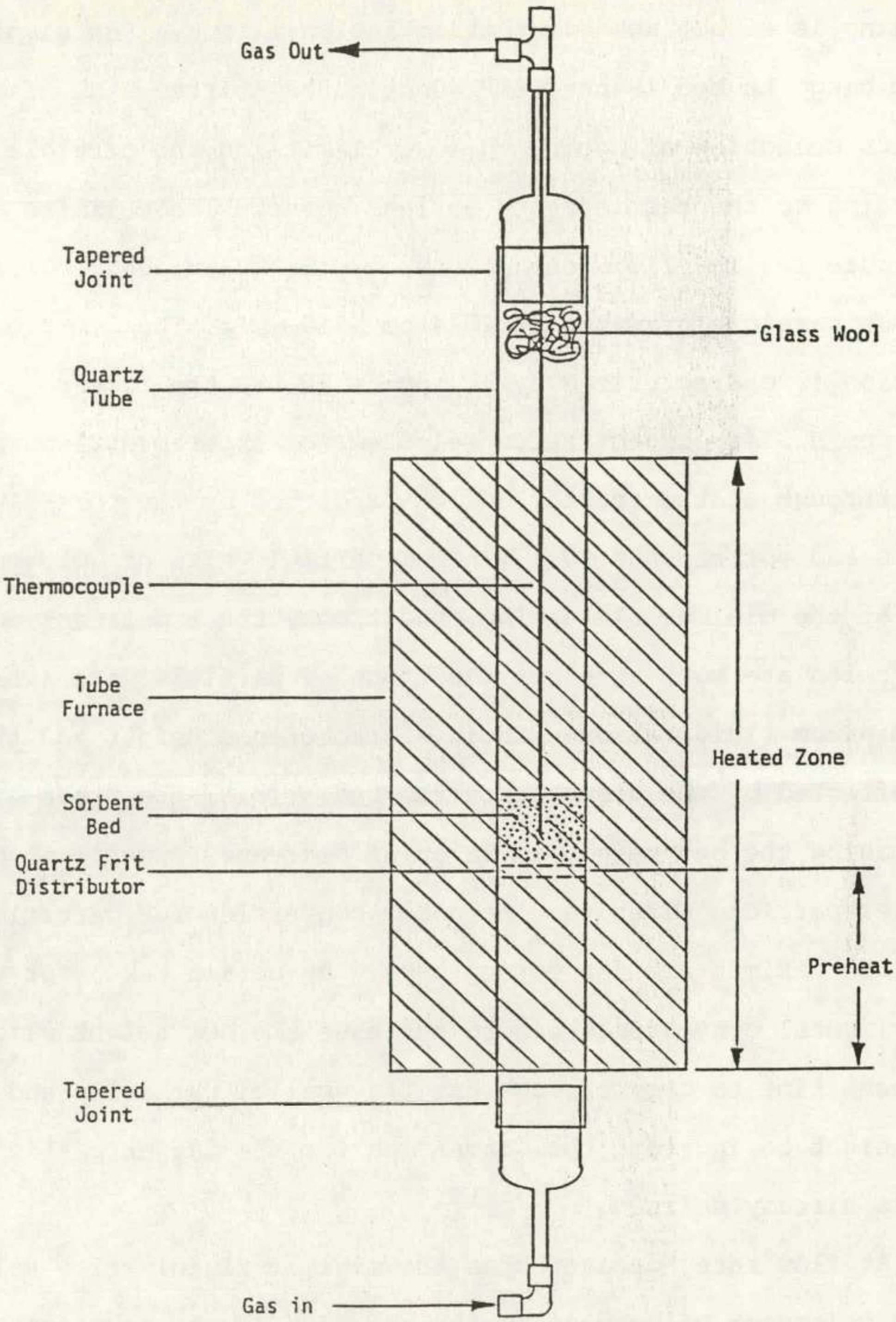


Figure 7. Fluidized Bed Reactor

conditions. The bed is most easily described under these conditions where bubbling is either non-existent or insignificant. The simplest model for describing the bed is the CSTR (Continuous Stirred Tank Reactor) which permits selection of upper and lower limits on the particle size used according to the requirements defined above. These limits are illustrated in Figure 8. The limit on conversion, $(C_o/C_i) = .005$, corresponds to a maximum particle diameter of .074 cm (740 μm). The limit on experimental duration is characterized by t_{10} ppm = 20 hr, the time required to reach a 10 ppm H_2S (a concentration selected for experimental purposes) breakthrough at the reactor outlet predicted by the pore-plugging and CSTR models and corresponds to a minimum particle size of .015 cm (150 μm).

At the minimum fluidizing conditions, the experiment duration and conversion are much stronger functions of particle size (which determines the minimum fluidization velocity) than of bed height and they are not at all affected by the diameter of the bed. Thus, the trade-offs of decreasing the bed-height in favor of decreased experiment duration for smaller particle sizes vs. increased conversion for particle sizes larger than the maximum are not strong ones. An option taken for the sake of experimental convenience was to decrease the bed height slightly to decrease time to breakthrough for the smaller particles and increase the bed height to increase the conversion for the larger particles within the limits already defined.

At flow rates greater than the minimum fluidization velocity, U_{mf}, the development of bubbles in the bed adds to the complexity of any model used to describe the system. Bubbles will shorten the contact and residence time distributions for a fraction of the gas flow and will reduce the overall conversion achieved by the reactor. Bubbles will also

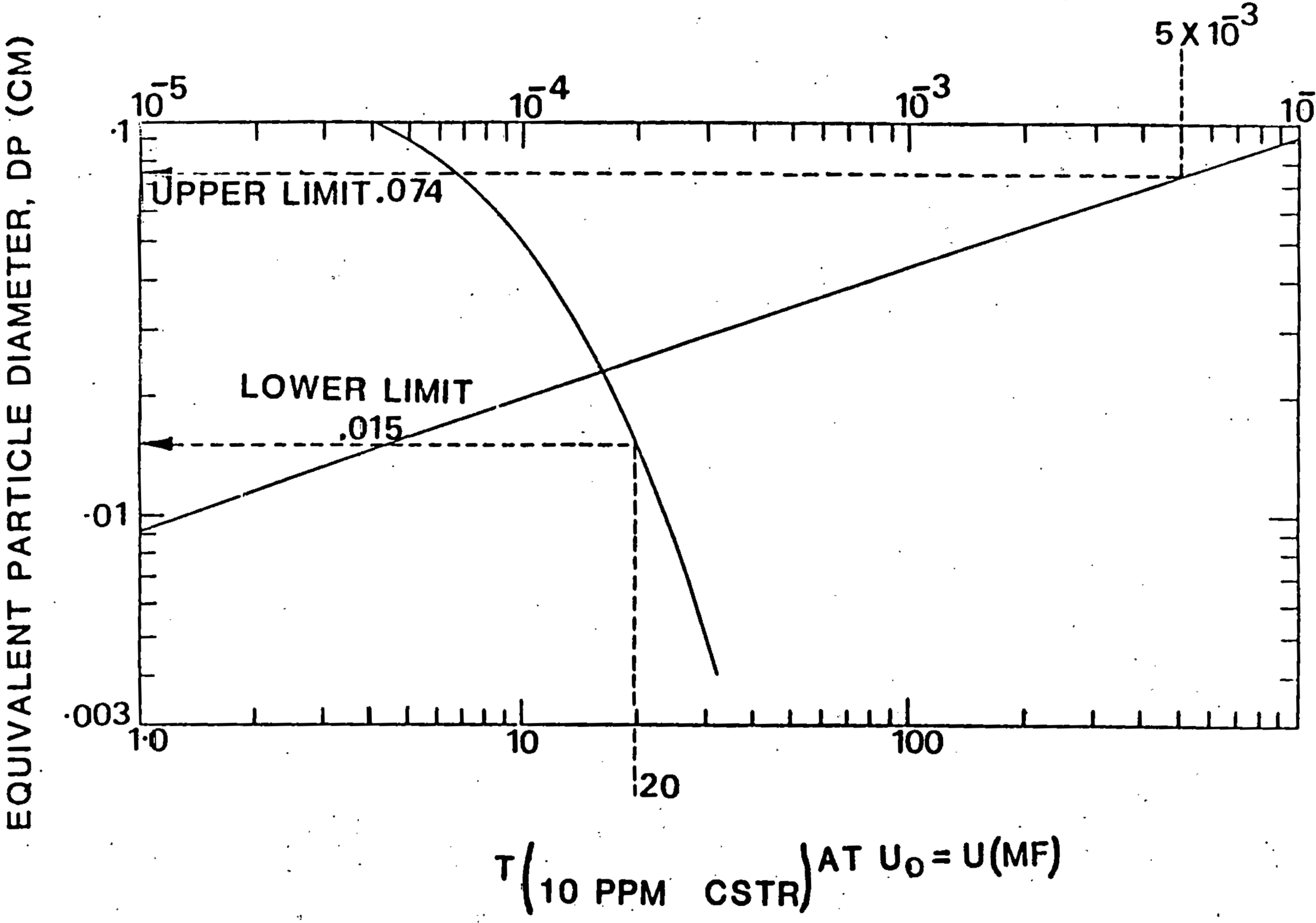


Figure 8. Location of Maximum and Minimum Particle Sizes at $U_o = U_{MF}$ and $H_{MF} = 5$ cm

increase the dispersion of the particles and a fraction of the gas which resides in the inter-particle or emulsion phase. Because of these complexities, the initial experiments were performed at conditions close to minimum fluidization -- conditions which should discriminate more clearly between different sorbent materials and different particle structures. Once a "best" sorbent and particle structure were defined at minimum fluidizing conditions, experiments were performed at higher flowrates, in a bubbling bed, in order to explore separately the "reactor effects" on the desulfurization process.

Fluidization tests established the characteristics of zeolite support material, Linde SK500, which had been crushed and sieved into four fractions according to particle size: -30/+ 50 mesh (600 μm to 300 μm), -50/+ 70 mesh (300 μm to 200 μm), -70/+ 100 mesh (200 μm to 150 μm), and -100/+140 mesh (150 μm to 100 μm). Samples of 100cc each were loaded into the reactor tube and tests were conducted both at room temperature and at elevated temperature (650^{O}C). Figures 9 and 10 show the pressure vs. flowrate curves for two different particle fractions at room temperature, -50/+70 mesh and -100/+ 140 mesh respectively. Both curves demonstrate the early pressure peak which is characteristic of fluidized systems and which represents the point at which the settled bed "unlocks" with the voidage increasing slightly accompanied by a decrease in pressure drop. The flowrate must then be increased slightly to establish fluidization after which the pressure drop increases slowly. The curve for the decreasing flowrate is used to determine the minimum fluidizing flowrate because the pressure peak associated with the bed "unlocking" phenomenon does not occur. The minimum fluidizing flowrate is found where the slope of the pressure drop curve changes. The observed minimum fluidization

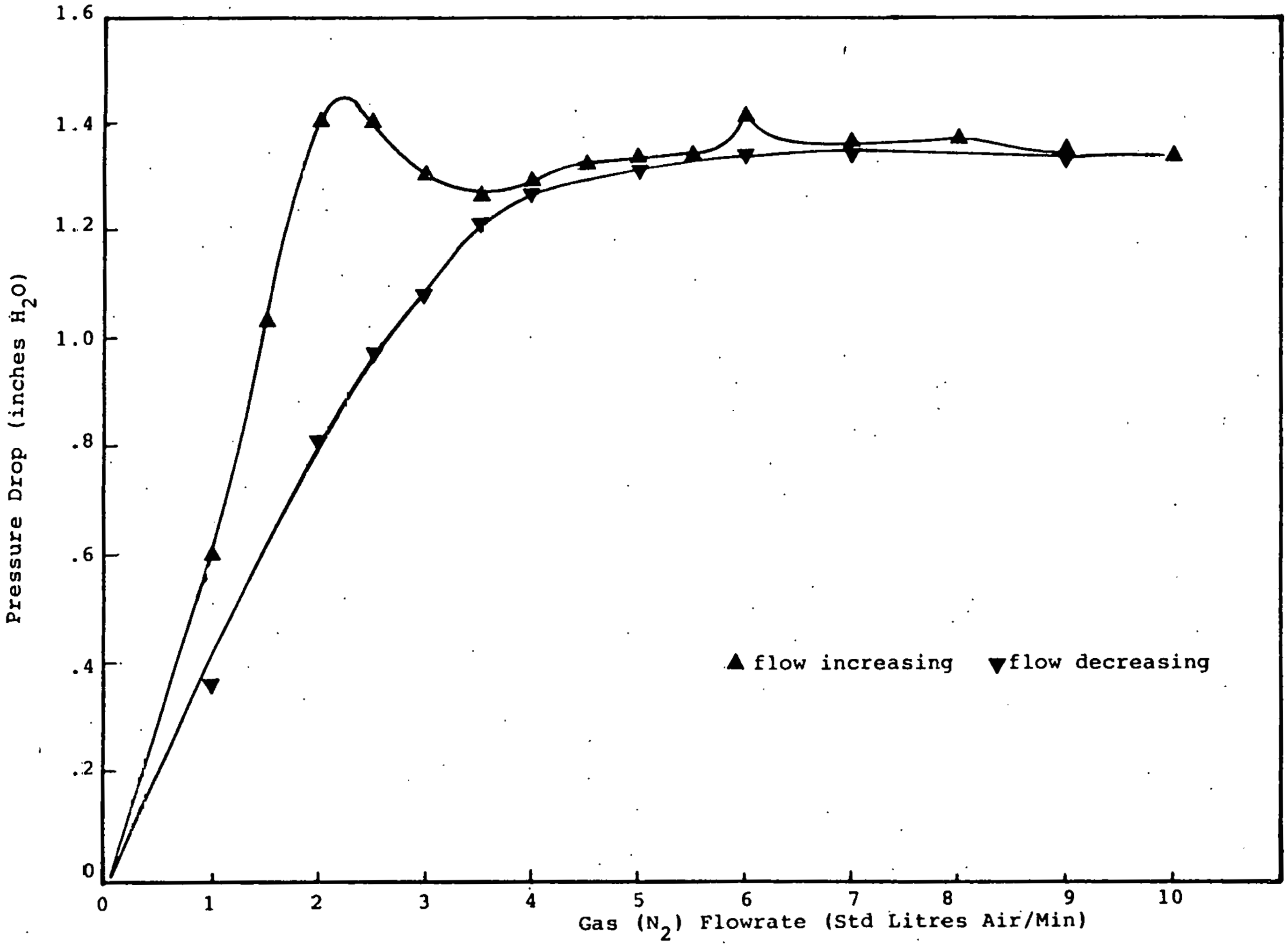


Figure 9. Sk 500, -50 + 70
Pressure Drop Across Bed vs. Flowrate

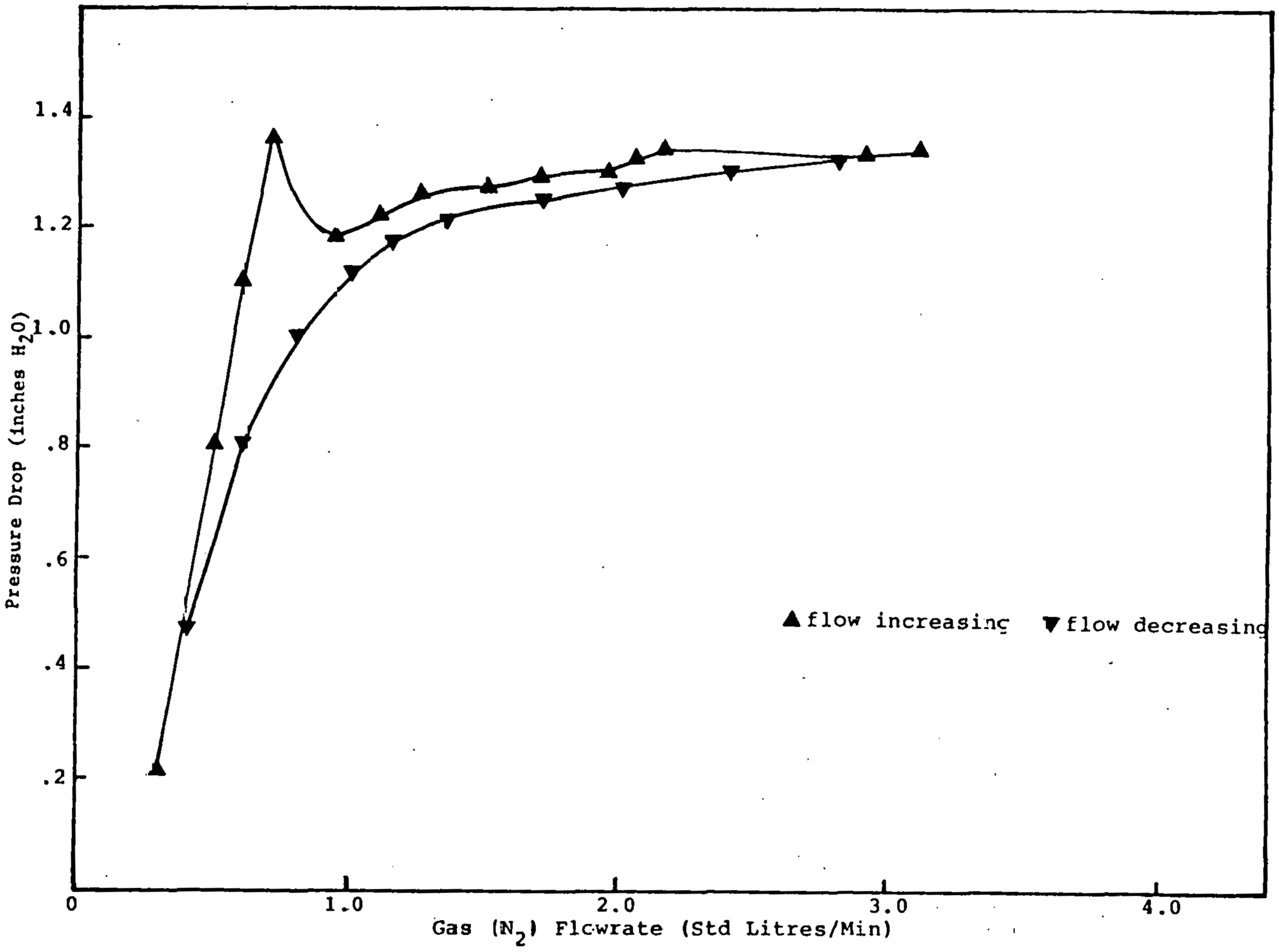


Figure 10. Sk 500, -100 + 140
Pressure Drop Across Bed vs. Flowrate

velocity compares well with values calculated from the Ergun equation which assumed a bed voidage of 0.50 and a particle sphericity of 0.80 (Figure 11). The bed expansion, too, correlates well with calculated values assuming the value $A_o = 0.01$ where A_o is the distributor plate area of the orifice (Figure 12).

At elevated temperatures, the fluidization behavior is altered somewhat from the behavior exhibited at room temperature. Figure 13 shows the pressure-drop vs. flowrate curves of -30/+ 50 mesh particle fraction at room temperature and 650°C. At higher temperature, the pressure drop increases faster initially and peaks earlier than at room temperature. The minimum fluidizing condition also occurs earlier at 650°C than at room temperature with minimum fluidizing velocities of 8.5 vs. 10.0 l/min., respectively.

B. Sorbent Selection

The elements receiving consideration to date have been selected largely on an empirical basis from essentially every group of the periodic table (Table 6). One effort to make a systematic examination of candidates for the hot desulfurization of low BTU fuel gases is that of Westmoreland and Harrison (1976). In their approach they made use of the free energy minimization method of Van Zeggeren and Story (1970) and resulted in a selection of 11 out of 28 elements considered. These potential candidates for fuel gas desulfurization within the temperature range of 400-1200°C were Fe, Zn, Mo, Mn, V, Ca, Sr, Ba, Co, Cu, and W. Based on thermodynamic considerations, Westmoreland and Harrison (1977) selected MnO, CuO, V_2O_3, and ZnO for kinetic studies and found MnO to have the most favorable kinetics.

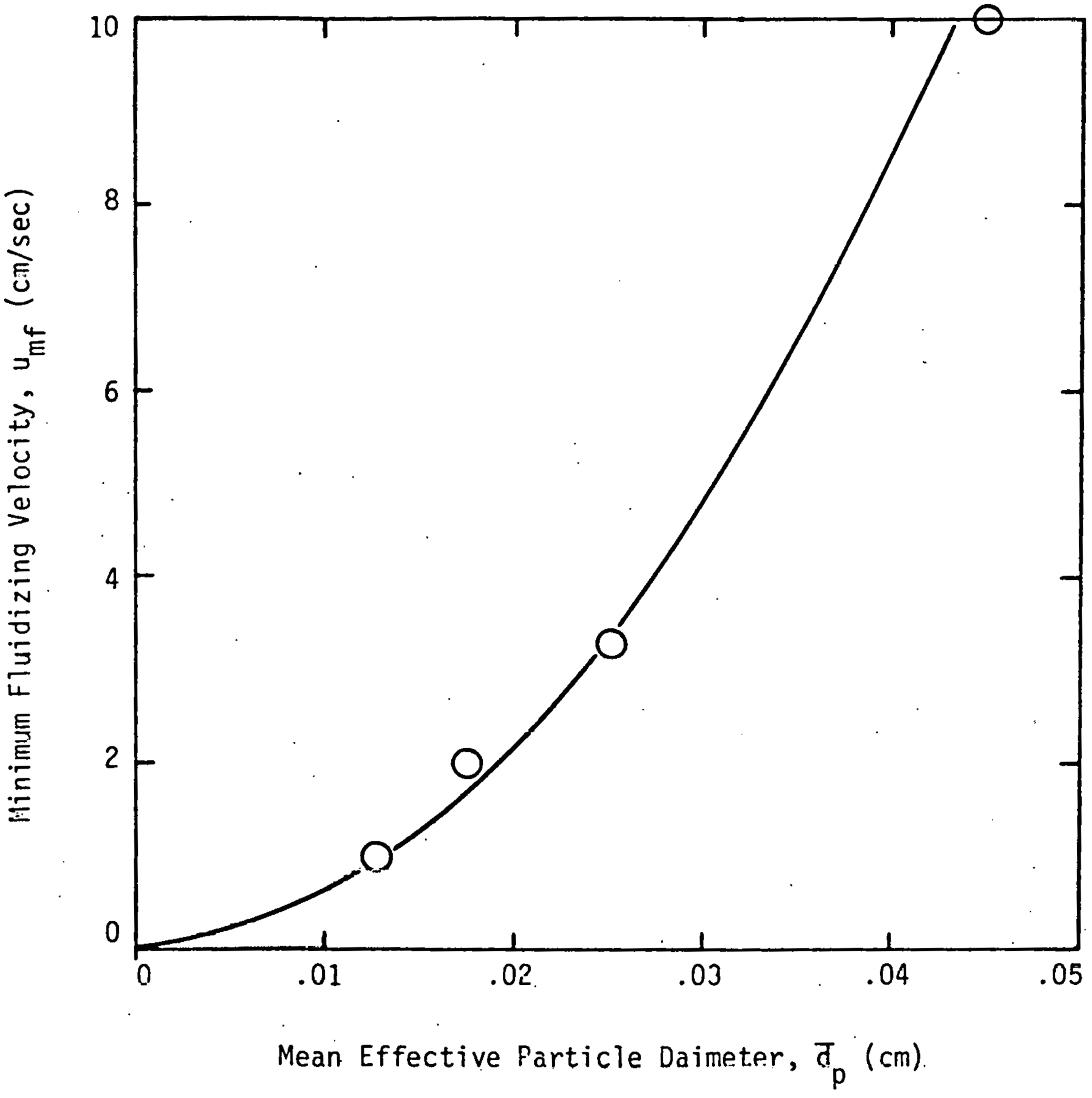


Figure 11: Comparison of experimentally determined minimum fluidizing velocity, u_{mf} (circles) to theoretically calculated values (solid line) for ϕ_s = 0.80 and ϵ_{mf} - 0.50.

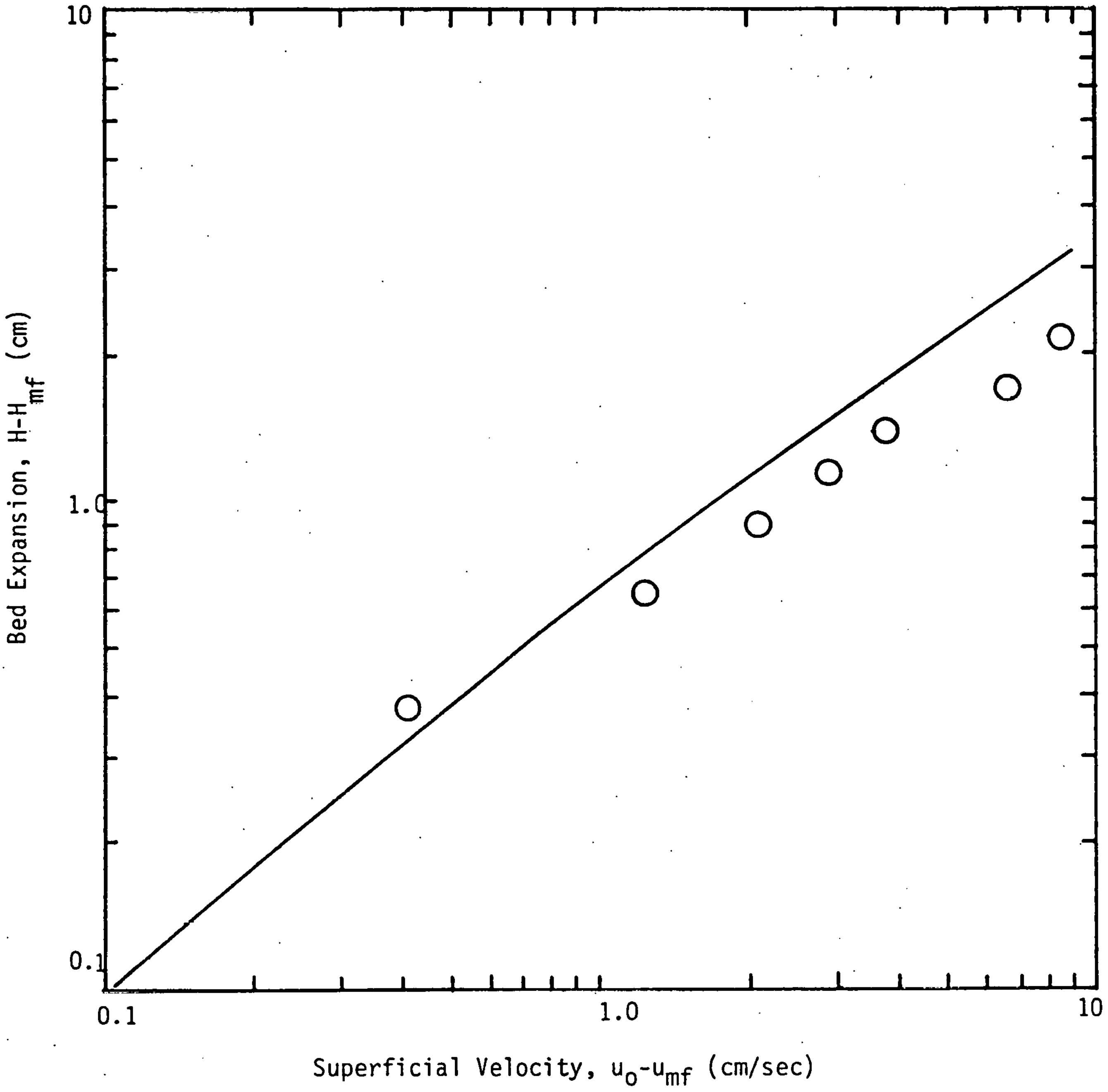


Figure 12: Comparison of experimentally observed bed expansion (circles) to theoretically calculated values (solid line) for $A_o = 0.01$.

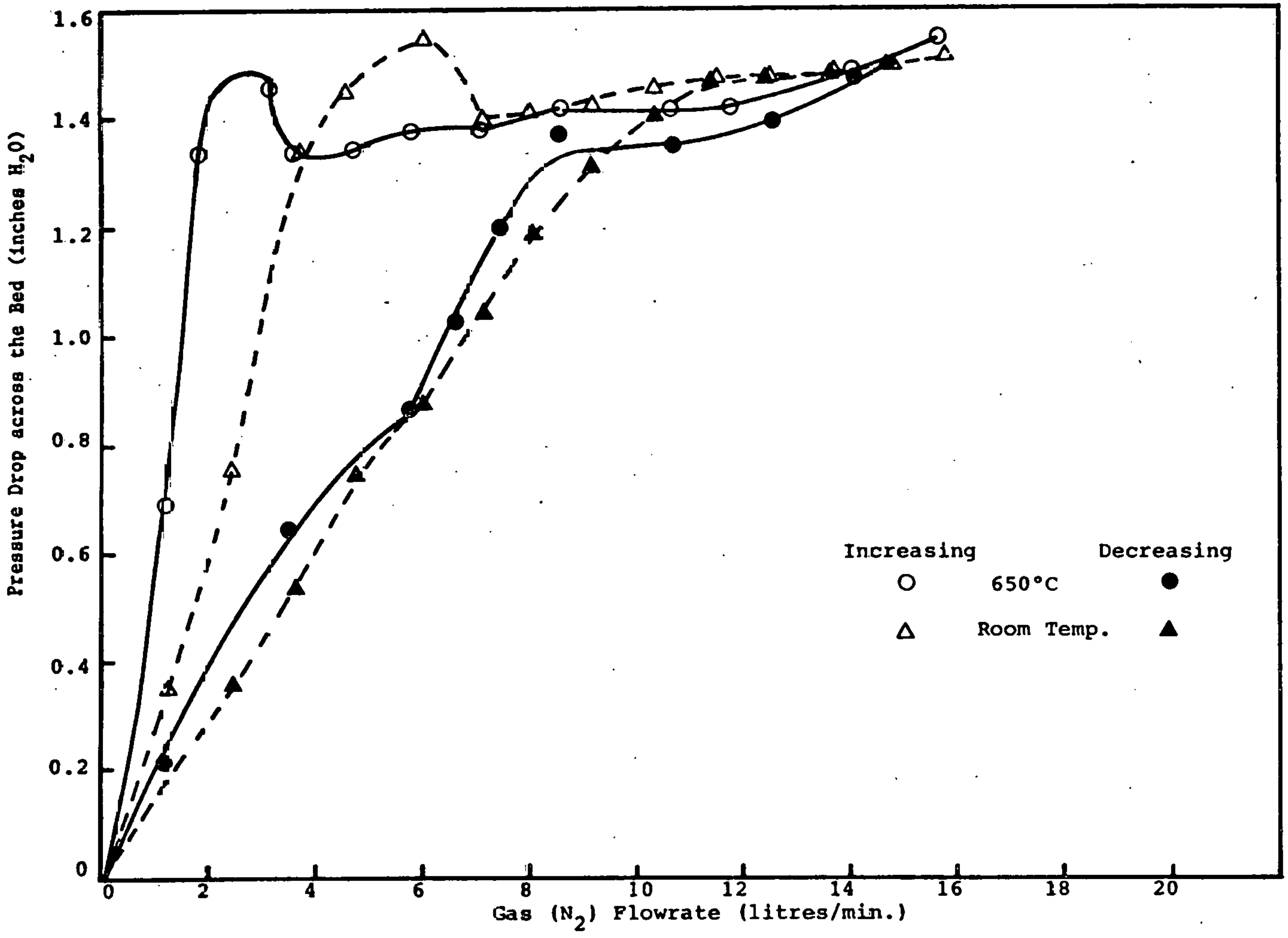


Figure 13. Pressure Drop Across Bed vs. Flowrate

Table 6. Fuel Desulfurization Candidates

Periodic Group	Potential Candidates	References*
Ia	Li, Na, K	1, 2, 3, 4, 5
Ib	Cu, Ag	1, 6, 7, 8, 9, 10, 11, 12
IIa	Mg, Ca, Sr, Ba	1, 13, 14, 15, 16, 17, 18, 19, 20
IIb	Cd, Zn	1, 6, 8, 21, 22, 23, 24
IIIa	La	25, 26
IIIb	Ga, Al	27, 28
IVa	Ti	29
IVb	Pb	8, 30
Va	V	1, 6, 7, 21
Vb	--	--
VIa	W, Mo, Cr	6, 7, 29, 31, 32
VIb	--	--
VIIa	Mn	6, 33, 34
VIIb	--	--
VIII	Ni, Fe	28, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47
Lanthanides	Ce	7
Actinides	U	7

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*See footnote attached.

FOOTNOTE Table 6

1. Onursal, 1979
2. Moore, 1975
3. Moore, 1977
4. Cover, 1973
5. Botts, 1976
6. Westmoreland, 1977
7. Hutt, 1936
8. Nachod, 1948
9. Meyer, 1978
10. Agrawal, 1980
11. Lewis, 1963
12. Benard, 1965
13. OBrien, 1976
14. Lemezis, 1974
15. Feinman, 1980
16. Squares, 1971a
17. Leum, 1968
18. Squares, 1971b
19. Kawahara, 1980
20. Curran, 1973
21. Jalan, 1979
22. Grindley, 1982
23. Gutman, 1969
24. Gibson, 1980
25. Wheelock, 1976
26. Wheelock, 1977
27. Laudan, 1968
28. Slayer, 1972
29. Metsuda, 1982
30. Meissner, 1976
31. Massoth, 1970
32. Massoth, 1975
33. Batchelor, 1963
34. Hudson, 1974
35. Reeve, 1958
36. Buresui, 1967
37. Schultz, 1970
38. Oldaker, 1975
39. Oldaker, 1976
40. Joshl, 1977
41. Steiner, 1977
42. Setzer, 1969
43. Kirkpatrick, 1951
44. Colsom, 1964
45. RostrupNielsen, 1968
46. Gautherly, 1974
47. Doren, 1969

A more recent systematic examination primarily using thermodynamic criteria for selection of candidates for the hot regenerable desulfurization of coal gases for advanced fuel cell applications is that of Jalan (1979). Criteria that must be kept in mind as a guide for selection of appropriate sorbent candidates consist of: low equilibrium H_2S concentrations at applicable temperatures for typical fuel gas compositions and the removal agent; rapid sulfidation kinetics; high conversions of the removal agent to the sulfided state under conditions applicable; rapid regeneration kinetics; thermal and mechanical stability for the removal agent under both conditions of sulfidation and regeneration; a compatibility of the removal agent with other more reactive gas components.

The principal initial criteria used for selection of the particular sulfur removal agents evaluated in this study was based on thermodynamic considerations such as attainable equilibrium H_2S concentrations for gas compositions typical of coal gases and at temperatures of about 650°C typical of the effluents from a hot iron oxide sorbent bed and on the regenerability of the sulfided adsorbents (Jalan and Wu, 1979; Jalan, 1981a, 1981b).

Following are the reactions of primary concern in desulfurization:

$$aMe + bH_2S \rightarrow Me_aS_b + bH_2 \qquad (1)$$

$$Me_aO_b + bH_2S \rightarrow Me_aS_b + bH_2O \qquad (2)$$

in sorbent reduction;

$$Me_aO_b + bH_2 \rightarrow aMe + bH_2O \qquad (3)$$

$$cMe_aO_b + fH_2 \rightarrow aMe_cO_d + fH_2 \qquad (4)$$

with $cb = ad + f$

and in regeneration;

$$2cMe_aS_b + (2cb + ad)O_2 \rightarrow 2aMe_cO_d + 2cbSO_2 \qquad (5)$$

$$2cMe_aS_b + adSO_2 \rightarrow 2aMe_cO_d + (2cb + ad)\ S \qquad (6)$$

$$aMe_cO_d + fSO_2 \rightarrow cMe_aO_b + fS \qquad (7)$$

with $ad + f = cb$

with the possible side reaction of:

$$Me_aS_b + 2bO_2 \rightarrow Me(SO_4)b \qquad (8)$$

Employing a temperature of 650°C (923°K), and a typical fuel composition (47% N_2, 20% H_2, 17% CO, 10% CO_2, 6% H_2O and 6000 ppmv H_2S) minimization of Gibbs free energy was used as the criteria of thermodynamic feasibility for desulfurization reaction 1 and 2. Reactions 3 and 4 are of importance for metal oxides such as CuO, WO_3 and V_2O_5 which will be reduced to lower oxidation states in the fuel gas environment. Regeneration of the sulfided metal by oxidation to the metal oxide, reaction 5, was also an important concern in the selection of sorbent candidates.

Reactions such as 6 and 7 for the reaction of SO_2 with the sulfided or oxidized metal and the stability of metal sulfates formed (reaction 8) in oxidation of the sulfided metals were also considered in the initial selection of candidate sorbents.

Of 42 metals and oxides initially examined, 12 candidates (Fe, Co, Pb, Mo, Cd, W, Zn, V, Mn, Sr, Ba, Cu) were evaluated in some detail (Fig. 14). Four candidates, ZnO, Cu, WO_2, and V_2O_3, were selected as meriting experimental evaluation of their desulfurization and regeneration performance. Interferences from carbon deposition and water-gas shift reactions were critically analyzed. The amount of water necessary to avoid carbon deposition and to maintain water-gas shift reaction equilibrium was theoretically determined, and its effects on the desulfurization ability for each candidate were calculated. Even in adverse conditions,

Figure 14. Screening Results of First 92 Elements

SCREEN OUT DUE TO CHEMICAL AND PHYSICAL PROPERTIES

Ar, At, Au, B, Br, C, Cd, Cl, F, H, He, Hg, I, In, Ir, Kr, Mn, Mo, N, Ne, Nd, O, Os, P, Po, Pr, Pt, Re, Rh, Rn, S, Sc, Se, Te, Tl, Xe, Y

SCREEN OUT DUE TO RARE AND EXPENSIVE NATURE

Ac, Dy, Fr, Ho, Lu, Pa, Pd, Pm, Ra, Tb, Tc, Tm, Yb

SCREEN OUT DUE TO UNFAVORABLE THERMODYNAMICS

Al, Ag, As, Be, Bi, Ce, Cs, K, La, Li, Mg, Na, Rb, Ru, Sb, Si, Sn, Th, Ti, U, Zr

INADEQUATE INFORMATION

Cr, Nb, Ta, Hf, Er, Eu, Gd, Sm

LOW TEMPERATURE (298-600°K) AND/OR 200 PPM LEVEL SULFUR REMOVAL CANDIDATES

Fe, Co, Ni, Ga, Ge, Pb

HIGH TEMPERATURE (600-950°K) CANDIDATES (RECOMMENDED FOR EXPERIMENTAL STUDY)

Zn, V, W, Cu

SUPER HIGH TEMPERATURE (1300°K OR HIGHER) CANDIDATES

Ca, Sr, Ba

all four candidates (ZnO, V_2O_3, Cu and WO_2) look attractive for low level desulfurization.

The desulfurization agents evaluated experimentally during the past two years have consisted of CuO, ZnO, the binary mixture of CuO/ZnO, and V_2O_5. These agents have been examined principally on supports such as alumina or zeolite but also as unsupported sorbents, notably for the binary mixture CuO/ZnO, ZnO and V_2O_5. Commercially available sorbents were used but a number of experimental sorbents were prepared as well.

C. Sorbent Preparation

The experimental supported sorbents were prepared by solution impregnation and cation exchange on a prestabilized alumina and on a commercial zeolite. These experimental sorbents were prepared by saturation of precalcined (500°C) sorbents with aqueous nitrate solution followed by dehydration at 150°C and thermal decomposition of the absorbed nitrate in air at 500°C. Metal loadings as cupric oxide or zinc oxide were established gravimetrically. The alumina support selected was Harshaw AL4133, prestabilized in a packed-bed reactor by flowing simulated H_2S free fuel gas at 700 cc/min. at 650°C for four hours, followed by exposure to an air-steam (75-25 volume percent) gas mixture at 700 cc/min. at 650°C for one hour. The zeolite selected as a support consisted of a high surface area, hydro-thermally stable, rare earth loaded faujasite (Linde SK500).

The mixed CuO/ZnO/zeolite sorbents were prepared by cation exchange using the same zeolite with aqueous nitrate solutions followed by dehydration of the exchanged zeolite at 150°C in air and calcining at 500°C in air to decompose residual nitrates. Three exchange procedures were used in view of the known range of exchange sites in various positions on the surface of the zeolite lattice and the possible introduction of selectivity factors in the exchange process. In addition, a range of Cu/Zn loading ratios was desired. The first preparation (A) involved a two step exchange in which the zinc was exchanged initially and subsequently, the copper was exchanged, the second preparation (B) was also two stage except that copper was exchanged initially, and the third preparation (C) was conducted in a single step with both copper and zinc present in a 1:2 molar ratio of CuO to ZnO. Preparation B and C are comparable to the commercial CuO/ZnO material, (United Catalyst 66B) with a CuO/ZnO mole ratio of 0.5. Preparation A provided a wide difference in the copper content from either sorbent B or C. The compositions of CuO and ZnO obtained on the zeolite support are given in Table 7.

D. Desulfurization Performance

A brief summary of the work accomplished on the immediately preceeding contract (Jalan, 1981b) is given here (Table 8). Based on thermodynamic calculations of the equilbrium H_2S concentrations for gas compositions typical of coal gases and at temperatures of 650°C typical of the molten carbonate fuel cells and the criteria cited above in section IV.C the sorbent candidates selected for evaluation consisted of V_2O_5, CuO, WO_3 and ZnO.

Experimental evaluation tests were conducted on a fixed bed bench scale reactor to establish sulfur removal at 650°C from a simulated coal gas (25.8% H_2, 47.2% N_2, 15.5% CO_2, and 11.5% CO on dry basis) containing 200 ppm H_2S. Sulfur capacities of the sorbent at about 10 ppm H_2S effluent concentration and the regenerability of the sorbents were determined. Tests conducted with the unsupported oxides, V_2O_5, CuO, WO_3, provided sulfur loadings of 0.14, 0.7, and 0.5 mole percent, respectively, corresponding to the sulfides V_2S_3, Cu_2S, and WS_2, at breakthrough

TABLE 7

Composition of CuO/ZnO/Zeolite Sorbents

Preparation Method	CuO w%	ZnO w%	CuO/ZnO Wt. Ratio
A	9.83	6.47	1.52
B	5.93	11.11	0.54
C	1.65	3.12	0.53

Table 8. Summary of Desulfurization Studies on Metal Oxide Sorbents

Desulfurization of Simulated Coal Synthesis Gas Containing 200 ppm H_2S

Sorbent	Desulfur Agent wt %	Support	Sulfur Capacity at 650°C$^+$		Regeneration Condition				Sulfate Decomposition Temp. °C
			Wt. Basis△	Mole %●	Oxidation Temp. °C		Reduction Temp. °C		
Cu(CuO)	37.5 CuO	None	0.14	0.7	Air	650	H_2	650	700-860
		SiO_2	1.7	22.5*	Air	600	H_2	500	
$V_2O_3(V_2O_5)$	10 V_2O_5	None	0.07	0.14	Air	650	Fuel	650	100-200
		Al_2O_3	0.13	2.5	Air	650	Fuel	650	
$WO_2(WO_3)$ pellet	100 WO_5	None	0.14	0.5	Air	650	H_2	650	-
powder		None	0.52	1.9	Air	650	H_2	650	
ZnO	80 ZnO	None	1.9	5.9	Air	750	None		600
			3.6	11.6	Steam & Air	650	None		
Cu/ZnO	33 CuO 65 ZnO	None	3.2	9.7	Steam & Air	750	H_2	250	600-800

$^+$ At 10 ppmv H_2S in effluent

*Desulfurization at 500°C

△ lbs. sulfur removed per 100 lbs. of charge based on active components in highest oxidation state (CuO, V_2O_5, WO_3, ZnO) and support, if any.

● Assumed conversion to Cu_2S, V_2S_3, WS_2, and ZnS respectively.

concentrations of 10 ppm H_2S for removal of 200 ppm H_2S at 650°C from a simulated fuel gas (Table 8). All these sorbents received prior reduction to V_2O_3, Cu and WO_2 which had been predicted to be the active species. Regenerability was achieved by air oxidation at 650°C to displace the adsorbed sulfur as SO_2 for all three of these agents. The low specific surface areas of these unsupported oxides was considered the principal limiting factor leading to the low sulfur loading capacities obtained with these agents.

Commercial ZnO pellets and commercial supported V_2O_5 sorbents were also evaluated. Sulfur loadings of 5.9 to 11.6 mole percent were obtained for ZnO at 650°C for scrubbing 200 ppm H_2S to 10 ppm H_2S. The larger of these sulfur loadings was obtained for a ZnO regenerated with a mixture of air and steam (25 volume percent steam) indicating a promising alternative to air as a regenerant. The commercial supported V_2O_5 sorbent provided sulfur loadings up to 2.5 mole percent for systems regenerated by prereduction at 610-650°C for sulfur scrubbing tests at 650°C for reduction from 200 ppm H_2S to 10 ppm H_2S.

A commercial copper supported on silica and a commercial mixed oxide CuO/ZnO were also evaluated as sulfur removal sorbents. A sulfur loading of 22.5 mole percent for copper supported on silica was obtained at 500°C for scrubbing 200 ppm H_2S in simulated coal gas to 10 ppm H_2S after air regeneration at 600°C and a prereduction at 500°C. Similar tests with the mixed oxide, CuO/ZnO, resulted in sulfur loadings of 9.7 mole percent at 650°C after air regeneration at 750°C and a prereduction at 240-250°C.

Some exploratory evaluations were also conducted with Cr_2O_3, $BaCO_3$, and $SrCO_3$ which indicated that at 1000°C, $SrCO_3$ can achieve efficient sulfur removal to 10 ppm H_2S from 200 ppm H_2S in simulated coal gas. The observed sorbent utilization was 47 percent of theory suggesting further evaluation would warranted for very high temperature desulfurization beyond the scope of this study.

Extensive physical characterization of ZnO pellets was conducted using low temperature nitrogen adsorption, scanning electron microscopy and microanalysis and established significant semiquantitative information on the surface structure of the pellets accompanying desulfurization, regeneration with air and steam,and thermal sintering. The principal results obtained include the positive identification the pore plugging in the coarser pores, which accompanies the sulfidation of the ZnO pellets. Microanalysis provided further evidence of the pore plugging during sulfidation and the limitation it imposes on efficient utilization of the of the pellet to depths in excess of 250μ. Finally, considerable effort was expended in devising a pore plugging model which could utilize experimentally accessible parameters to permit design of more effective sulfur removal sorbents.

1. Desulfurization Performance in Fixed Bed

a. Desulfurization Over United Catalyst C125

Exploratory test evaluations conducted in a fixed bed reactor with a simulated fuel gas at 650°C with a proprietary sorbent, United Catalyst C125, commonly used for a combination of sulfur and chloride removal from hydrocarbon gases, showed a consistently reproducible sulfur loading of 1.5 to 2.0 weight percent. This result was obtained after regeneration by air-steam oxidation and thermal decomposition in nitrogen at 650 to 750°C. In addition to this regenerable desulfurization capacity, attributable to one component of the sorbent, there was a consistent sulfur removal onto a second, largely unregenerable component. Later it was identified as calcium oxide and this discouraged further investigation of this sorbent.

b. Desulfurization Over Vanadium Sesquioxide

Giner, Inc. had previously reported a very favorable thermodynamic analysis of the reaction

$$V_2O_3 + H_2S \rightarrow V_2S_3 + 3H_2O$$

based on the heat of formation of V_2S_3 obtained from the National Bureau of Standards (Wagman, et al., 1971). Our experiments, however, showed very small reactivity of V_2O_3 with H_2S (Jalan,1981a,1981b). After re-examination of the literature and consultations with METC (Table 9), it was decided that the National Bureau of Standards value of the heat of formation of V_2S_3 (-227 Kcal/mole) was suspect.

In parallel investigations, workers at METC reported that a 10 ppm H_2S fed into a bed of vanadia catalyst (containing 0.043 wt% S) resulted in 100 ppm H_2S at the exit and increased the sulfur content of the vanadia catalyst to 0.147 weight percent (run 54, Grindley, 1983). A simple material balance for sulfur indicates an unknown source of sulfur outside the vanadia bed. This could be due either poor performance of ZnO bed (ruled out by run 55, Grindley, 1983) or contaminated reactor walls. An important conclusion, however, is that with 27% water vapors present in the coal gas mixture, at 649°C, vanadium oxide reacted with low concentration H_2S (10-100 ppm) to increase the sulfur content of the catalyst from 0.043 to 0.147 weight percent (see Table 3 of Grindley, 1983). It is important to note that the preferred value of the heat of formation of V_2S_3 (-125 Kcal/mole) will not permit the reaction of V_2O_3 with H_2S in the presence of 27% water vapors. It is possible that a sulfur compound other than V_2S_3 is formed.

TABLE 9

THERMODYNAMIC DATA FOR V_2S_3

M.P. °C of V_2S_3	ΔH_f° kcal/mole	ΔG kcal/mole	T °K	Source
	-230±4		298	Gmelin, 1967
	-227		298	Wagman, 1971
	[-125]		298	Miles, 1974
		-55	1000	Merc, 1978
		-87.2	923	Jalan, 1981
∿650				CRC, 1975
d >600				
d 850-950 invacuo				Sandrock,1976

The Harshaw vanadia catalyst was retested in our bench scale packed bed reactor. Furthermore, to determine the reactivity of H_2S with V_2O_3, "steady state" experiments were conducted in a quartz reactor with unsupported, high purity V_2O_5 (Union Carbide), V_2O_5/Al_2O_3 (Harshaw) obtained directly and via METC, and V_2O_5/alumina prepared at Giner, Inc. Mixtures of hydrogen with 6 to 10 percent H_2S and 6 to 26 percent water vapor at 650°C were reacted with the various V_2O_5 samples for five hours. Based on chemical analyses for sulfur and vanadium and assuming the sulfide to be V_2S_3, the measured conversions of V_2O_3 to V_2S_3 were 0.8 to 1.1 percent for unsupported V_2O_3 and 198 percent for highly dispersed V_2O_3 on alumina (Table 10). It is speculated that the anamolously high sulfur value of 198 percent is possibly attributable to formation of a surface compound such as $V(HS)_3$, analogous to sulfur compounds formed with alumina and silica.

The results of tests in both the packed bed stainless steel reactor and in the exploratory quartz reactor, along with METC results, have confirmed our previous experiments that V_2O_3 does have the ability to react at 650°C with H_2S, and that the conversion of V_2O_3 was very small for H_2S effluent concentrations less than 10 ppm. It is concluded that at the present state of understanding, V_2O_5 would not make a good sorbent.

c. Desulfurization Performance of Zinc Oxide and Copper Oxide

A summary of the results of the desulfurization performance tests conducted under the current program with single component and binary component systems, unsupported and supported, are given in Tables 11 and 12. With the objective of improving utilization efficiency, the earlier studies with CuO and ZnO were extended to highly dispersed supported sorbents for the hot, regenerable removal of sulfur from simulated coal gas. Specifically,

TABLE 10

DESULFURIZATION OVER V_2O_3 IN QUARTZ REACTOR

SORBENT	SURFACE AREA	SULFUR LOADING AT 650°C	
		Wt % S	MOLE %V_2S_3
V_2O_3 UNSUPPORTED (Union Carbide)	LOW	1.1	2.1
V_2O_3 (10 Wt%)/Al_2O_3 (Harshaw)	MODERATE	0.8	17
V_2O_3 (13.8 Wt%)/Al_2O_3 (Giner, Inc.)	HIGH	12.7	198

REACTANT GAS MIXTURE 6% H_2O, 6% H_2S, AND 88% H_2

Wt % S BY CHEMICAL ANALYSIS OF PRODUCT

TABLE 11

DESULFURIZATION SUMMARY-SINGLE COMPONENT SYSTEMS

Sorbent	Composition		Sorbent	Prehistory			Desulfurization					
	CuO w/o	ZnO w/o	wt.g	Pretreat	Regeneration Atmosphere	Temp. °C	Space Velocity hr^{-1}	Test Duration hr	Sulfur Loading mol %	Reactor	Duty Cycles	Test No.
ZnO (unsupported)	--	100	20.8	None	Fresh	650	5500	25.75	15.5	S.S	1	1
					Air	"	5500	11.25	6.8		3	3
ZnO (unsupported)	--	80	5.2	None	Fresh	650	19350	4.75	7.1	S.S	1	47
					Air/Steam	"	19350	6.38	11.6		4	50
ZnO Zeolite	--	17.8	4.5	None	Fresh	650	3780	6.00	20.0	Q	1	143
	--	17.8		None	Air/Steam	"	3780	2.17	7.0		2	144
	--	17.8	4.5	None	Fresh	650	3780	7.2	24.0	Q	1	146
	--	17.8		None	Air/Steam	"	3780	2.17	7.0		3	148
CuO/SiO_2	37.5	--	10.0	None	Fresh	500	700	14.0	4.5	S.S	1	21
	37.5	--		None	Air	500	700	4.08	1.3		4	24
	37.5	--		H_2 Red	Fresh	550	700	30.17	9.6	S.S	1	34
	37.5	--		H_2 Red	Air	550	700	71.0	22.5		2	35
CuO/Al_2O_3	17.8	--	5.2	Red H_2S Free Fuel Gas	Fresh	650	5000	1.6	8.7	S.S	1	75
	17.8	--		H_2 Red.	Air	"	5000	2.14	11.7		5	79
	17.8	--	5.0	H_2 Red.	Fresh	650	2030	3.42	6.9	S.S	1	83
	17.8	--		H_2 Red.	Air/Steam	"	2030	2.75	5.4		5	87
CuO/Zeolite	10.6	--	6.5	H_2 Red.	Fresh	650	1550	8.42	17.8	S.S	1	90
	10.6	--		Red H_2S Free Fuel Gas	Air	"	1550	7.42	15.6		4	93
	10.6	--	6.4	H_2 Red.	Fresh	650	1550	10.8	22.9	S.S	1	95
	10.6	--		H_2 Red.	Air/Steam	500	1550	29.5	62.6		4	98
	10.6	--	3.7	H_2 Red.	Fresh	650	1700	2.0	5.2	Q	1	173
	10.6	--		H_2 Red.	Air	650	1700	2.5	6.5		2	174
	14.07	--	7.0	H_2 Red.	Fresh	650	1730	2.75	5.0	INCOLOY 800H	1	175
	14.07	--	5.7	h_2 Red.	Fresh	650	1560	9.0	16.3	S.S.	1	178

TABLE 12

SUMMARY OF DESULFURIZATION TESTS

CuO and ZnO - BINARY SYSTEMS

Sorbent	Composition		Sorbent wt.g	Prehistory		Desulfurization			Sulfur loading mol %	Duty Cycles	Test No.	Reactor
	CuO w/o	ZnO w/o		Pretreat	Regeneration Atmosphere	Temp. °C	Space Velocity hr^{-1}	Test Duration hr				
CuO/ZnO	33	65	5.0	None	Fresh	650	24970	2.83	4.1	1	51	S.S.
	33	65		H_2 Red	Air/Steam	"	12500	12.0	8.9	10	60	
CuO/ZnO Zeolite Prep. A	9.8	6.4	8.77	H_2 Red	Fresh	650	3850	5.0	>12.9(4)*	1	124	Q
	9.8	6.4		H_2 Red	Air/Steam	"	3850	0.13	0.4	4	127	
	9.8	6.4	8.00	H_2 Red	Fresh	650	4300	4.25	12.0	1	128	Q
	9.8	6.4		H_2 Red	Air/Steam	"	4300	1.17	3.3	9	136	
CuO/ZnO Zeolite Prep. B	5.9	11.1	8.5	H_2 Red	Fresh	650	3900	7.07	>15.0(0)*	1	137	Q
	5.9	11.1		H_2 Red	Air/Steam	"	3900	2.75	5.9	5	141	

Notes = * - Values in parentheses indicates PPM H_2S corresponding to reported S loading
S.S - Stainless Steel
Q - Quartz

CuO, ZnO, and mixed sorbent CuO/ZnO dispersed on hydrothermally stable alumina and zeolite supports were examined (Tables 13 and 14, Figures 15-20). Unless other wise, stated all experiments were carried out with simulated coal gas (on dry basis: 25.8% H_2, 47.2% N_2, 15.5% CO_2, and 11.5% CO) containing 200 ppm H_2S. The desulfurization runs were terminated when exit H_2S concentrations above 10 ppm were measured. Parameters evaluated consisted of the role of the support, effective particle size of the sorbent, temperature, water partial pressure, wall effects, reproducibility, pretreatment history, and regeneration mode. These results are discussed in detail in the sections that follow starting with unsupported ZnO.

i. Zinc Oxide-Unsupported

Most of the desulfurization runs were terminated when effluent H_2S concentrations above 10 ppm were measured. However, in order to generate data for the model discrimination (see Section IV F),desulfurization performance of unsupported ZnO was measured in the fixed bed reactor till breakthrough concentrations approached the injection concentration of 200 ppm H_2S.

The unsupported ZnO sorbents consisted of United Catalyst, UCI C72-1; Strem 30-270 and Harshaw 0401. These tests were conducted in a quartz-lined fixed bed reactor with dry simulated coal gases in a space velocity range of 15000 to 23000 hr^{-1}; for a typical height of 5cm, this corresponds 21 to 32cm/sec. Initial sulfur loadings on fresh sorbents were determined to be 6.0, 2.3 and 5.1 mole% for the UCl, Strem and Harshaw materals, respectively, at 20ppm H_2S in the effluent gas. The sulfur capacity of the UCI ZnO, after the first regeneration, dropped to 1 mole %, but remained constant over subsequent duty cycles (Figure 21). Similarly regnerated batches of Strem and Harshaw ZnO sorbents demonstrated initial declines in sulfur loadings (Figures 22 and 23). These declines were

TABLE 13

Summary of Desulfurization Tests

CuO Supported on Al_2O_3

Prereduction and Desulfurization at 650°C

No. of Tests	Prior Regeneration Temp. °C Oxidant/N_2 Decompn.	Oxidant	Prereduction Gas	Sulfur Conversion Mole % at 10 PPMV
Fresh	None	--	Fuel Gas[o]	8.7
Fresh	None	--	2% H_2 in N_2	6.9
2	650/650	Air/N_2	Fuel Gas[o]	0.50
2	650/650	Air & Steam/N_2	Fuel Gas[o]	4.6
2	650-750/750	Air/N_2	2% H_2 in N_2	10.3
3	650-750/650-750	Air & Steam/N_2	2% H_2 in N_2	6.6

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[o] H_2S Free Fuel Gas

TABLE 14

Summary of Desulfurization Tests

CuO Supported on Zeolite

Prereduction and Desulfurization at 550°C

	Prior Regeneration			Sulfur Conversion Mole %	
No. of Tests	Temp. °C Oxidant/N_2 Decomp.	Oxidant	Prereduction Gas	500°C at 10 PPMV	650°C
Fresh	None	—	2% H_2 in N_2	—	17.8
Fresh	None	—	2% H_2 in N_2	—	22.9
1	650/750	Air/N_2	Fuel Gas[o]	—	15.6
2	650/750	Air/N_2	2% H_2 in N_2	—	15.3
2	650-750/750	Air & Steam/N_2	2% H_2 in N_2	—	13.7
1	650-750/750	Air & Steam/N_2	2% H_2 in N_2	79.7	—

---

[o] H_2S Free Fuel Gas

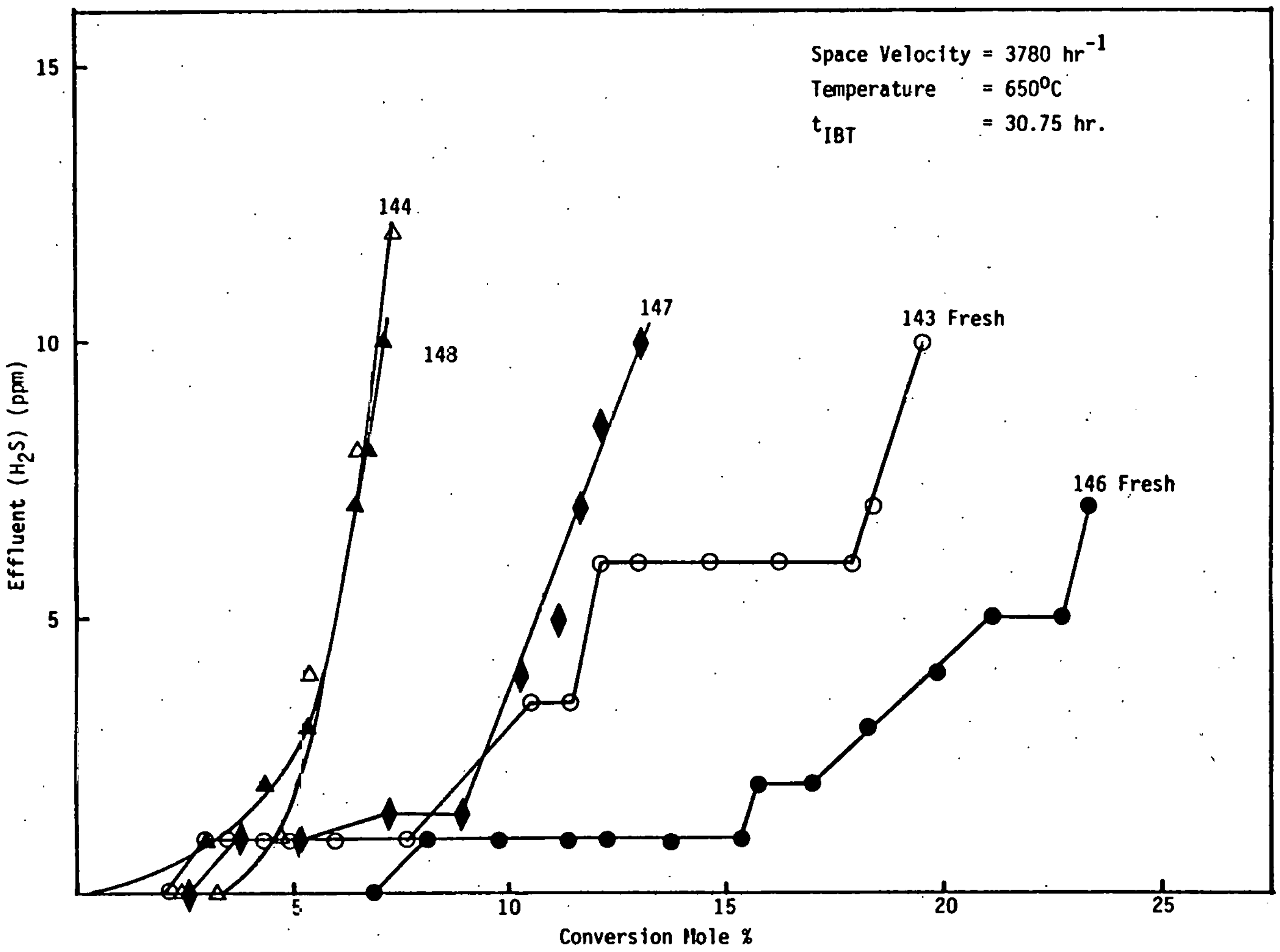

Figure 15. H_2S Uptake Curve for Supported ZnO (17.81 wt% ZnO/zeolite)

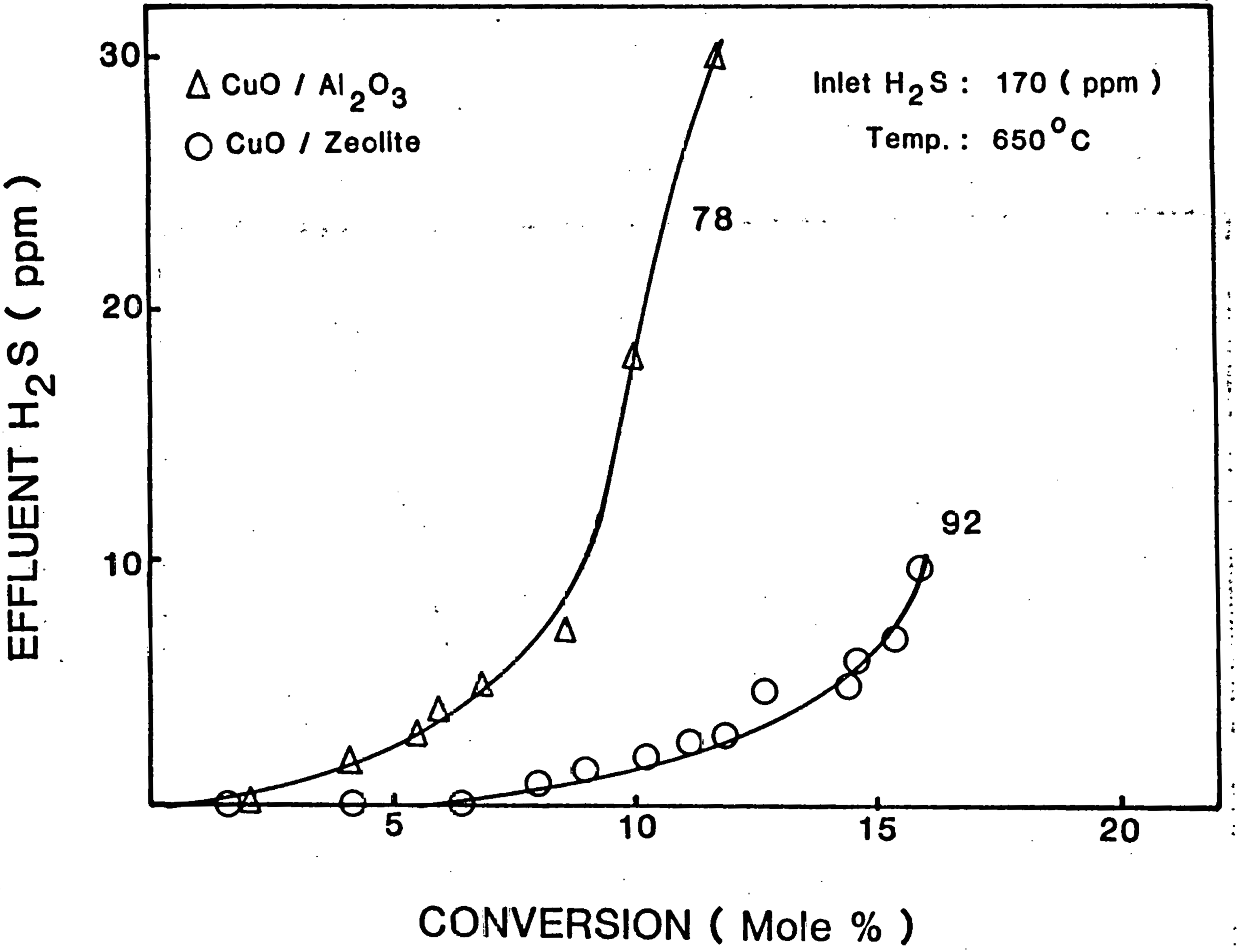

Figure 16. A Comparison of the Desulfurization Performance of Copper Oxide Supported on Alumina and on Zeolite, Air Regenerated.

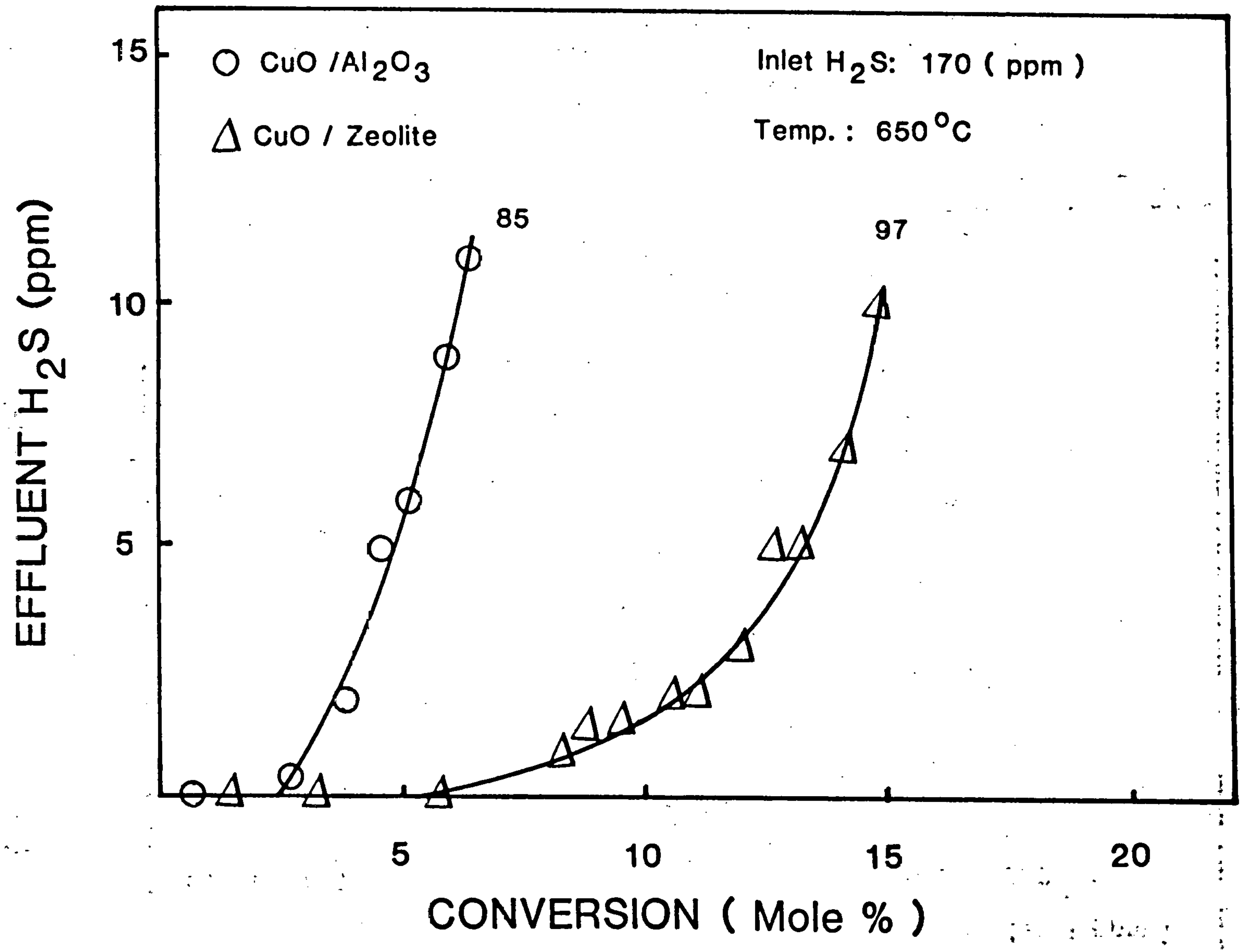

Figure 17. A Comparison of the Desulfurization Performance of Copper Oxide Supported on Alumina and on Zeolite, Air-Steam Regenerated.

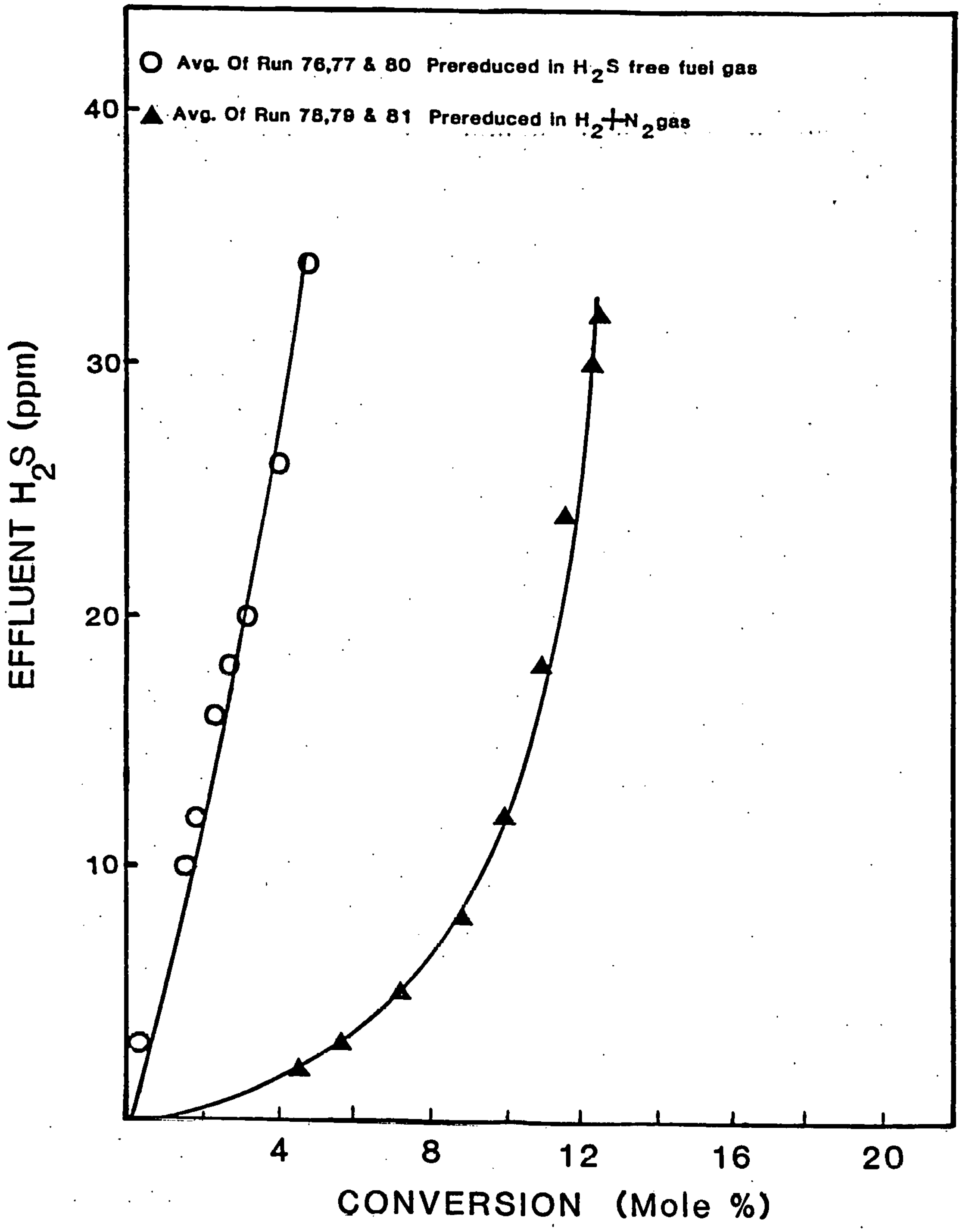

Figure 18. The Effect of Prereduction at 650°C with Hydrogen and Fuel Gas on the Desulfurization Performance at 650°C of Copper Oxide Supported on Alumina (Stabilized).

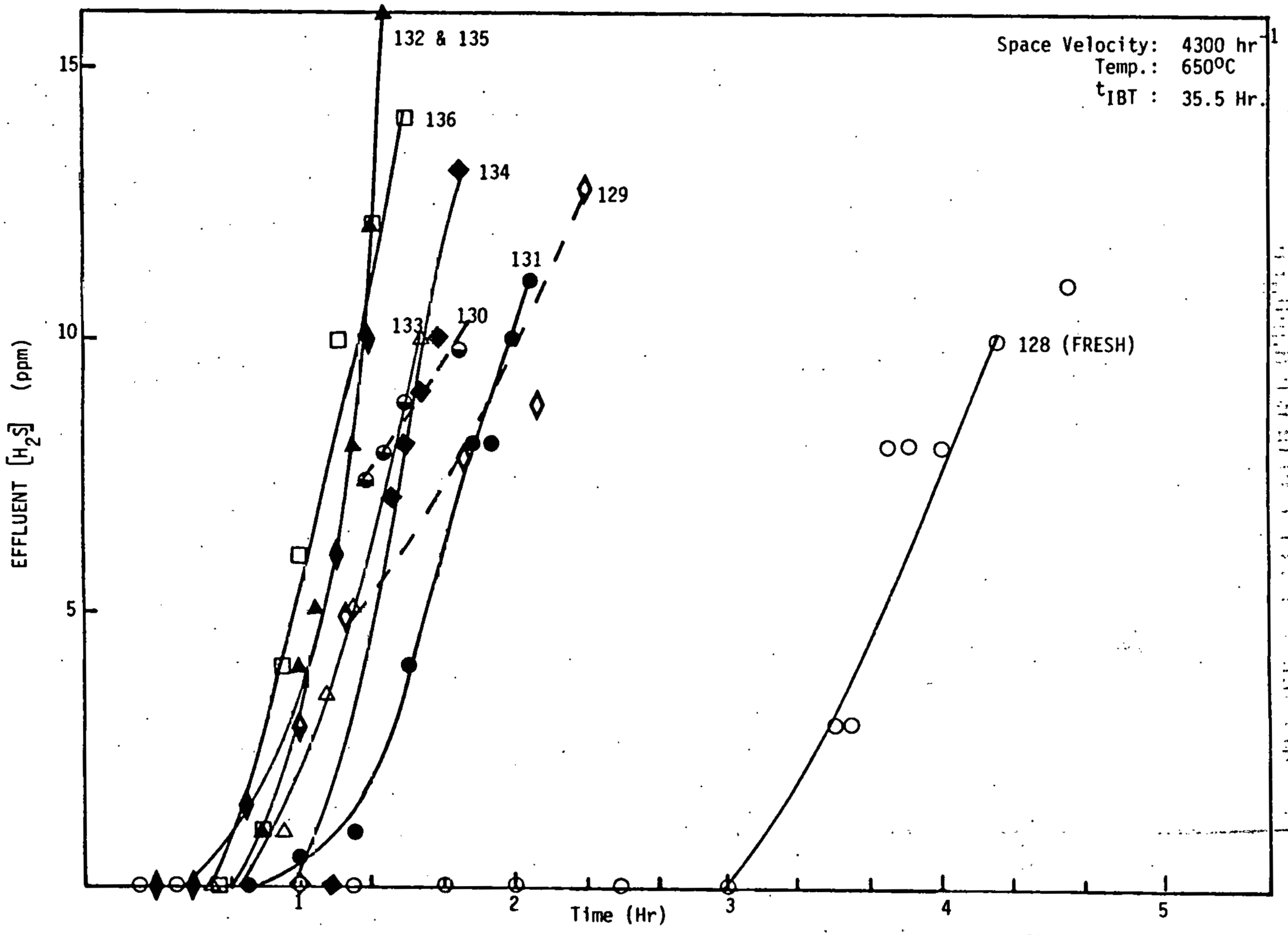

Figure 19. H_2S Uptake Curve for CuO/ZnO Supported on Zeolite (Prep.A)

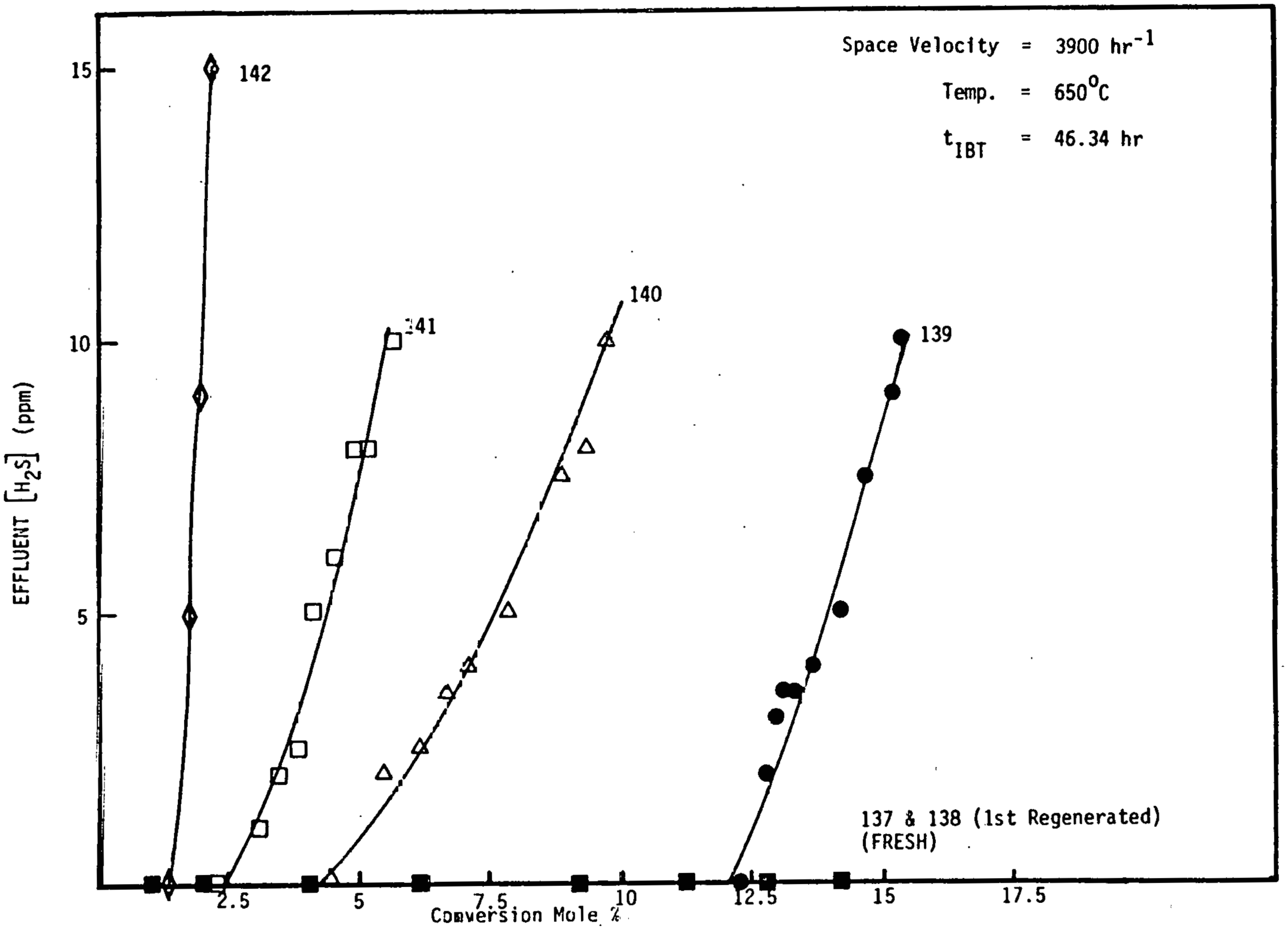

Figure 20. H_2S Uptake Curve for CuO/ZnO Supported on Zeolite (Prep.B)

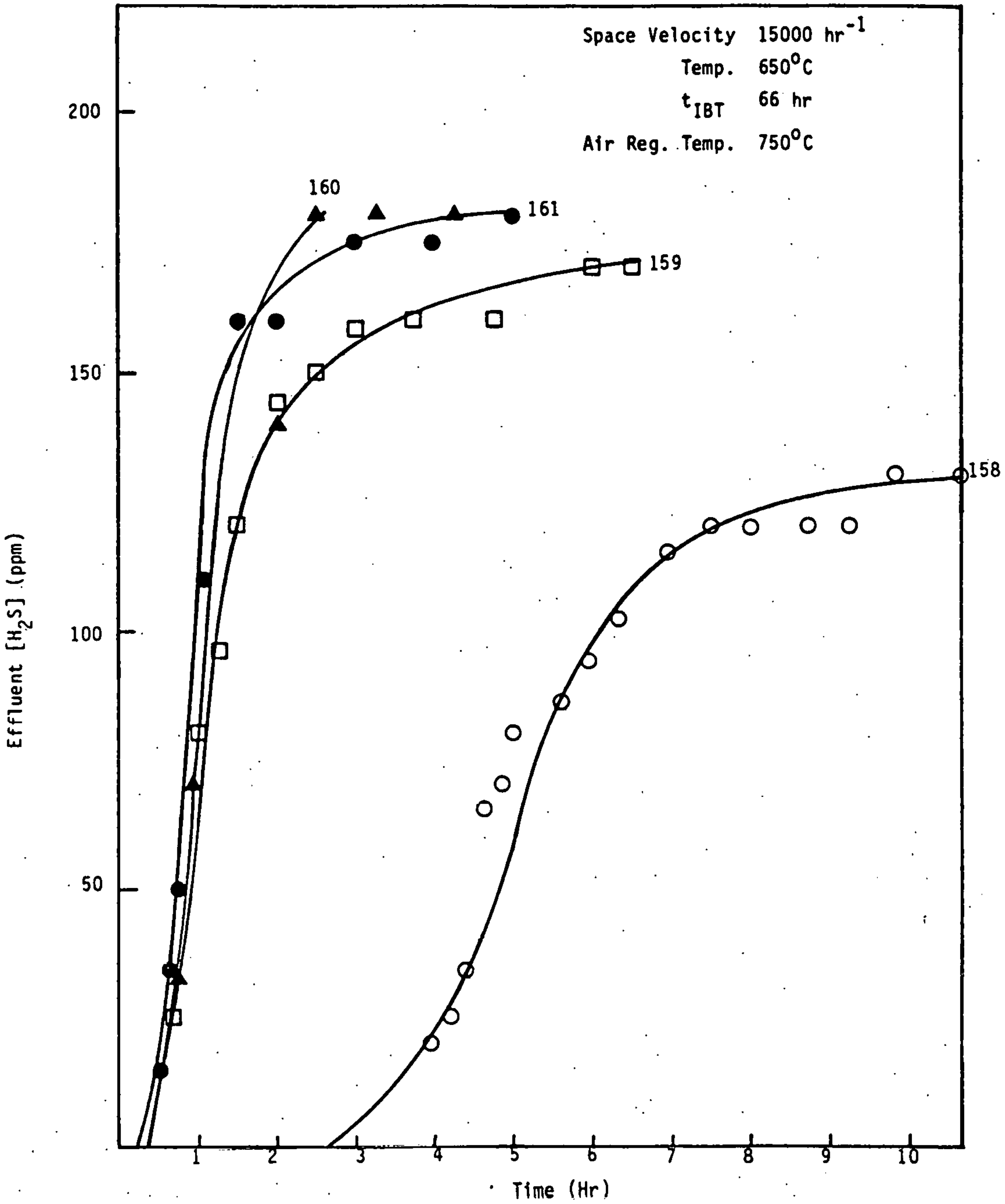

Figure 21. H_2S Uptake Curve for ZnO (United Catalyst)

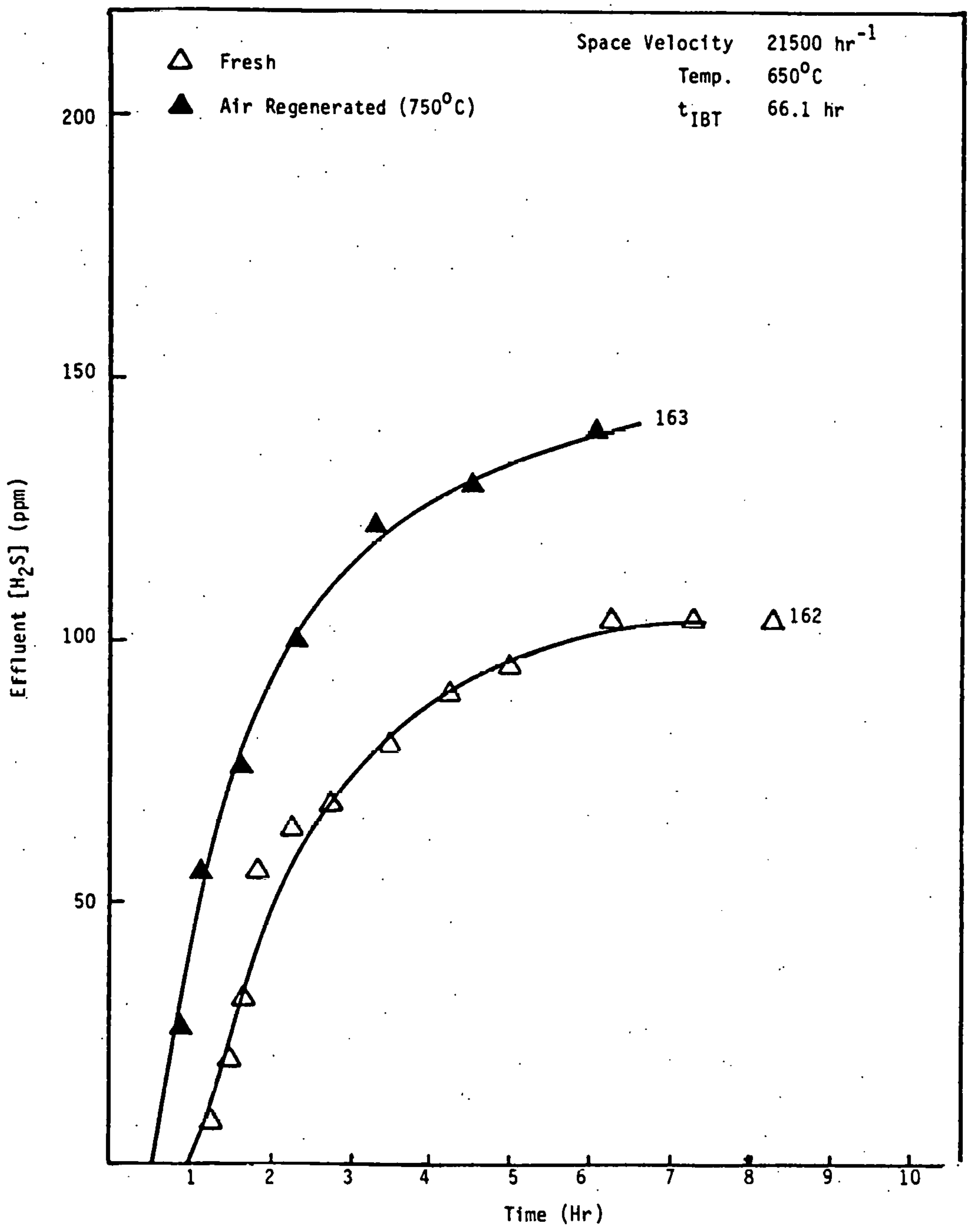

Figure 22. H_2S Uptake Curve for ZnO (Strem Chemical)

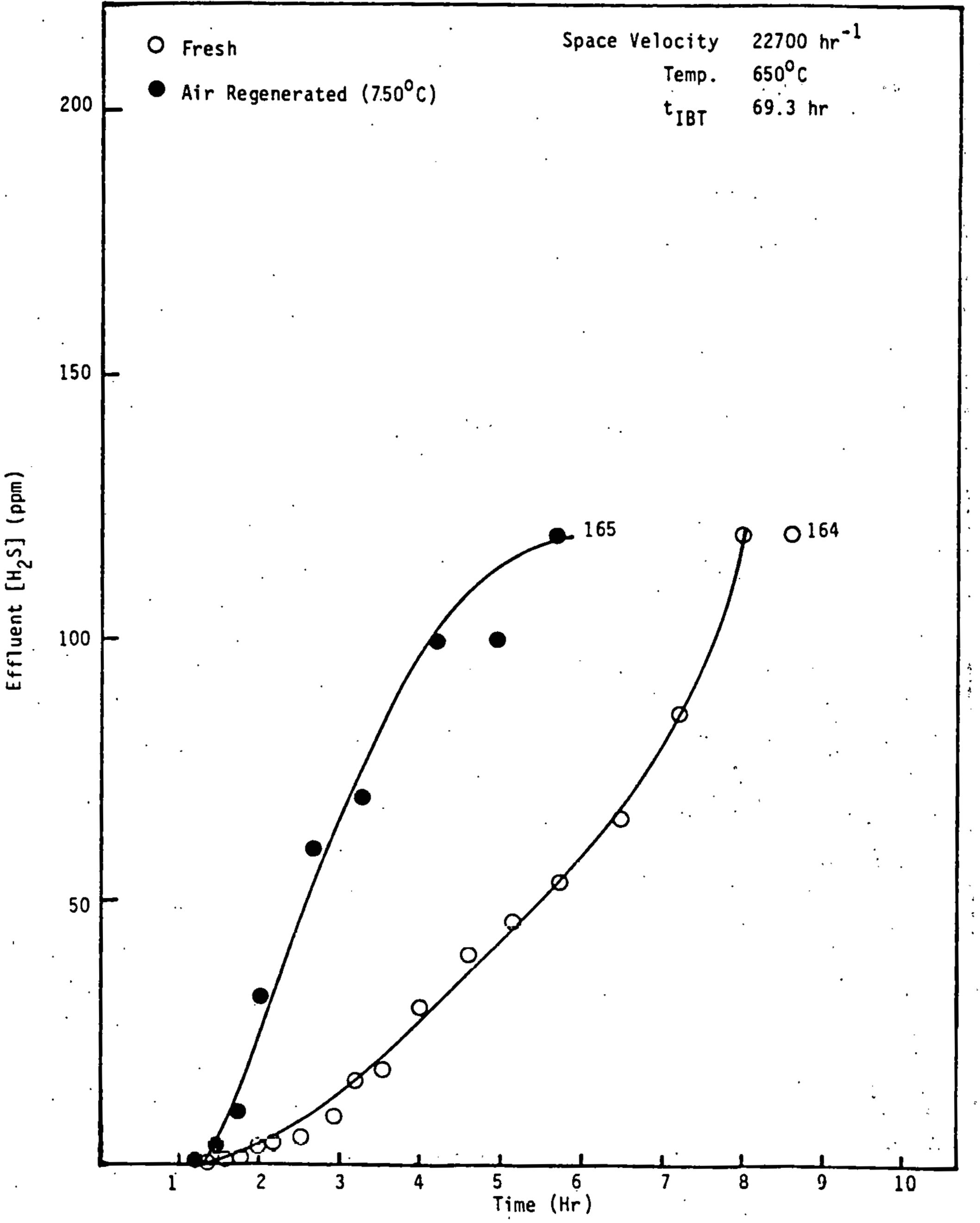

Figure 23. H_2S Uptake Curve for ZnO (Harshaw Chemical)

attributed to the sintering and volatilization of elemental zinc in dry gas observed above for the supported ZnO/zeolite sorbent. The data from these desulfurization-regeneration tests with unsupported ZnO are discussed below with the modeling calculations.

ii. Zinc Oxide - Supported

Desulfurization performance of ZnO supported on zeolite was measured in simulated coal gas mixture containing 200ppm H_2S and 6% H_2O. It was anticipated that very high surface area of the sorbent would yield high sulfur uptake capacity and the spatial dispersion would inhibit sintering and provide better regenerability.

Zinc oxide supported on zeolite (17.8 wt% ZnO) exhibited 20 mole percent conversion at 10ppm H_2S breakthrough concentration, but the initial performance was not maintained on subsequent regeneration/desulfurization duty cycles (Figure 15). This degradation was attributed to a combination of a small amount of sintering and reduction of very small particles of zinc oxide and subsequent volatilization at 700°C in the relatively dry hydrogen rich simulated coal gas. To test this, using the quartz lined fixed-bed reactor, a dry mixture of 20% H_2 in nitrogen was passed over the ZnO/zeolite sorbent at 650°C. Zinc volatilization from the sorbent bed and condensation on the cold walls at the exit end of the reactor was observed.

A conclusion based on these test data is that exposure to high temperature reducing atmospheres during desulfurization of sulfur-laden coal gases would cause volatilization of microparticles of zinc. However, under these conditions, zinc sulfidation becomes a strongly competitive reaction with reduction of the ZnO. In addition, zinc volatilization will be further inhibited by water partial pressures in the range 9-27 percent typical of air-blown gasifier and even higher for oxygen-blown gasifiers.

iii. Copper Oxide - Supported

The desulfurization tests conducted in a bench scale, fixed bed reactor configuration at 650°C with CuO on a prestabilized commercial alumina consistently provided sulfur capacities of 6 to 12 mole percent when prereduced in hydrogen (2 to 26 mole percent) at 650°C and with either air regeneration at 650°C plus sulfate decomposition in nitrogen at 750°C or regeneration at 650°C with air and steam mixture. The desulfurization performance of this CuO/Al_2O_3 sorbent at 650°C is superior in terms of stoichiometric conversion by an order of magnitude to results obtained previously at 500 to 600°C for desulfurization over a commercial copper oxide/silica sorbent, United Catalyst G108B (compare results Table 8 and Table 13). Experience to date indicates that desulfurization capacity at 500°C significantly exceeds the capacity of CuO at 650°C (Table 8 and 14). Prereduction of CuO/Cu sorbents with H_2S-free fuel gas was found to be less efficient than with hydrogen-nitrogen gas mixtures, due apparently to inhibition of sorbent reduction by the presence of oxidizing gases (CO_2 and H_2O) in the fuel gas (Figure 18).

For reduction of H_2S from 200ppm to 10ppm in a simulated fuel gas, sulfur capacities at 500°C were determined to be about 63 mole percent with the zeolite (a commercial rare-earth loaded faujasite-Y) support, compared to 1.3 to 4.5 mole percent with the silica support (Table 8 and 14), whereas sulfur capacities at 650°C ranged from about 16 to 23 mole percent with CuO/zeolite to 0.7 mole percent for unsupported CuO.

Air oxidation and thermal decomposition in nitrogen in the temperature range 650 to 750°C provide better than 90 percent regeneration of the sulfided sorbents. The use of air-steam regeneration mixtures enhances sulfur removal efficiency. Prereduction in hydrogen at 250 to 650°C provides sufficient preconditioning and availability of copper for efficient desulfurization. These experimental tests demonstrated that the desulfurization capacity can be increased from less than one percent for unsupported CuO to in excess of 63 percent for CuO/zeolite sorbent. Structural stability combined with high dispersion of the CuO appear to be key factors in optimizing the desulfurization performance of these experimental supported CuO sorbents.

Additional data summaries for the CuO supported sorbents with the prestabilized alumina and the zeolite showing the effects of temperature, regeneration mode (air or air/steam) and prereduction with fuel gas versus dilute hydrogen/nitrogen mixtures are given in Tables 13 and 14 and Figures 16 and 17. The mole percent conversion capacity for the copper supported on zeolite was approximately double that for the copper supported on alumina.

Supported systems, such as either CuO or ZnO on zeolite, show consistently higher sorbent utilization efficiency at 10ppm H_2S breakthrough concentration, compared with unsupported sorbents. The supported CuO systems show consistent improvement in sorbent utilization when going from silica to alumina, to zeolite as the support, The CuO/zeolite demonstrated a significantly high conversion of about 63 mole percent at 500°C, compared with about 23 mole percent at 650°C for silica.

Both CuO/alumina and CuO/zeolite sorbents show promising maintenance of conversion efficiency in the range of 5.4 to 16.0 mole percent at 650°C after 4 to 5 duty cycles. The initial declines in conversion efficiency observed for the early tests with these experimental sorbents can be attributed to the fact that pretreatment and regeneration conditions had not yet been optimized and the state of dispersion of the desulfurization agent had not been stabilized.

Prereduction under relatively mild conditions, such as 250°C, is sufficient for reduction of CuO and minimizes sintering. In the case of highly dispersed ZnO, high temperature (650-750°C) reduction, in the absence of appreciable water partial pressures, would lead to voltilization of elemental zinc.

Air or oxygen regeneration at relatively high temperatures such as 650-750°C is required for efficient decomposition of either copper or zinc sulfates formed during sulfide oxidation. Air/steam regeneration combined with an inert gas decomposition at 650-750°C contribute to the more efficient regeneration of both CuO and ZnO sorbents.

iv. CuO/ZnO Sorbent - Fixed-Bed Tests

Three mixed CuO/ZnO sorbents A, B, and C were prepared as described under sorbent preparation (Section IVC) with composition as given in Table 7. Early work (Table 8) performed with commercial mixed CuO/ZnO materials led to promisingly high desulfurization capacity. Therefore, it was considered important to establish the advantages provided by using supported CuO/ZnO mixtures with high states of dispersion. These sorbents were prereduced in 20% H_2 in nitrogen at 650°C in preparation for the desulfurization tests with simulated coal gas containing 200 ppm H_2S at 650°C. Regeneration was conducted with steam/air at 650°C.

The results for sorbent A, in which the ZnO was the first agent impregnated are shown in Figure 19. Nine consecutive duty cycles were run with 170ppm H_2S injection concentration and a space velocity of 4300 hr^{-1}. The initial sulfur capacity was 12 mole percent on the fresh sorbent, but capacity declined and stabilized to about 5 percent on subsequent duty cycles.

The results for sorbent B, in which the CuO was the first agent impregnated, are shown in Figure 20. Six consecutive duty cycles were run with 170ppm H_2S injection concentration and a space velocity of 3900 hr^{-1}. The initial sulfur loading on the fresh sorbent was 28.5 mole percent (run 137). This capacity was maintained after one regeneration (run 138). Subsequent duty cycles led to a decline in capacity which attained 4 mole percent after the fifth regeneration. Sorbent C, which was prepared by simultaneous impregnation of a copper-zinc nitrate solution with a 2:1 atomic ratio, was tested under the same conditions as sorbent A and B. The initial capacity on fresh sorbent was 8 mole percent at 10 ppm H_2S breakthrough concentration. This capacity declined to 1 mole percent after the first regeneration. It is not possible to offer an explanation for the superior, desulfurization capacity of sorbent B, of the three sorbents, but it is apparently related to zinc occupying more favorable cation exchange sites. The supported mixed oxides (Table 7 and Figures 19 and 20) demonstrated relatively high initial desulfurization capacities, but underwent rapid decreases in capacity on subsequent tests and provided no clear advantage over the single component supported sorbents, whether CuO or ZnO (Table 11).

d. Interference From Reactor Material

Particular consideration was given to the role of possible interferences in the fixed-bed stainless steel reactor by installing a quartz liner and repeating the desulfurization tests with both copper and zinc sorbents. Earlier blank tests run with an empty stainless steel reactor at 500-650°C indicated negligible sulfur removal to the walls for the simulated coal gas mixtures containing 200 ppm H_2S. Based on these earlier blank tests, no significant differences in sulfur removal capacities were anticipated for quartz versus stainless steel reactors.

This result was substantiated for tests run under similar conditions in quartz and stainless steel reactors for ZnO and V_2O_5 (Table 15), but surprisingly was not applicable to the CuO/zeolite sorbent.

A desulfurization test run over CuO/zeolite in stainless steel (Test 178) was in essential agreement with an earlier run (Test 90) under the same conditions but gave consistently greater sulfur loading than could be obtained in either quartz or a high nickel alloy (Incoalloy 800H) (Figure 24 and Table 15). Since the tests with empty stainless steel reactor and with ZnO and V_2O_5 in the stainless steel reactor did not show such analomous behavior, it is clear that this increased sulfur absorption is not a simple reaction with the stainless steel reactor.

The apparent explanation for this marked discrepancy is that a new desulfurization component results from an interaction between the copper and stainless steel. This new desulfurization component is very likely an iron-copper ferrite type product resulting from interaction of the copper with the 316 stainless steel reactor wall. The enhanced desulfurization capacity added by this new "scale product" suggests that copper-ferrite merits evaluation. Copper-ferrite might prove as significant as the zinc-ferrite under investigation at METC.

e. Comparison of Desulfurization Sorbents

A comparison of the principal desulfurization sorbents examined here is summarized in Table 16. The principal conclusions apparent from these results are the following:

> The highest mole percent conversions are realized with zeolite supported CuO and ZnO. However, with these two systems decreases in sulfur loading were observed during repeated desulfurization/regeneration cycles. The initially high capacity is believed to be

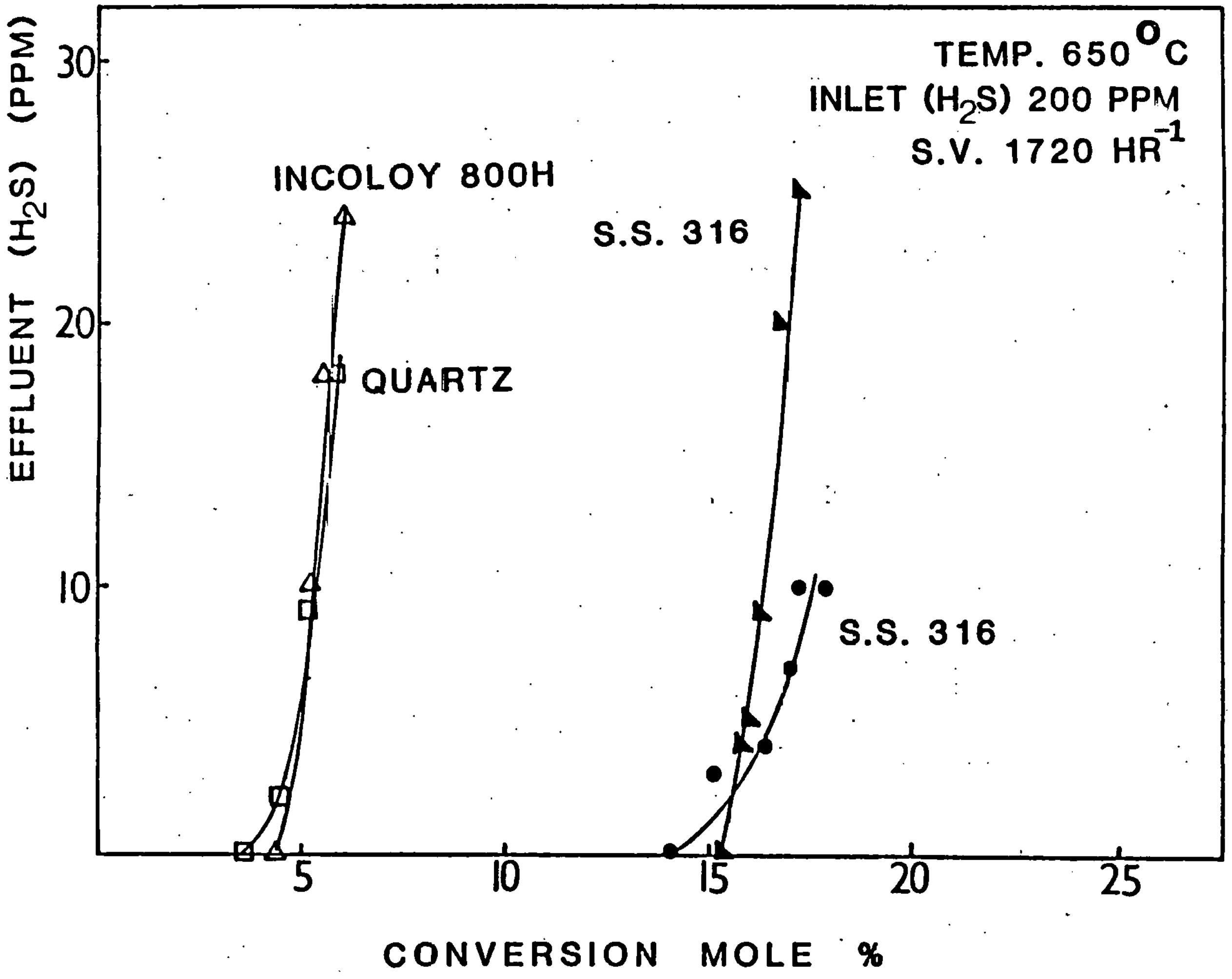

Figure 24 CuO/Zeolite Sorbent in Various Reactors.

TABLE 15

EFFECT OF REACTOR MATERIAL ON SORBENT CAPACITY

SORBENT	RUN#	REACTOR	MOLE %S
ZnO (United Catalyst)	44	STAINLESS STEEL	5.85
	158	QUARTZ	5.93
V_2O_5 (Union Carbide)	14	STAINLESS STEEL	0.25
	121	QUARTZ	0.28
CuO/Zeolite (Giner, Inc.)	90	STAINLESS STEEL	17.5
	178	STAINLESS STEEL	16.2
	173	QUARTZ	5.5
	175	INCOLOY 800 H	5.4

TABLE 16

DESULFURIZATION SUMMARY(1)

SORBENT	MOLE % S LOADING(2)	
	FRESH	AFTER (n) CYCLES
11% CuO/Zeolite	18	16(4)
18% ZnO/Zeolite	24	7(3)
6% CuO-11% ZnO/Zeolite	15	6(5)
33% CuO-65% ZnO	8	9(7)

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(1) DESULFURIZATION CONDUCTED AT 650°C, PREREDUCED IN H_2, 200ppm H_2S IN SIMULATED FUEL GAS WITH 6% WATER PARTIAL PRESSURE.

(2) SULFUR LOADINGS GIVEN AS CONVERSION TO SULFIDE (Cu_2S or ZnS) AT EXIT (H_2S) 10 (ppm).

due to very high dispersion of metal oxides on the zeolite support. The subsequent decrease in capacity can be attributed to crystallite growth or sintering and, in the case of zinc to volatilization.

Both the CuO/ZnO mixed sorbent and the CuO/zeolite demonstrate the capability of maintaining the H_2S concentrations below 1 ppm at significant loadings as shown in Figure 25. The mixed CuO/ZnO sorbent has demonstrated a remarkable maintenance of desulfurization capacity over seven duty cycles.

From a practical engineering point of view, the mixed sorbent CuO/ZnO provides larger sulfur loadings on either a weight or volume basis than the best of the supported sorbents tested, CuO/zeolite (Table 17). For this reason, the mixed CuO/ZnO sorbent was selected for further study in the fluidized-bed reactor.

2. Fluidized Bed Reactor Tests on CuO/ZnO

In view of the promising desulfurization performance with the mixed sorbent, CuO/ZnO, additional tests were conducted with the fluidized reactor to evaluate the role of sorbent particle size, water partial pressure, temperature, and desulfurization performance with selected organic sulfur compounds. A summary of the results of desulfurization tests in the fluidized-bed reactor is given in Table 18.

a. Effects of Particle Size

A series of desulfurization tests were conducted with CuO/ZnO in the fluidized-bed reactor with different particle sizes, i.e., 450 μm, 250 μm, and 175 μm, at a constant temperature (600°C) and with constant water partial pressure (26%). The fresh sorbent for each test was prereduced in dilute H_2. The superficial gas velocities at minimum fluidization conditions for 450 μm, 250 μm, and 175 μm, particle size were found to be 3.0,

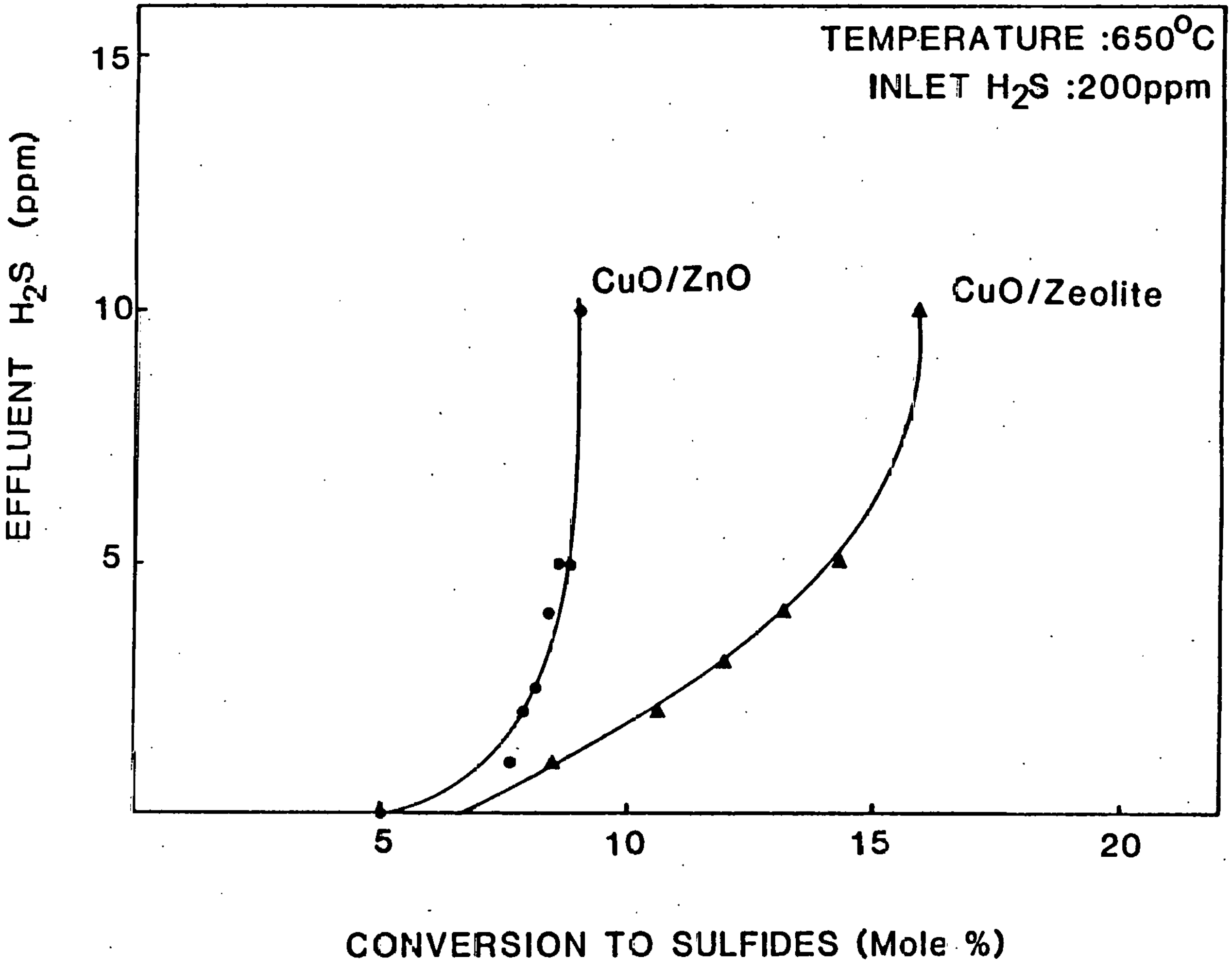


Figure 25. Comparison of CuO/ZnO and CuO/Zeolite

TABLE 17

ENGINEERING CONSIDERATIONS OF SELECTED SORBENTS

SORBENT	SULFUR CAPACITY AFTER FOUR REGENERATION CYCLES		
	MOLE % AS Cu_2S AND ZnS	GM. OF S PER 100 GM. OF SORBENT BED	KG OF S PER M^3 OF SORBENT BED
11% CuO/ZEOLITE	16	0.33	2.8
33% CuO-65% ZnO	9	2.9	44

TABLE 18

SUMMARY OF DESULFURIZATION TESTS IN FLUIDIZED BED REACTOR

Sorbent	Composition Wt %	Sorbent Wt. g	Desulfurization Particle Size μm	Desulfurization Temp. °C	Desulfurization Inlet PH_2O	Desulfurization S.V. hr^{-1}	Desulfurization Test Duration hr	Sulfur Loading Mole %	Run #
CuO/ZnO	33% CuO 65% ZnO	1	450	650	22	1990	2.0	32	204
CuO/ZnO	33% CuO 65% ZnO	1	450	650	9	1990	2.67	42	210
CuO/ZnO	33% CuO 65% ZnO	1	450	650	26	1990	1.75	28	211
CuO/ZnO	33% CuO 65% ZnO	1	450	650	15	1990	2.92	46	212
CuO/ZnO	33% CuO 65% ZnO	1	450	600	26	2330	2.00	37	213
CuO/ZnO	33% CuO 65% ZnO	1	450	550	26	2660	1.00	21	214
CuO/ZnO	33% CuO 65% ZnO	1	450	500	26	2790	2.00	45	216
CuO/ZnO	33% CuO 65% ZnO	1	250	600	26	1200	4.42	42	217
CuO/ZnO	33% CuO 65% ZnO	0.5	175	600	26	800	4.67	59	218
ZnO Harshaw	100% ZnO	1	450	600	26	2330	1.33	20	226
CuO/SiO_2	30% Cu	3.3	450	600	26	2330	0.067	1.6	227
CuO/SiO_2+ ZnO	30% Cu 100% ZnO	1 CuO 0.65 ZnO	450	600	26	2330	1.45	26	228
ZnO/Zeolite	3.22% ZnO	16.7	450	600	26	1200	0.5 to 1.00	8 to 16	237
CuO/ZnO Zeolite	6.83% CuO 4.22% ZnO	13.0	450	600	26	900	2.25	16	239
CuO/Zeolite	14.5% CuO	13.5	450	600	26	900	1.30	8.4	240

1.53, and 1.0 cm/sec, respectively. A reduction in particle size increases the specific surface area of the sorbent resulting in an additional increment in sulfur capacity. The sulfur capacities were observed to be 36, 43 and 59 mole % for 450 μm, 250 μm, and 175 μm, particle size respectively (Figure 26). These desulfurization tests with CuO/ZnO sorbent for the three different particle sizes showed that the sulfur capacity of the sorbent can be increased by increasing surface area with small particles. There is a practical limit on size reduction, however, to avoid excessive entrainment and attrition.

b. The Role of Water Pressure

Experiments were conducted with the mixed sorbent CuO/ZnO in the fluidized-bed reactor to examine the effect of water partial pressure on the desulfurization capacity at 600°C and 650°C. A particle size of 450 μm and water partial pressures between 9 and 26%, which encompass the range from air-blown to oxygen-blown gasification, were used in these tests (Figure 27). The sulfur capacities at 650°C cover the CuO/ZnO sorbent in Figure 27 were observed to be 42, 46, 32, and 27 mole %, respectively, corresponding to the water partial pressures of 9, 15, 22 and 26% in the simulated coal gas containing 200 ppm H_2S. A similar curve with a maximum at 15% water partial pressure was obtained at 600°C also.

Based on thermodynamic considerations alone, the water partial pressure would be expected to affect the desulfurization performance over ZnO, but not over Cu, since the H_2O is a product for sulfidation of ZnO, but not of Cu. A maximum in the desulfurization performance between 9 and 26% water partial pressure over this mixed sorbent, CuO/ZnO, indicates that both components are actively involved in the desulfurization process. A possible explanation for the maximum observed at 15% water pressure for

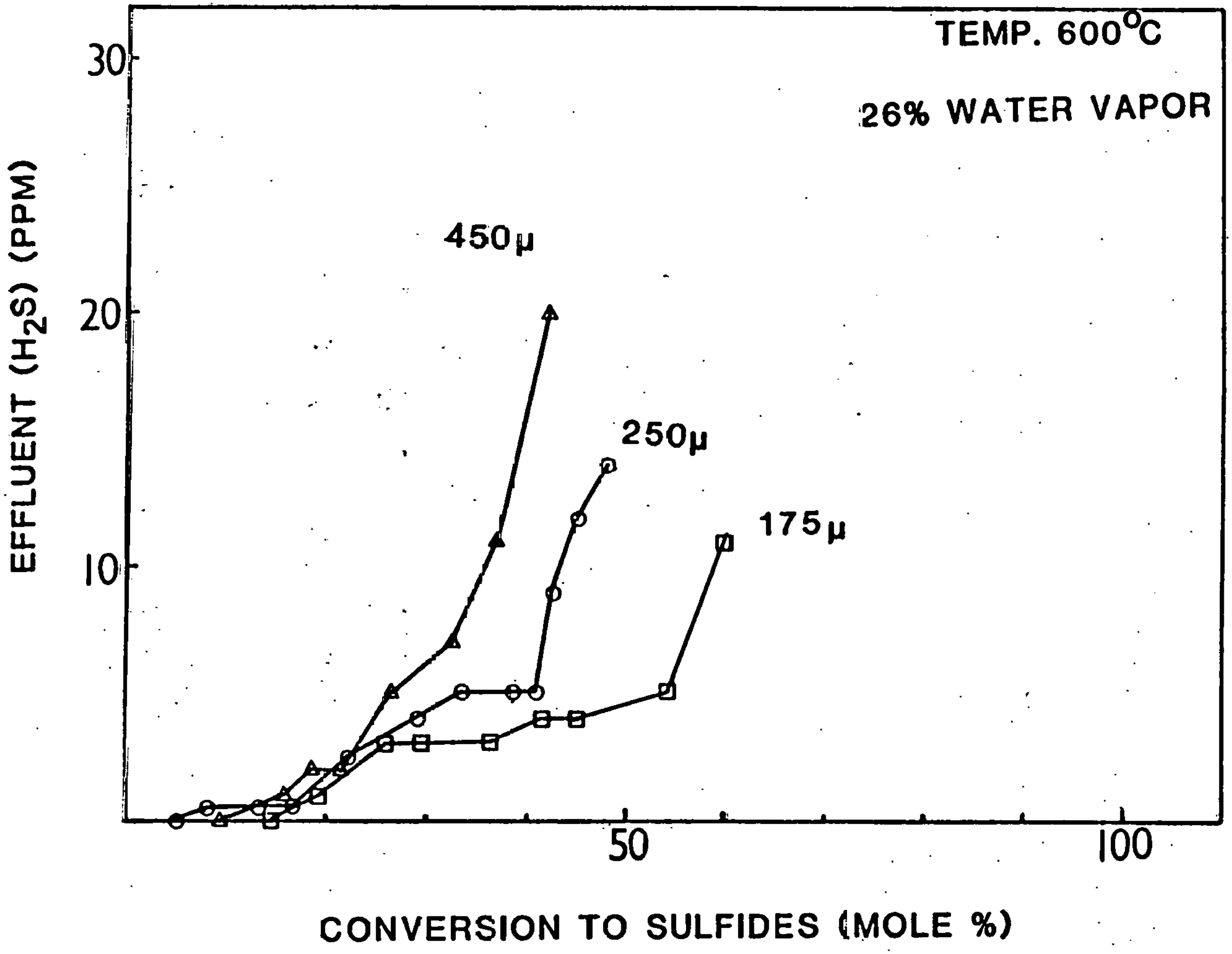


Figure 26. Effect of Particle Size on the Sulfur Capacity of CuO/ZnO.

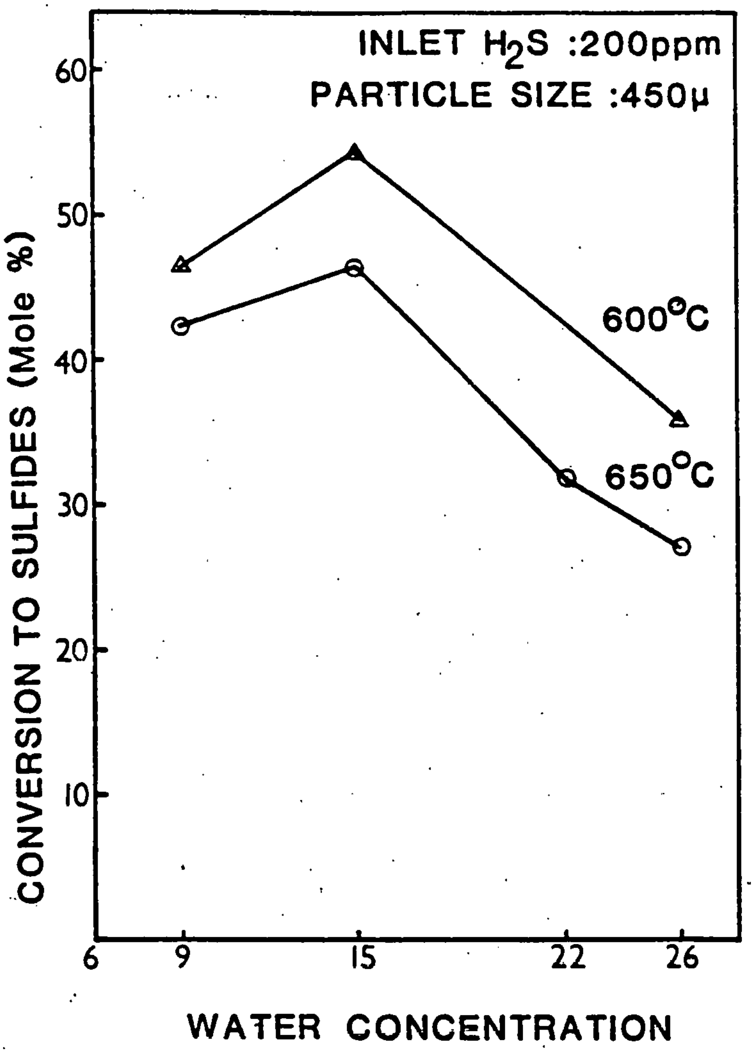


Figure 27. Effect of Water Concentration on Sulfur Capacity of CuO/ZnO.

CuO/ZnO at 600°C and 650°C is discussed later (see General Discussion)

c. The Role of Temperature

The effect of temperature between 500 and 650°C on desulfurization of simulated coal gas containing 200 ppm H_2S over the mixed sorbent, CuO/ZnO, and over unsupported ZnO was evaluated in the fluidized-bed reactor. A particle size of 450 μm, and a water partial pressure of 26% was used. The results of these tests are presented in Figure 28. For the mixed oxide sorbent, the overall trend is for a decline in desulfurization capacity in going from the maximum observed at 500°C to the highest temperature of 650°C. There is a surprising minimum at 500°C (reproduced in two separate tests) for which an explanation cannot be offered at this time. The desulfurization tests over ZnO show a weak dependence upon temperature between 500 and 650°C with a maximum at 600°C.

d. Verification of Packed-Bed Reactor Results in the Fluidized-Bed Reactor

In order to verify that the ranking of the desulfurization capacity derived from the packed-bed reactor was maintained in the fluidized-bed reactor, the desulfurization capacity of these sorbents in the fluidized reactor were determined. The results of these tests are presented in Figure 29, with the mixed CuO/ZnO sorbent exhibiting the highest mole conversion to sulfide at a 10 ppm breakthrough concentration of H_2S. The mixed sorbent also demonstrated a significant mole percent conversion at an H_2S concentration below 1 ppm. It is noteworthy that the desulfurization capacity of the physically blended CuO/SiO_2 (33%) and ZnO (66%) is greater than what would be expected based on the capacities of CuO/SiO_2 and ZnO alone. This suggests a synergistic effect between these sorbents, and this synergistic effect is considerably greater for the CuO/ZnO mixed oxide.

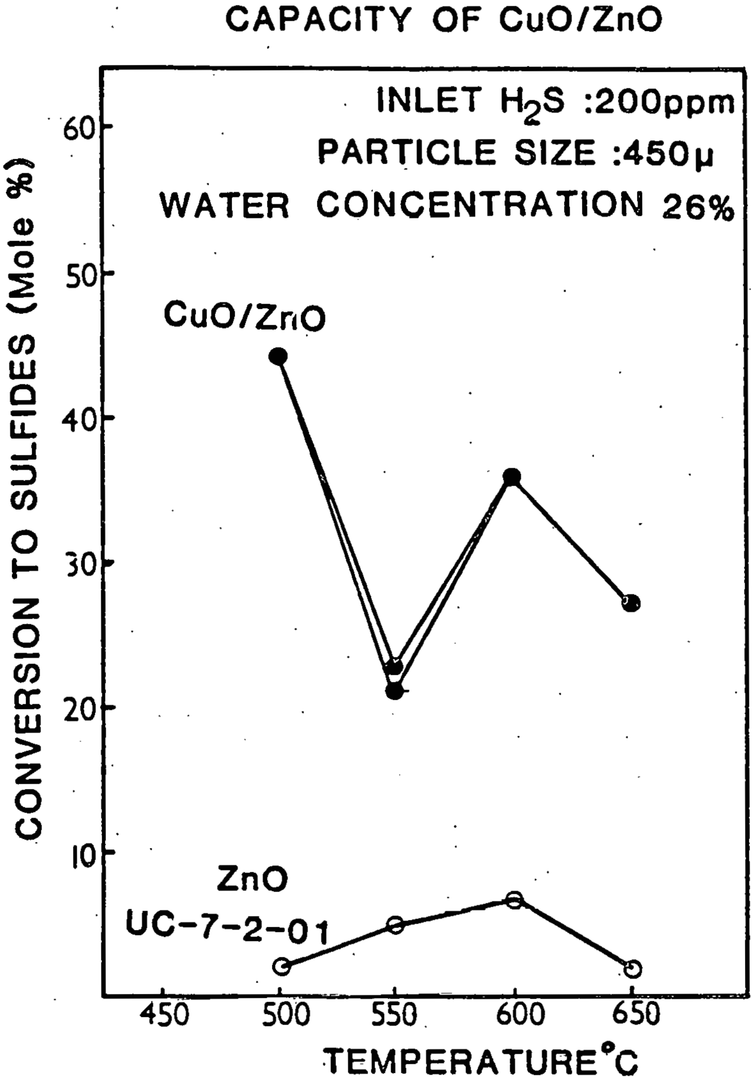


Figure 28. Effect of Temperature on Sulfur Capacity of CuO/ZnO and ZnO.

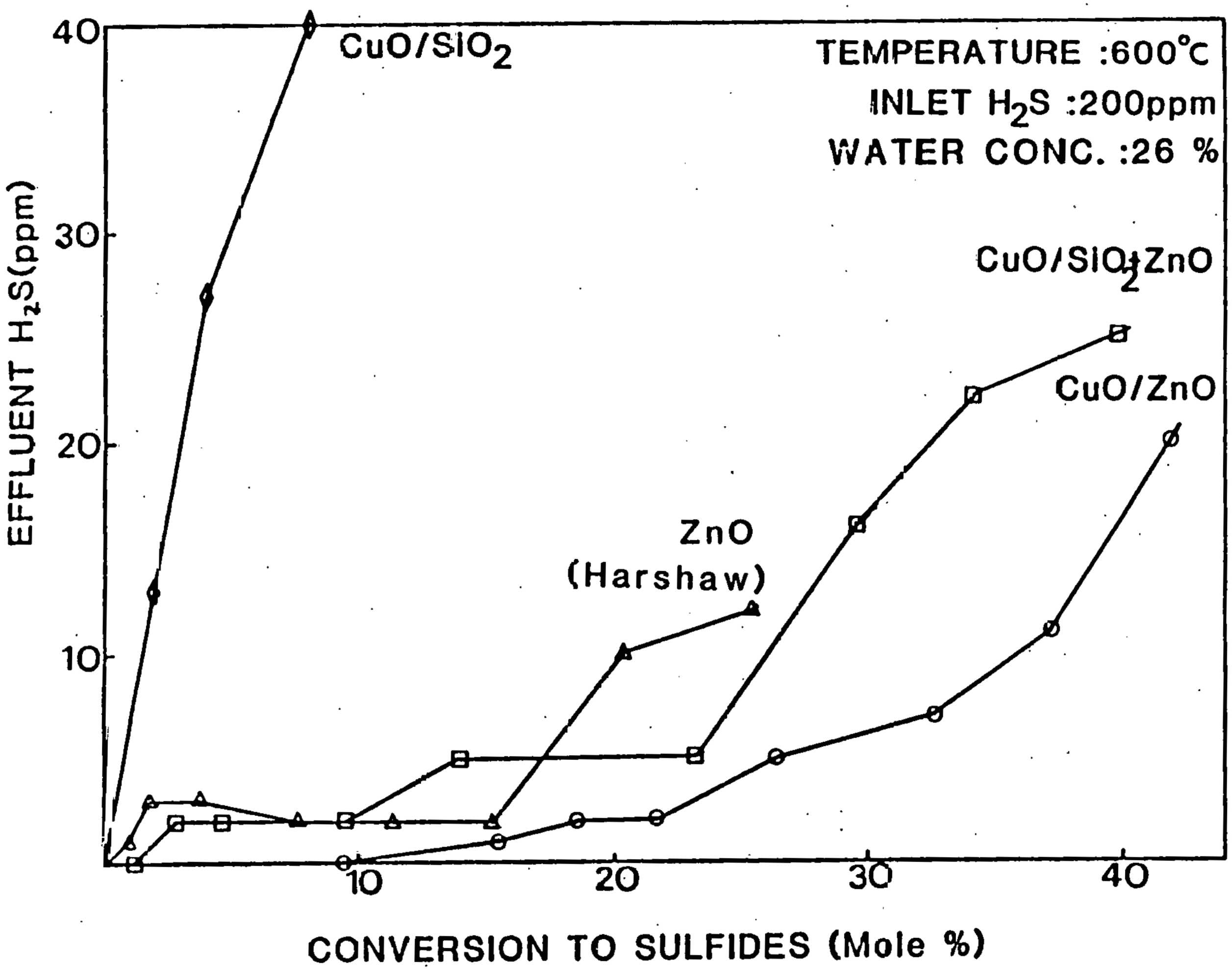


Figure 29. Comparison of Sorbents in Fluidized Bed

3. Desulfurization of Organic Sulfur Compounds

Desulfurization tests were conducted with the CuO/ZnO sorbent in the fluidized-bed reactor at 600°C with 450 μm, particle size sorbents for three organic sulfur compounds: COS, CS_2, and CH_3SH. Each compound was examined in dry and wet (15% water partial pressure) gas mixtures, and the results are given in Table 19. Promisingly high conversions (to Cu_2S and ZnS) were obtained for all three sulfur compounds. The presence of water partial pressure at 15% had comparatively little effect on the desulfurization capacity for COS, the capacity was enhanced for CS_2 and reduced significantly for CH_3SH.

E. Sorbent Characterization

1. ZnO Unsupported

In its high surface area form, ZnO showed high sulfur uptake and good chemical regenerability but poor structural regenerability. ZnO pellets were extensively characterized by SEM, microanalysis and low temperature nitrogen adsorption to investigate the pore structure and sulfur distribution as affected by sulfidation and regeneration. The ZnO pellets selected for this evaluation were retrieved from desulfurization tests conducted in a quartz reactor with a single layer of ZnO pellets as the reaction bed to minimize uncertainties due to non-representative sampling. Low temperature nitrogen adsorption isotherms were used to calculate the BET surface area, the pore volume, and the pore volume vs. pore size distributions.

The results of the low temperature nitrogen adsorption measurements are summarized in Table 20 and Figure 30. Pore volume analyses clearly show that the most significant changes in the pore structure of ZnO resulted from a heat treatment in nitrogen (inert) atmosphere, This

TABLE 19

SUMMARY OF ORGANIC SULFUR REMOVAL TESTS IN FLUIDIZED BED REACTOR

SORBENT - CuO/ZnO (G 66B), PARTICLE SIZE 450μ TEMP. 600°C

ORGANIC SULFUR	RUN#	INLET GAS COMPOSITION	SULFUR CAPACITY AS CU_2S AND ZnS (MOLE %
COS	232	N_2-74.2%, H_2-25.8%, COS-60 ppm	47 (10 ppm)
COS	233	N_2-59.2%, H_2-25.8%, H_2O-15%, COS-50 ppm	25-45 (10 ppm)
CS_2	241	N_2-48.2%, H_2-25.8%, H_2O-26%, CS_2-60 ppm	37-44 (15 ppm)
CS_2	245	N_2-100%, CS_2-100 ppm	9-18 (20 ppm)
CH_3SH	243	N_2-59.2%, H_2-25.8%, H_2O-15%, CH_3SH-30 ppm	25 (0 ppm)
CH_3SH	246	N_2-100%, CH_3SH - 100 ppm	56 (10 ppm)

Table 20. Low Temperature Nitrogen Adsorption Analysis of the Pore Structure of ZnO

History	N_2 BET Surface Area m^2/g	Pore Volume cm^3/g	Percent of Max. Pore Volume to 40 A ($0.1\ P/P_o$)	Percent of Max. Pore Volume to 425 A ($0.8\ P/P_o$)
Fresh	27.8	0.135	6	50
Heated at 750°C in N_2	13.0	0.055	4	45
After Desulfurization	9.9	0.029	10	34

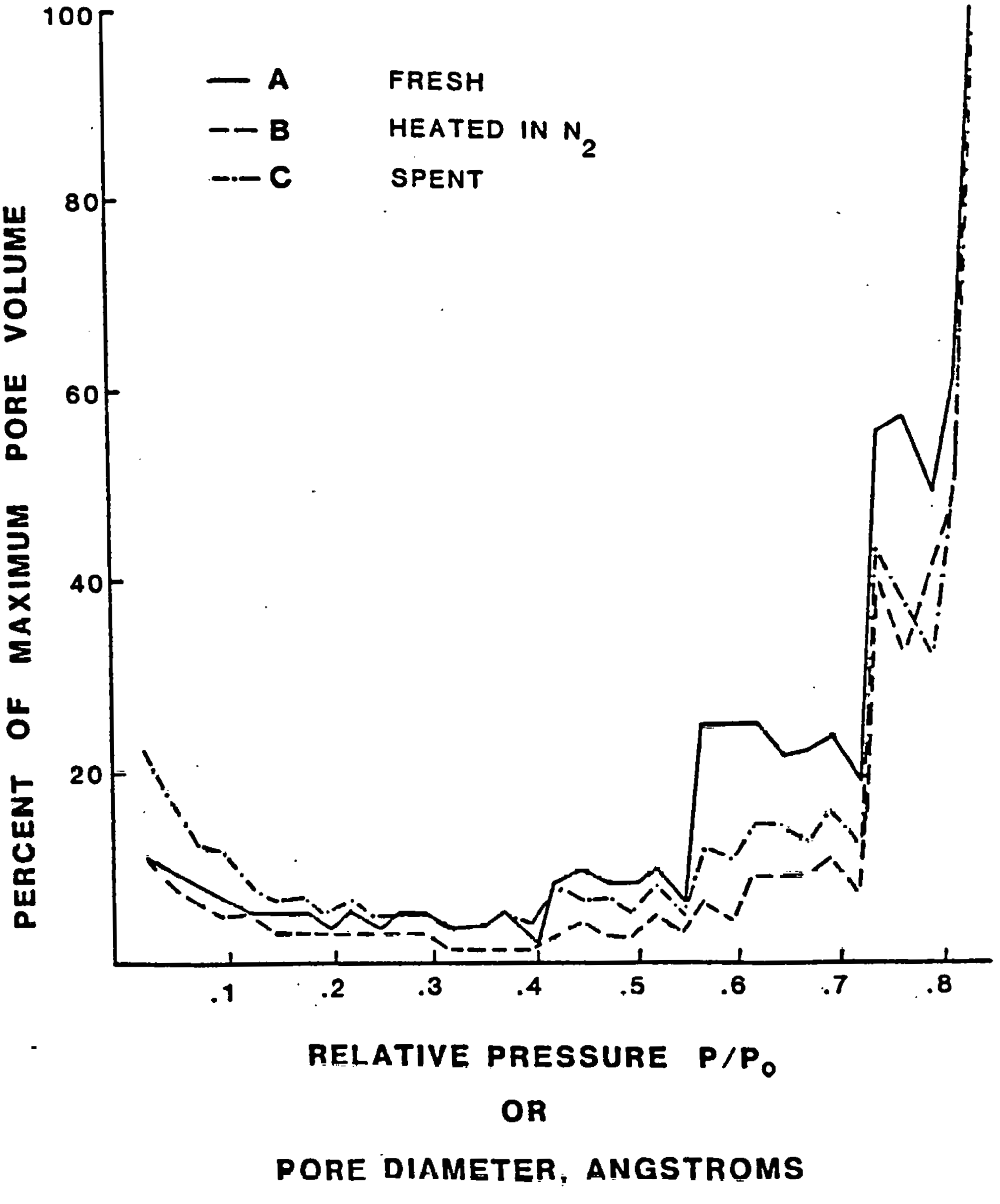
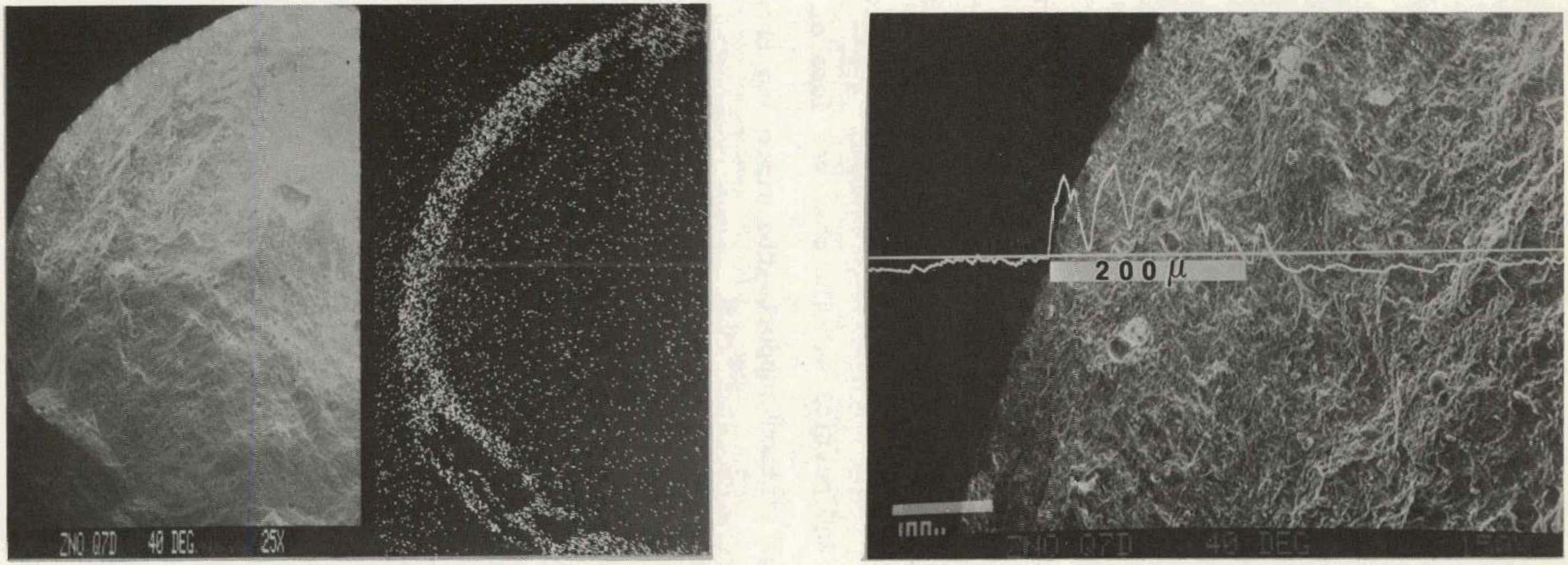


Figure 30. Pore Structure of ZnO From Low Temperature Nitrogen Adsorption - Percent of Maximum Pore Volume vs. Pore Size Distribution

indicates that thermal sintering of ZnO particles occurred in an inert environment and, further, that subsequent desulfurization produced relatively small changes in the pore structure. The small decrease in the total pore volume of the spent ZnO is attributed to a "swelling" of the pore walls due to the increase in molar volume associated with sulfidation of ZnO (see Pore-Plugging Model section). This explanation is supported by the results in Figure 30, which show the creation of new smaller diameter (< 40 Å) pores in the spent ZnO (curve C) when compared with the heat treated ZnO (curve B). A sample of ZnO regenerated by air oxidation showed significant further decrease in the specific surface area.

Regeneration by air oxidation of ZnS (spent ZnO) is a highly exothermic reaction. This could lead to very high temperatures locally and cause sintering of ZnO particles. The observed loss of specific surface area during regeneration supports the sintering theory and identifies the sintering during highly exothermic reaction to be a major cause for a severe decrease in the activity of regenerated zinc oxide.

Electron microscopy, microanalysis, and surface area measurements were obtained and examined in conjunction with a pore-plugging model that accounted for the geometric changes occurring in this type of gas solid reaction when the molar volume of product solid (ZnS: 24.4 ml/mole) is larger than the molar volume of reactant solid (ZnO: 14.4 ml/mole). If diffusional limitations in the pores are important the porosity decrese will be greater near the surface of the porous pellet, and pores will plug, limiting access to the inner part of the ZnO pellet. Figure 31 is a scanning electron micrograph of a section of a spent sorbent pellet and corresponding sulfur x-ray dot map and sulfur scans and shows concentration of sulfur at the outer 200 Å of the pellet. This and other microanalytical results confirm



A B C

Figure 31

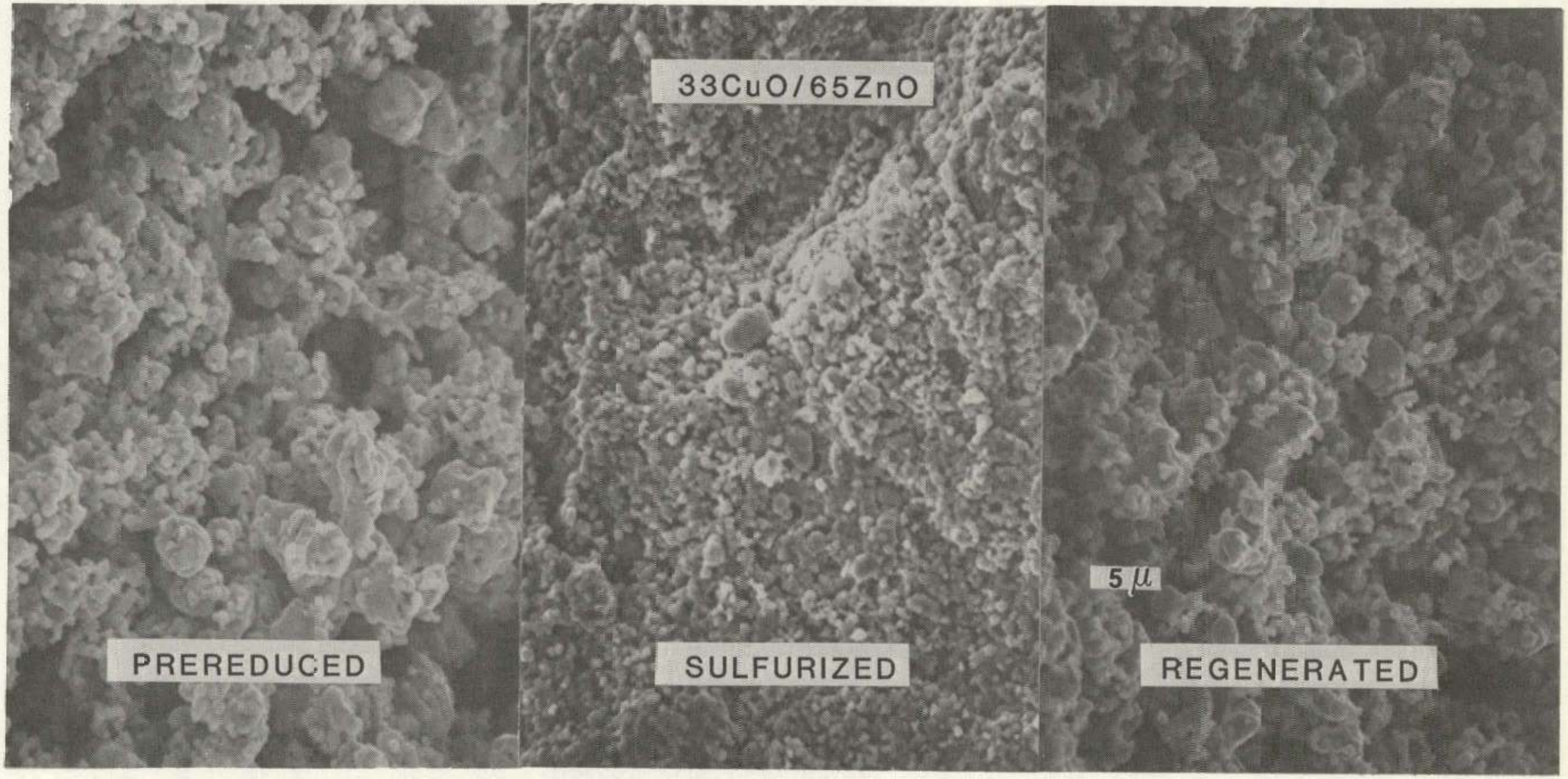
SCANNING ELECTRON MICROGRAPH (A), SULFUR DOT MAP (B) AND SULFUR SCAN (C) OF A SPENT ZnO PELLET that sulfur penetration in the ZnO pellet is limited to an outer thin layer of the pellet.

Earlier work had shown that upon regeneration in air, ZnO had lost its sulfur uptake activity. Sintering of ZnO particles during air oxidation was identified as a major cause for this. The investigation of regeneration alternatives to air oxidation of ZnO sorbents has now revealed that a combination of steam and air enhanced regeneration efficiency. Steam is known to provide pore widening in various adsorbent and catalyst systems and would offer a promising solution to the complicating effects of pore-plugging accompanying sulfidation which have been demonstrated in the present program.

Pore volume and pore size analyses identified closing of larger pores during sulfidation of ZnO and thermal sintering during heating and regeneration. Electron microscopy and microanalysis further demonstrated that the utilization of the presently used ZnO pellets was limited to about 200 Å. The pore plugging model provides guidelines to design improved sorbent structures.

2. CuO/ZnO

Electron microscopy of the mixed CuO/ZnO (G66B) sorbent in the prereduced (Figure 32a), sulfided (Figure 32b) and oxidation regenerated (Figure 32c) states provides insight as to the surface structural changes accompanying these steps. The second micrograph (Figure 32b) shows that during sulfidation, a finer grain surface structure has developed, producing a filling in of the coarser pore spaces. This apparently results from a creation of relatively fine crystallites of the sulfided metals, copper and zinc. The third micrograph (Figure 32c) indicates a return to the coarse open pore structure of the prereduced sorbent (Figure



(a) (b) (c)

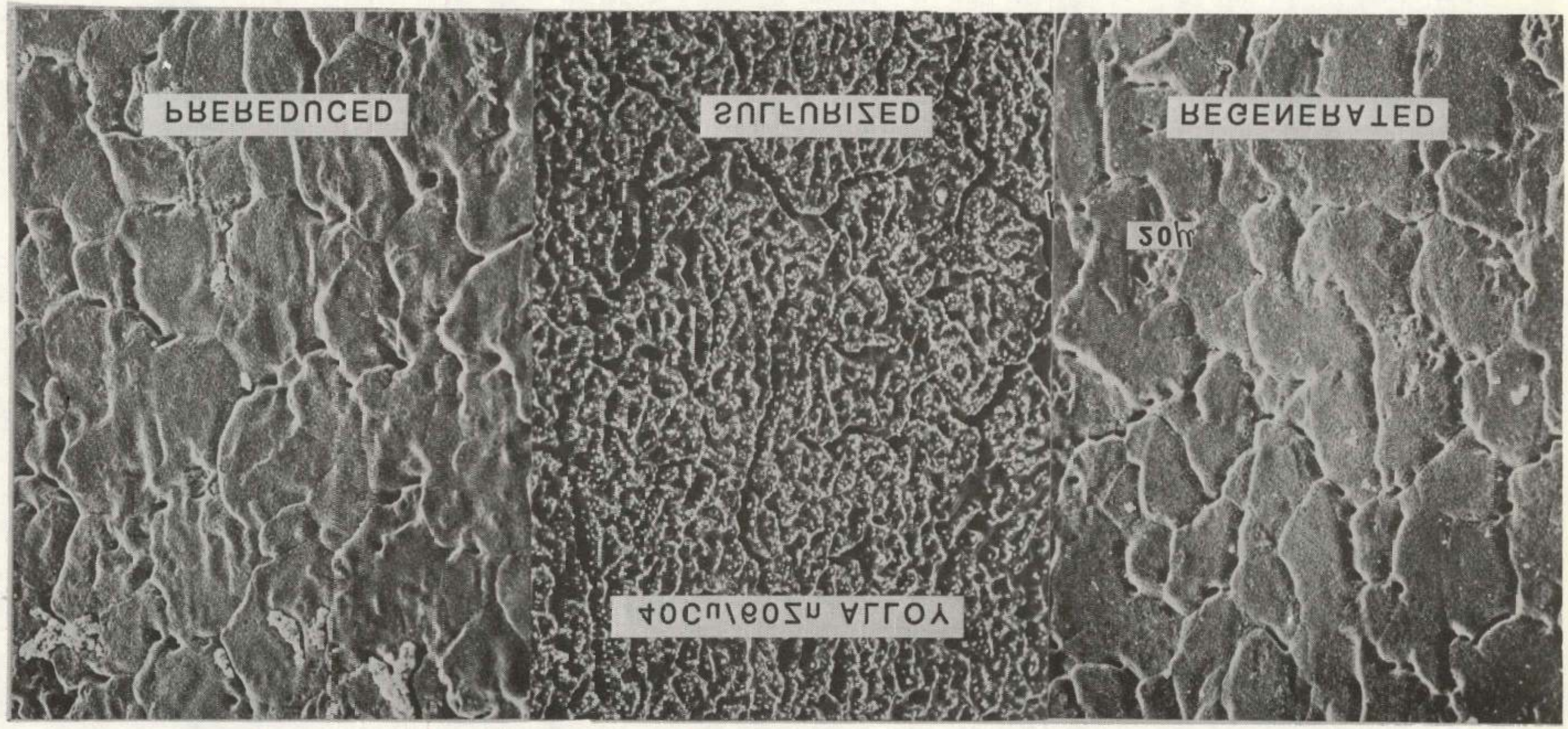
Figure 32. Electron Microscopy Characterization of CuO/ZnO Sorbent in the (a) Prereduced, (b) Sulfurized, and (c) Regenerated States.

32a) after oxidation of the sulfide.

The conditions of pretreatment used for prereduction might be expected to form a brass alloy on the surface of this CuO/ZnO. Sulfidation of this prereduced mixed oxide could be expected to form small crystallites of the new metal sulfide phases formed during desulfurization at the grain boundaries of the larger brass, CuO, and ZnO crystallites of the substrate. Exposure to reduction or oxidation conditions would be expected to cause sintering and generate relatively large brass or oxide crystallites, whereas the periodic sulfidation causes a drastic surface structural reorganization, countering the sintering, and the formation of the metal sulfide crystallites.

The validity of this concept was tested by electron microprobe and SEM examination of the surfaces of polished brass pellets (40 wt% Cu/60 wt% Zn) which had been consecutively oxidized in air at 650°C, prereduced in dilute hydrogen (20 vol % H_2 in N_2) at 250°C and sulfided with simulated coal gas at 650°C. Scanning electron micrographs of samples examined at each stage of treatment are shown in Figures 33a-33c. These micrographs clearly show that extensive surface structural reorganization accompanies the above gas/solid reaction steps: oxidation creates a rough gas-solid, fissured oxide scale; hydrogen reduction leads to a sintering of the oxide scale platelets; and the sulfidation process generates small crystallites of the new sulfide phases, Cu_2S and ZnS, on the surface of the reduced and sintered platelets of the metal oxide scale.

There is at least one documented instance for gas-solid reactions in which the repetitive recycling of a solid phase, FeTi alloy, between a hydrided state and a thermally dissociated state leads to progressive decrepitation of granular chunks of the alloy into a fine powder (Sandrock, 1976)



(a) (b) (c)

Figure 33. Electron Microscopy Characterization of Model Cu/Zn Alloy "Smooth" Surface in the (a) Prereduced, (b) Sulfurized, and (c) Regenerated States.

The present case of a gas-solid desulfurization reaction in which there has been repetitive recycling of a solid phase, mixed CuO/ZnO, between consecutive reactions of hydrogen reduction, sulfidation with H_2S, and oxidation provides one similarity to the FeTi-hydride system and one marked difference. The similarity consists of the alternation between reaction with and decomposition of the solid phase with a gaseous component, in this case H_2S, creates conditions of progressive decrepitation favorble for maintenance of a high state of dispersion of the CuO/ZnO sorbent. A principal difference between these two systems lies in the presence of a support structure in the case of CuO/ZnO which limits the disintegration of the sorbent during the consecutive formation and oxidation of the surface metal sulfide crystallites.

Extensive characterization of coprecipitated CuO/ZnO mixtures of the composition 33 wt% CuO/67 wt% ZnO have been conducted in view of the applicability of these systems to shift conversion and methanol systhesis reactions (Mehta, 1979; Bulko, 1979; Sengupta, 1981). There is very definitive evidence from XRD, TEM, STEM, SEM and some gas adsorption studies that under oxidizing conditions the copper has considerable solid state solubility as Cu^{2+} and/or Cu^{+} in the ZnO phase, whereas under reducing conditions, the copper appears as highly dispersed segregated copper crystallites within the matrix of ZnO crystallites. This is a very significant finding for high temperature desulfurization processes where surface area loss due to sintering during regeneration has been identified as a major cause of activity degradation. The mixed oxide, CuO/ZnO, provides a "structurally self regenerating" system. The results of characterization made for systems used under "steady state" reaction conditions must be used with reservations. However, until information can be obtained as to their applicability to the relatively short term alternation of reduction and oxidation conditions typical of a regenerable desulfurization sorbent.

F. Modeling Studies

A relatively simple pore-plugging model developed in earlier Giner, Inc. contract work demonstrated a good fit with the experimental data. Unfortunately, the two parameters which are derived in fitting the model to the data, TP (the pore-plugging constant) and Da (Damkohler number), do not relate well to process parameters, in particular the regeneration sequence. Subsequently, the model has been modified to obtain six different semi-empirical models describing the pore-plugging behavior of sorbents in a packed-bed desulfurization reactor.

These models have been identified as follows:

1. First generation linear model.
2. First generation exponential model (our original model).
3. Second generation linear model.
4. Second generation exponential model.
5. Third generation linear model.
6. Third generation exponential model.

In these titles, "linear" and "exponential" refer to the expression of the Damkohler number as either a decreasing linear or declining exponential function with respect to time. The different generations refer to increasingly more sophisticated expressions of the pore-plugging parameters, Tp.

Model Descriptions

The primary complication in applying a simple plug flow reactor model to the desulfurization of gases by metal oxides in a fixed-bed reactor is the phenomenon of pore-plugging. The metal oxides react with H_2S in the gas to form sulfides in the desired desulfurization reaction. The metal sulfides generally have a higher molar volume than the metal oxides. This causes the porosity of the sorbent material to decrease as the reaction progresses, eventually causing the pores to plug. The detailed reaction-diffusion problem related to this pore-plugging phenomenon has been treated extensively in the literature.

However, the incorporation of the complete reaction-diffusion model for the individual particle in an overall reactor model would require a cumbersome numerical scheme. In order to avoid the complexities of a full reaction-diffusion model, we have examined several empirical models which are based on a simplified pore-plugging model developed during our earlier work.

The reactor models considered here are based on the equation for a first-order irreversible reaction in a plug flow reactor:

$$\frac{dy}{d\xi} = -Day \qquad (1)$$

where

y = reactant concentration

ξ = reactor position coordinate

Da = effective Damkohler number

The models differ in the way in which the Damkohler number is computed. The Damkohler number includes kinetic resistances, external mass-transfer limitations, and internal sorbent diffusion limitations. As the reaction progresses pore-plugging causes a decrease in the Damkohler number.

First Generation Model

The available data is given as the reactor exit concentration versus time. The simplest treatment of the pore-plugging is to express the

Damkohler number as a function of time alone. For example,

$$\text{(2)} \qquad Da = Da_0 \exp\left(- \frac{t}{\tau p}\right)$$

or

$$\text{(3)} \qquad Da = Da_0 \left(1 - \frac{t}{\tau p}\right)$$

Integration of equation (1) with Da given by equation (2) gives the first generation exponential model:

$$\text{(4)} \qquad \frac{y}{y_i} = \exp\left(- Da_0\, \xi \exp\left(- \frac{t}{\tau p}\right)\right)$$

The solution of equations (1) and (3) yield the first generation linear model:

$$\text{(5)} \qquad \frac{y}{y_i} = \exp\left(- Da_0\, \xi \left(1 - \frac{t}{\tau p}\right)\right)$$

These first generation models take no account of the variation in the extent of sorbent reaction within the bed.

The <u>linear expression</u> for pore-plugging can be derived from an idealized picture shown in Figure 34 in which reaction occurs uniformly over a thickness of δ at the entrance region of each pore. The pores are all of uniform size, dp, and the H_2S is reacted completely. This visualization results in an expression for τp:

$$\text{(6)} \qquad \tau p = \frac{\delta \varepsilon op \; 6(1-\varepsilon)V}{a\, V_{sorb}\, \alpha\, C_{H_2S,O}\, G d_p}$$

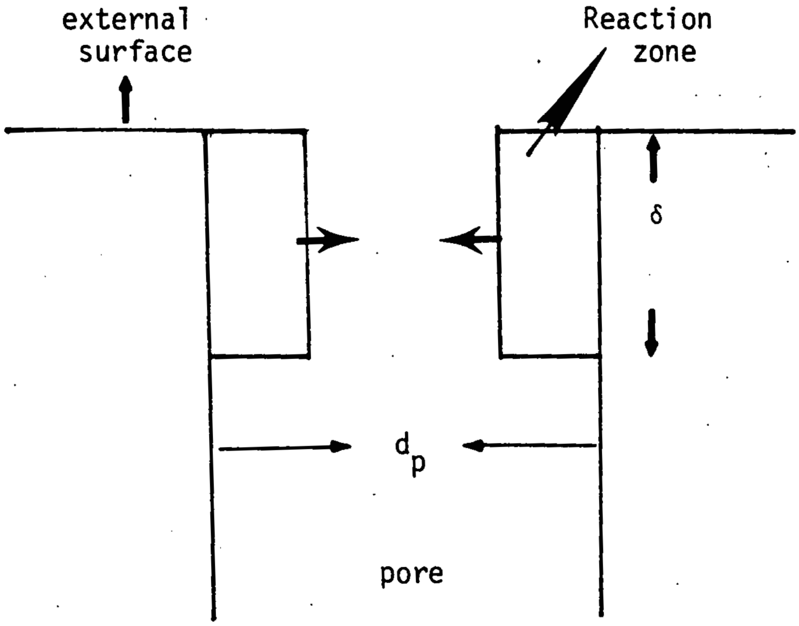


Figure 34. Idealization of Pore Plugging Phenomenon.

where,

τ_p = Time for pores to plug (in sec.)

δ = Thickness of reaction zone (in cm.)

ε_{op} = Initial sorbent porosity

ε = Reactor voidage

V = Reactor volume (cm^3)

a = Mole of sorbent reacted/mole of H_2S

V_{sorb} = Molar volume of sorbent (cm^3/mole)

α = Ratio of sulfide molar volume to oxide molar volume.

$C_{H_2S,O}$ = Inlet H_2S concentration (mole/cm^3)

G = Gas volumetric flow rate (cm^3/sec)

dp = Pore diameter

Using the value of τ_p in the first generation linear model which best fit the data in run #44, equation (6) yields a value of δ, the reaction zone thickness, of 72 μm. Microanalysis of the sorbent used in run #44 indicated that the ZnO sorbent was partially reacted within 250 μm of the particle surface. This verifies that the value of τ_p determined is physically reasonable.

The exponential expression takes account of the fact that pores are not all of a uniform size. While the linear model predicts that reaction will cease in a finite period of time, the exponential model predicts an exponential decay in reaction rate.

Second Generation Model

The reaction rate of the sorbent is proportional to y, the concentration of H_2S, so a second generation of models can be formulated by making the characteristic pore plugging time, T_p, inversely proportional to the local H_2S concentration, y:

$$(7) \quad T_p = \frac{p}{y}$$

This modification yields the second generation exponential and linear models, equations (8) and (9), respectively:

$$(8) \quad \frac{dy}{d\xi} = Da_o y \exp\left(-\frac{ty}{p}\right)$$

$$(9) \quad \frac{dy}{d\xi} = Da_o y \left(1 - \frac{ty}{p}\right)$$

The second generation linear model, equation (9) can be integrated in to give:

$$(10) \quad y = \frac{yiP\exp(Da_o\xi)}{Ptyit\left(\exp(D_{ao}\xi)-1\right)}$$

The second generation exponential model, equation (7), must be integrated numerically. The second generation models take account of the variation in H_2S concentration through the bed. However, these models are limited because they consider the local pore plugging time a function of y at time t alone.

Third Generation Model

A more realistic third generation of models can be formulated by recognizing that the pore-plugging time is a function of the local reaction rate integrated between times 0 and t. For this purpose, we introduce the extent of sorbent reaction, $\alpha = \alpha(\xi, t)$, and the characteristic extent of reaction for pore-plugging,   . The time rate of change in the extent of sorbent reaction is proportional to the local rate of H_2S reaction:

$$(11)\quad \frac{d\alpha}{dt} = -K\,\frac{dy}{d\xi}$$

The H_2S reaction rate can be expressed as a linear or exponential function of:

$$(12)\quad \frac{dy}{d\xi} = -Da_o y\left(1-\frac{\alpha}{\alpha p}\right)$$

$$(13)\quad \frac{dy}{d\xi} = -Da_o y\,\exp\left(-\frac{\alpha}{\alpha p}\right)$$

Equations (11) and (12) can be solved to give a third generation linear model. Equation (12) is integrated in ξ to give:

$$(14)\quad \ln\left(\frac{y}{y_i}\right) = -D_{ao}\xi + \frac{D_{ao}}{\alpha p}\int_0^{\xi}\alpha\,d\xi$$

Differentiation by t yields:

$$(15)\quad \frac{1}{y}\,\frac{dy}{dt} = \frac{D_{ao}}{\alpha p}\int_0^{\xi}\frac{d\alpha}{dt}\,d\xi$$

Substitution for $\frac{d\alpha}{dt}$ from equation (10) and integration in ξ gives:

$$(16)\quad \frac{1}{y}\,\frac{dy}{dt} = \frac{Da_o}{\alpha p}\,K\,(y-y_i)$$

This equation can be integrated in time to yield the third generation linear model:

$$(17) \quad y = \frac{yi}{1-[1-\exp(Da_o\xi)]\ \exp\left(\dfrac{-yiDa_oKt}{\alpha p}\right)}$$

The third generation exponential model requires the numerical integration of equations (11) and (13) in both t and ξ this would involve considerable numerical work.

Numerical Methods

Five of the models mentioned above were fit to data obtained at Giner, Inc. in a fixed-bed desulfurization reactor operating at 650°C. The data are given as H_2S exit concentration as a function of time.

For the first generation models the best fit values Da_o and Tp are easily derived by linear regression on a calculator. The second and third generation models can be reduced to single non-linear equations for outlet concentration, equations (10) and (17). A computer subroutine, RMIN, was used to iterate numerically to find the best values of the parameters.

The evaluation of the second generation exponential model requires numerical integration in ξ. This was accomplished using a fourth-order Runge-Kutta routine, RR, with variable step-size. The routine uses various step-sizes to achieve a prescribed maximum error. Again the parameters are iterated using RMIN to achieve the lowest sum of squares.

Results and Conclusions

All 20 test results were compared with the model predictions. For illustrative purpose, the data fit for the five models to experimental data for Run #47 with ZnO sorbent is shown Figures 35-39. All of the models fit the data well, except for the second generation linear model. The second generation model gives a theoretical curve which is generally too steep to fit the data. This problem is due partially to the linear functionality of

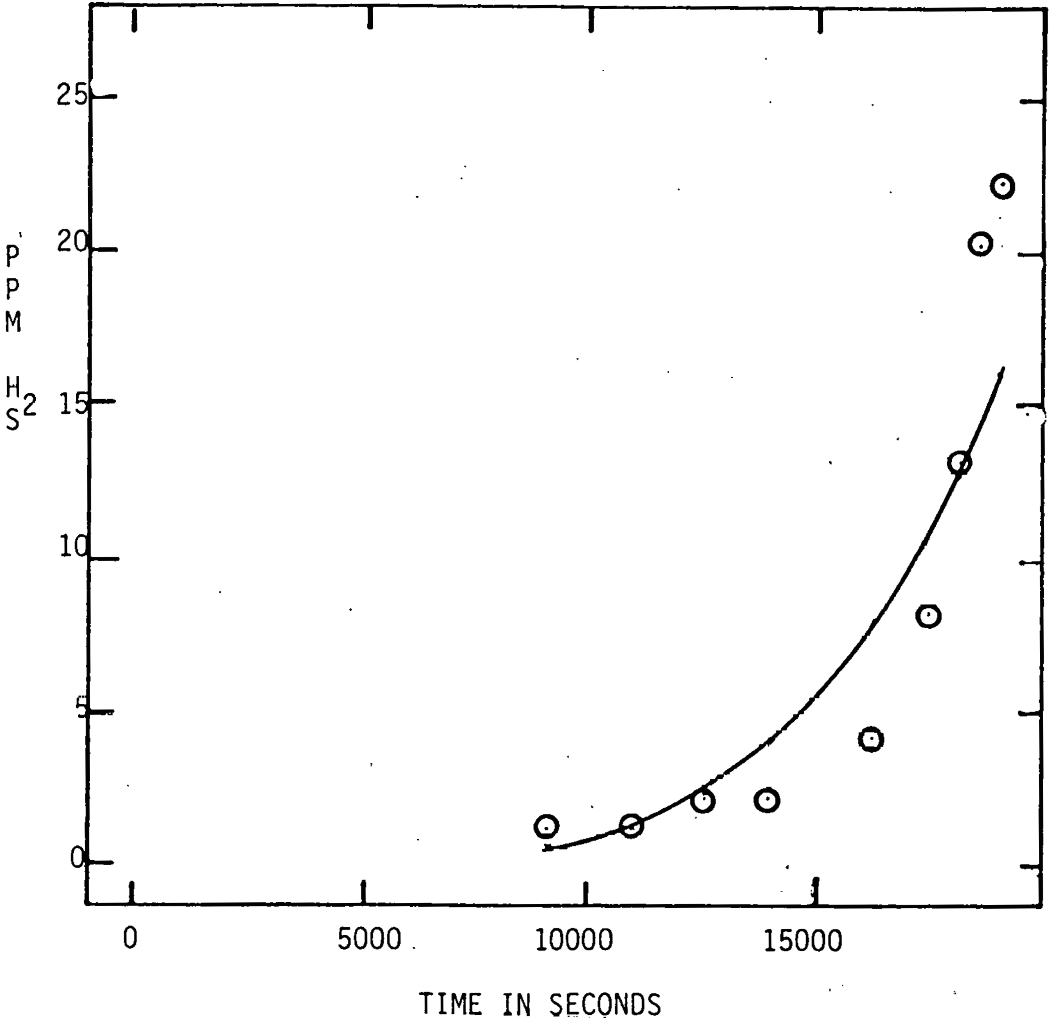


Fig. 35. 1ST GENERATION EXPONENTIAL MODEL RUN 47

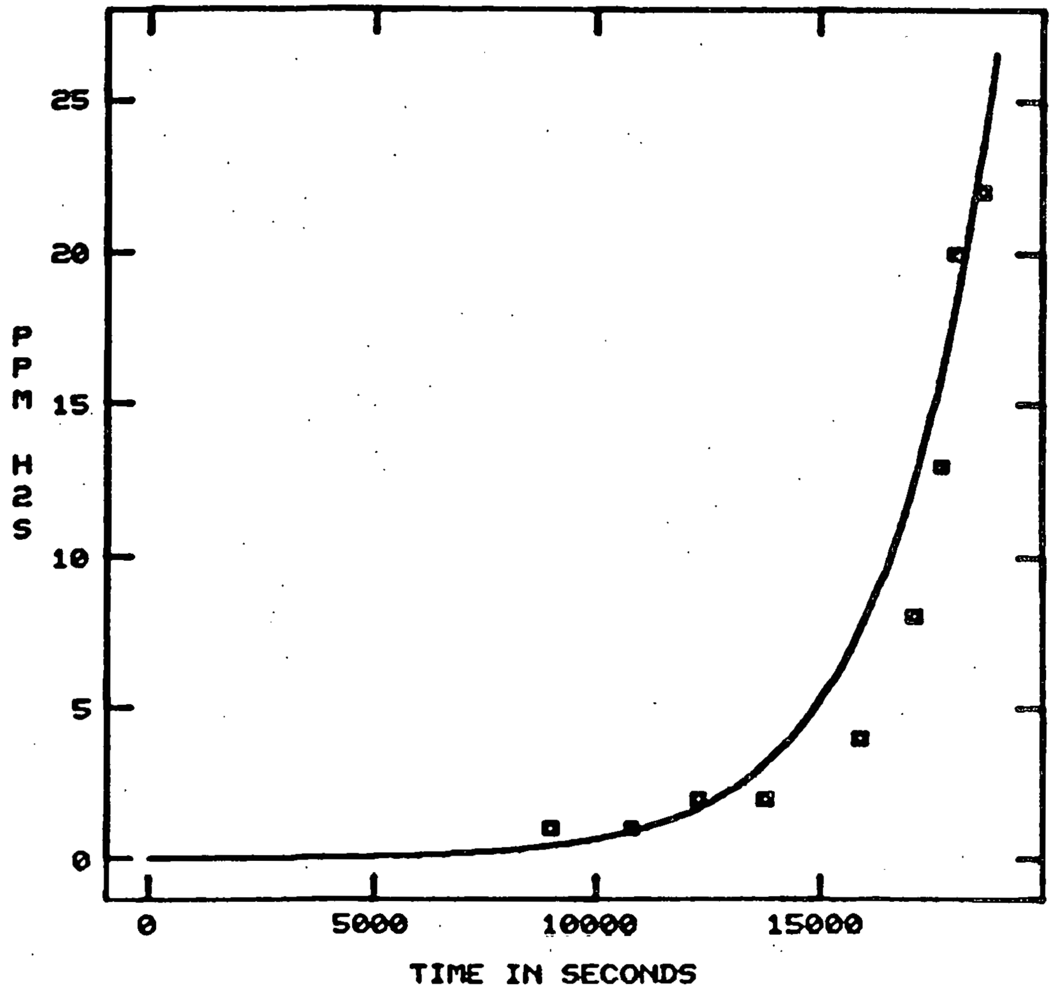


FIG. 36 1ST GENERATION LINEAR MODEL RUN 47

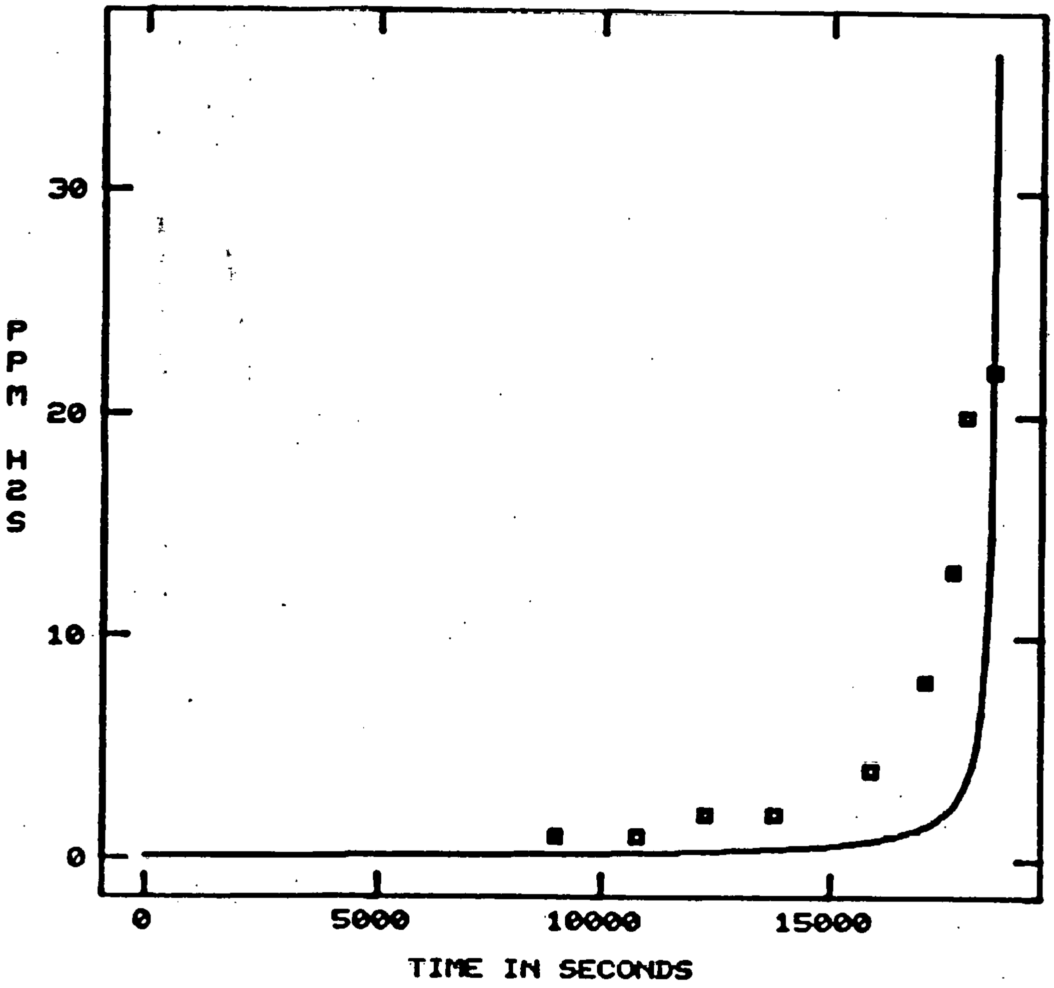


FIG. 37 2ND GENERATION LINEAR MODEL RUN 47

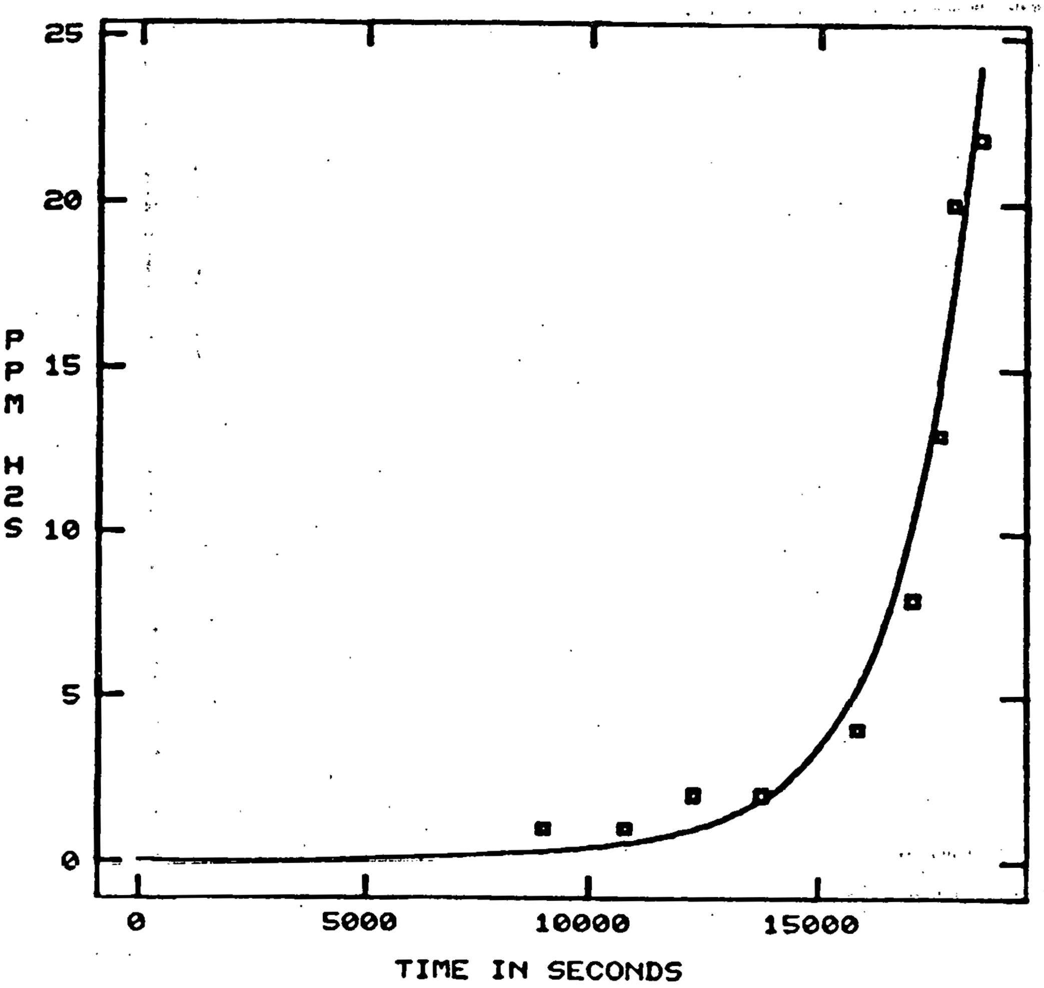


FIG. 38 2ND GENERATION EXPONENTIAL MODEL RUN 47

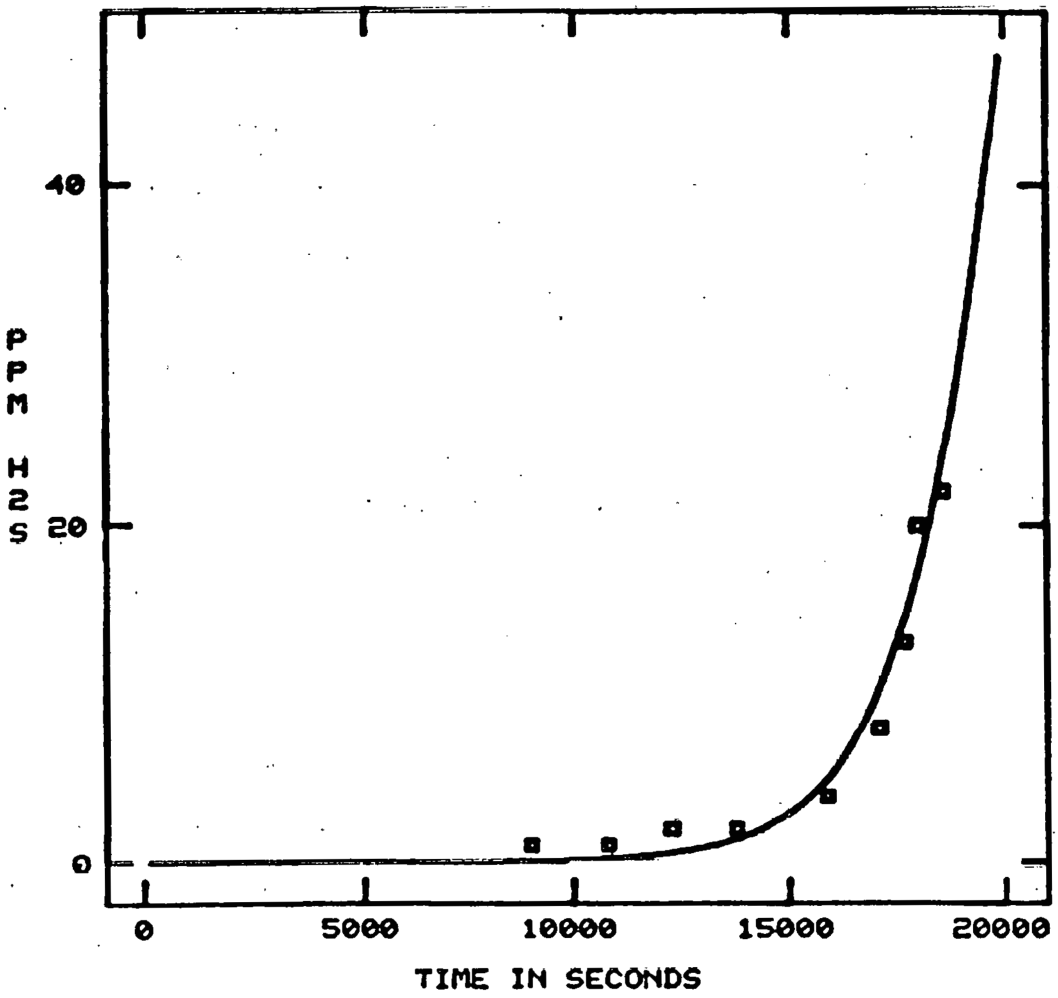


FIG. 39 3RD GENERATION LINEAR MODEL RUN 47 the Damkohler number with respect to time, which gives Da = 0 in a finite period of time. The problem is further exacerbated by the nature of the second generation models. In these models the Damkohler number depends on the current H_2S concentration, rather than the H_2S concentration history. To understand why this causes a steep concentration versus time curve, consider a point near the reactor exit. Through the early stages of reaction this point sees very little H_2S and so the sorbent remains fresh. As breakthrough begins, however, our reactor position begins to see substantial H_2S concentrations. Although the sorbent has adsorbed relatively little H_2S the second generation model tells us that because the current H_2S concentration is high and the reaction time is long, the sorbent will have a low activity. On the contrary, since the sorbent is fresh, it will have high activity.

The internal reactor profiles corresponding to the parameters which were fit to run #47 are given in Figures 40-41. The shapes of reactor profiles for the first generation models do not change with time, because Da is not a function of reactor position. The second generation models show some change in the shape of the reactor profile. The third generation model, however, is the only model which shows the kind of reaction front progression that one expects for this type of reaction. The shape of the reaction front remains the same as it progresses through the reactor because it continues to see relatively unreacted sorbent.

The values of the best fit parameters are given in Table 21 for a number of runs. For the second generation models we define an effective plugging time as:

$$Tp, \text{ eff} = \frac{p}{y}$$

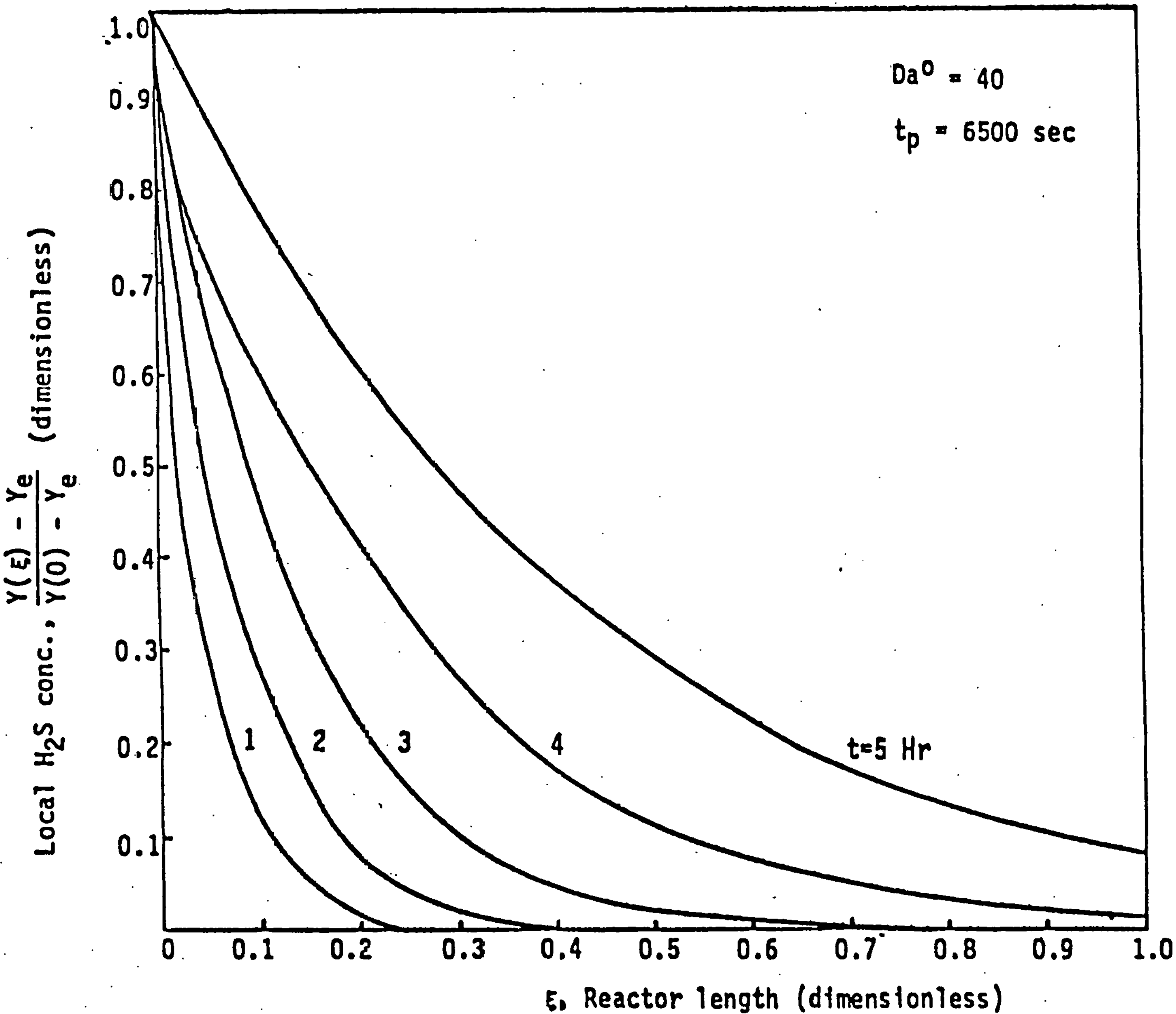


FIG. 40. 1ST Generation Exponential Model.
H_2S Concentration Profile in the Reactor at Various Times.

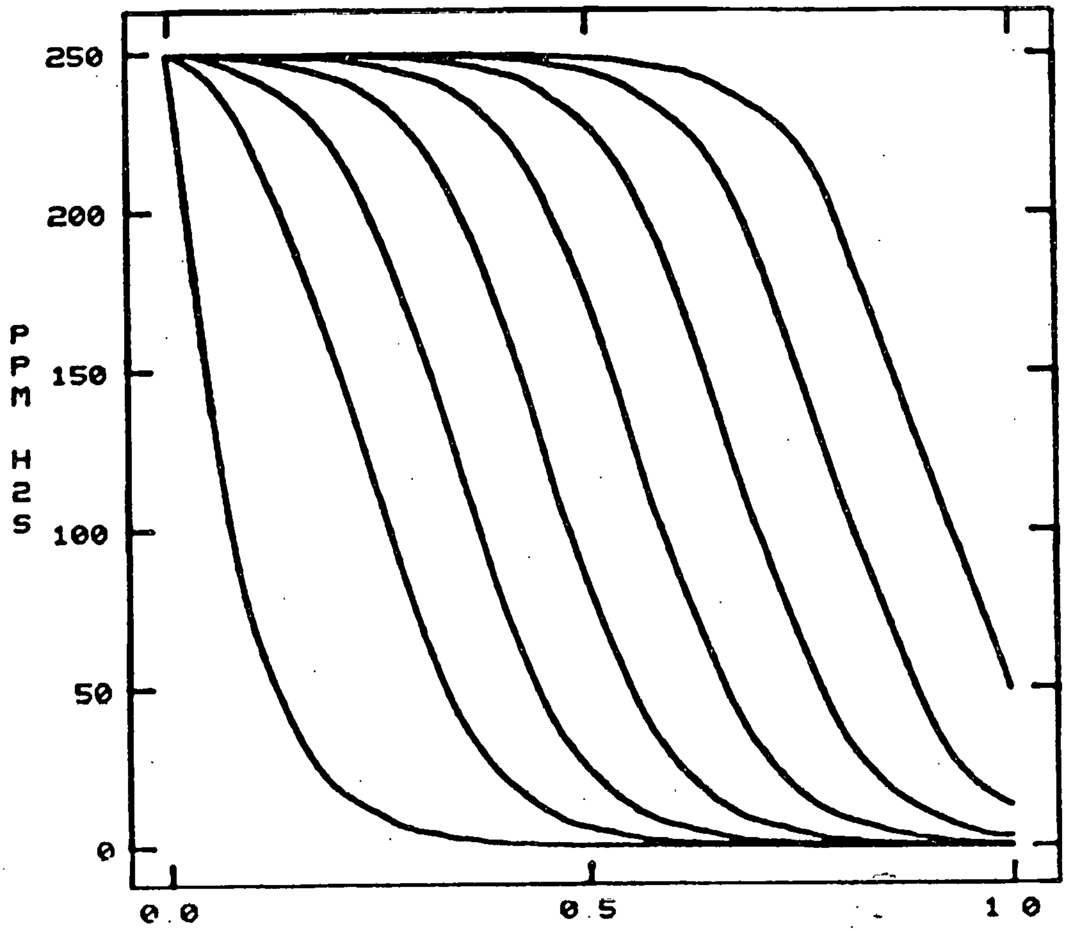


FIG. 41 XI-REACTOR POSITION

3RD GENERATION LINEAR MODEL RUN 47 REACTOR PROFILES

TABLE 21

Best Fit Parameter Values

Material	History	Run #	1st generation linear		2nd generation linear			3rd generation linear			1st generation exponential		2nd generation exponential		
			Da_o	seconds τ_p	Da_o	$p \times 10^{-6}$	seconds $\tau_{p,eff}$	Da_o	$p \times 10^{-6}$	seconds $\tau_{p,eff}$	Da_o	seconds τ_p	Da_o	$p \times 10^{-6}$	seconds $\tau_{p,eff}$
ZnO	fresh	47	10.11	24,298	7.58	4.67	18,680	13.56	5.57	22,279	141.5	10,836	8.57	1.73	6,905
United	1st steam regen.	48	8.60	33,187	5.09	6.40	25,586	8.83	8.37	33,484	14.1	13,932	6.64	2.77	11,071
Catalyst	3rd steam regen.	50	11.09	31,384	4.66	7.07	28,278	11.69	7.86	31,426	81.3	6,912	7.73	2.53	10,112

For the third generation model:

$$\mathrm{Tp,\ eff} = \frac{\alpha p}{Da_o Kyi}$$

The parameters for the first generation exponential model fail to show consistent trends, because there is a strong interaction between the two parameters. For example, in runs 47, 48, and 50, TP first increases then decreases with repeated regenerations, while Da_o first decreases then increases with regeneration.

Of the five models tested all except the second generation linear model fit the data adequately. The first generation exponential model, however, failed to give consistent parameter values. Thus, the first and third generation linear models and the second generation exponential models give satisfactory results. Of these the third generation linear model is preferable on theoretical grounds, because it makes the sorbent activity a function of the concentration history seen by the particle. A third generation exponential model should also work well. Although the numerical work involved in computing such a model would be greater, the third generation exponential model will be tested against the experimental results.

The internal reactor profiles predicted by the second and third generation models are distinctly different, especially at high exit concentrations of H_2S. In order to discriminate between these models with respect to how well they describe the packed-bed desulfurization reactor, a set of desulfurization experiments were performed in which each desulfurization cycle was allowed to run to high (100-200 ppm) exit concentrations of H_2S. The models were applied to these new data. A "best" model was identified which fit at the high concentrations.

V. GENERAL DISCUSSION

A survey of hot gas cleanup process technology (Onursal, 1979) indicates that Fe_2O_3 and CuO provided the widest range of compatibility with the various coal gasifiers available for sulfur removal capability. The results of the present work, along with that of the four preceding examinations (Huff, 1936; Nachod, 1948; Lewis,1963; Meyer, 1978) of copper systems, demonstrate that copper can effectively remove hydrogen sulfide at temperatures between 500°C to 650°C, and that regeneration can be achieved with combinations of air or air/steam in the temperature range of 500-800°C. The formation of copper sulfate had been a problem but the use of steam-air mixture or inert (or reducing) atmosphere decomposition minimizes this.

This review of earlier work on copper sorbents, in addition to providing evidence of the promise of copper as a desulfurization agent for cleanup of coal gases, reveals the deficiencies of the earlier systems. Earlier sorbents, whether unsupported mixed oxides or supported copper systems, failed to provide the structural and thermal stability adequate for sustained, desulfurization/regeneration duty cycles under simulated high temperature use conditions. Few of these studies provided an adequate examination of the conditions optimum for regeneration. The studies employing fluidized-beds and involving solids mixing and transfer (Meyer, 1978; Agrawal, 1980; Lewis, 1963) identified the problems, without finding solutions of gas-solid and solid-solid mixing and equilibration, notably in the regeneration reactions. In general inadequate sorbent structures, insufficient regeneration and inadequate materials performance such as corrosion limited the commercial application.

The present work indicates that copper sorbents, when optimized, can provide a high degree of sustained desulfurization capacity at temperatures around 500°C with regeneration using a combination of air/steam plus nitrogen at 650-750°C followed by reduction around 250°C. The low levels (< 1 ppm) to which sulfur, as H_2S, can be reduced in simulated coal gases have been demonstrated. This capability has particular application to systems such as the molten carbonate fuel cell and certain combined cycle power plants. The merits of using a hydrothermally stable support such as a rare earth loaded zeolite to provide a high order of dispersion of the copper and a high order of thermal and structural stability under the conditions of desulfurization, oxidation regeneration and reduction appropriate for the hot cleanup of simulated coal gases have also been demonstrated.

A very surprising, but advantageous finding is the ability of copper based sorbents to reduce H_2S level below 1 ppm. Thermodynamic analyses show that in a coal/gas environment, CuO would be reduced to metallic Cu which would react with H_2S to give Cu_2S. The equilibrium H_2S concentration, however, for the reaction

$$2Cu + H_2S \rightarrow Cu_2S + H_2$$

is greater than 200 ppm at 650°C. An explanation that copper can only reduce H_2S below 1 ppm by chemisorption on metallic Cu is not consistent with rather large sulfur uptake capacity (18 mole percent). A possible explanation is: kinetically limited, incomplete reduction of CuO in a thermodynamically reducing environment to provide presence of some Cu_2O. The equilibrium H_2S concentration for the reaction

$$Cu_2O + H_2S \rightarrow Cu_2S + H_2O$$

is about 0.01 ppm (Figure 42). Presence of high water vapors would increase the possibility of Cu_2O formation. This may explain why the maximum sulfur capacity occurs at 15% water vapor pressure as shown in Figure 27.

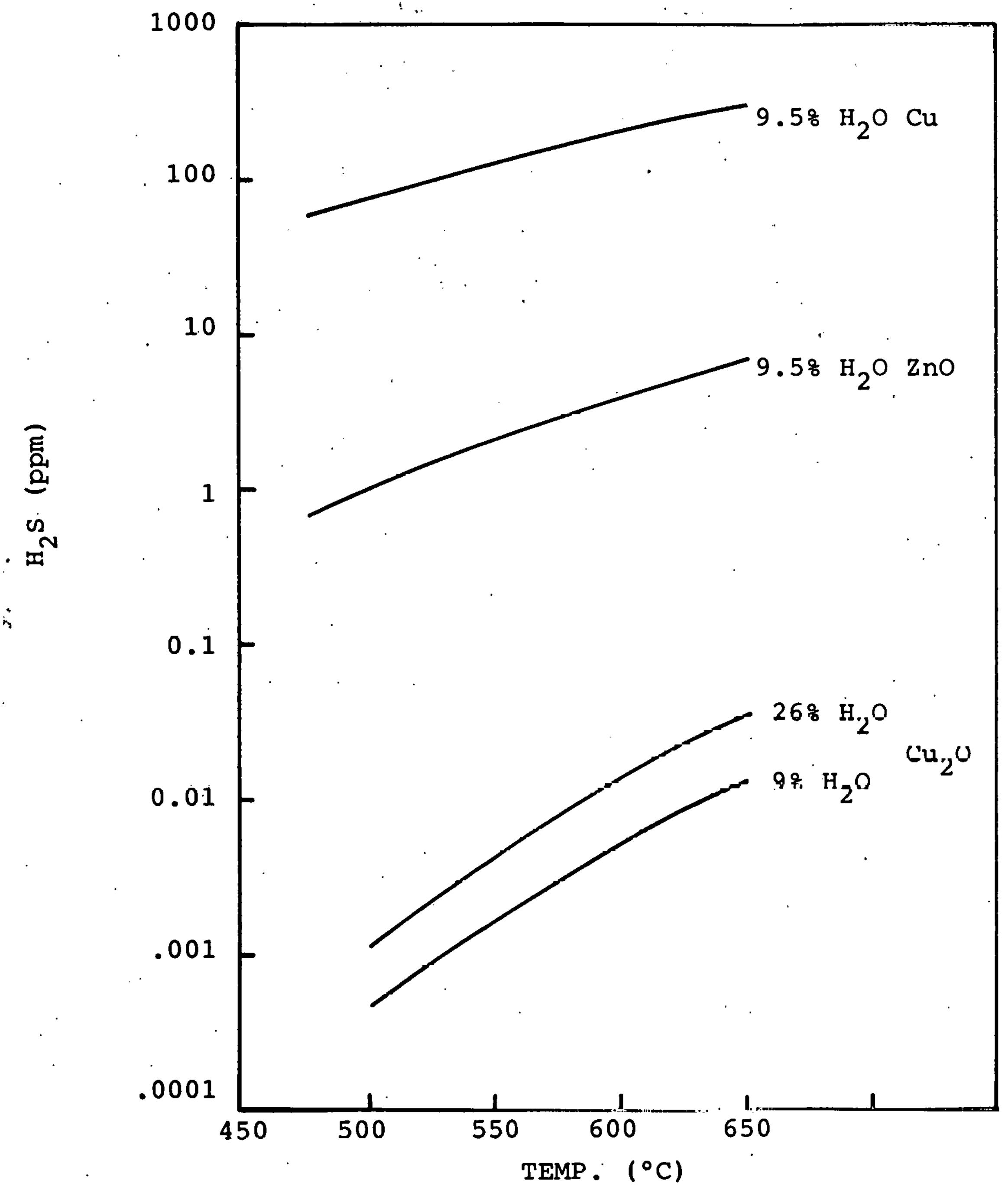


Figure 42. Equilibrium for H_2S Dry and Wet H_2 Over Cu, Cu_2O, and ZnO.

Another explanation is the formation of solid solutions ($Cu + Cu_2O$) and/or ($Cu + Cu_2S$); if so, the thermodynamic calculations based on individual components are invalid.

The desulfurization capacity of the mixed CuO/ZnO sorbent was greater than what would be expected from the desulfurization capacity of either component alone. This synergistic effect was also evident in the physical blend of CuO/SiO_2 and ZnO as seen in Figure 29. In addition to providing increased desulfurization capacity, the CuO/ZnO exhibited conversion to sulfides at an H_2S concentration below 1 ppm. Similarly, researchers at Kennecott (Meyer, 1978; Agrawal, 1980) have observed that the binary sorbent CuO/FeO_x was able to obtain lower ambient H_2S concentrations than either component based on thermodynamic calculations. The research at METC (Grindley, 1981, 1982, 1983) on another mixed sorbent, Fe_2O_3/ZnO, has been encouraging. The other promising observation regarding the mixed CuO/ZnO sorbent is its maintenance of desulfurization capacity after several regenerations.

VI. CONCLUSIONS AND RECOMMENDATIONS

This investigation has established that highly dispersed CuO on zeolite, highly dispersed CuO + ZnO on zeolite, and a coprecipitated CuO/ZnO are the three most promising sorbents in the temperature range of 500^{o}-$650^{o}C$ for reduction of H_2S from around 200 ppm to below 1 ppm H_2S in simulated coal gas. Based on engineering considerations, CuO/ZnO mixed sorbent is the most promising desulfurization agent (Figure 29, Table 17).

A structural reorganization mechanism, unique to mixed oxides, was identified: the creation of relatively fine crystallites of the sulfided components (Cu_2S and ZnS) counteract the loss of surface area due to sintering during regeneration. Studies with 9 to 26% water vapor in simulated coal gases show that sulfur levels below 1 ppm can be achieved in the temperature range of 500^{o} to $650^{o}C$. The ability of CuO/ZnO to remove COS, CS_2, and mercaptans (from about 100 ppm to less than 1 ppm) at these conditions was also demonstrated. Our research has also shown the feasibility of regeneration of spent sorbents by the simulated MCFC cathode exit gases., 5% O_2, 10% CO_2, 10% H_2O, and 75%5 N_2.

This program has been highly successful in meeting the overall objective, i.e., to develop a high temperature regenerable sorbent that can reduce H_2S concentration below 1 ppm. However, during the performance of the program, there were three major unexpected findings which required special attention. These findings were:

1) anomalous results of METC tests with vanadia sorbents: an apparent error in the thermodynamic value (heat of formation) of V_2S_3 in the National Bureau of Standards publication was uncovered. This required considerable additional work which, along with METC results, confirmed the previous experimental finding that V_2O_3 does react with H_2S

and the conversion of V_2S_3 as was previously believed. The possible formation of $V(HS)_3$ or a sulfided compound of vanadium eutectic with some impurity or support materials was suggested. It is understood that this work is being continued at the Jet Propulsion Laboratory.

2) Interaction of CuO with Stainless Steel Reactor: Quite unexpectedly, it was observed that there was a large discrepancy in the sulfur capacity of CuO/zeolite sorbent when run in quartz and stainless steel reactors. After painstaking efforts, it was established that there is a real synergistic effect between CuO and Fe, and it is proposed that mixtures of CuO/FeO_x be evaluated.

3) Higher than anticipated sulfur uptake capacity of CuO/ZnO in the fluidized-bed reactor: Based on the packed-bed studies, it was anticipated that the sulfur capacity of CuO/ZnO sorbent in the fluidized-bed reactor would be of the order of 10 mole/percent; instead, very large (up to 50%) sulfur capacities were observed. The mole percent conversion of CuO/ZnO to sulfides, in some instances, is inferior to CuO/Cu and ZnO supported on zeolite, but in terms of volume and weight percent sulfur loading, CuO/ZnO affords distinct advantages.

In view of the above findings, further work must be carried out before the technology can be packaged for engineering utilization. An extensive survey of the literature, predominantly patents and reports, reveals that many, if not all, hot gas desulfurization studies were terminated short of pilot stage evaluation. These processes have not been seriously considered by engineers even though only a few critical questions remain unanswered. Further work is recommended to take advantage of these findings and to tie up the loose ends. It is further suggested that, based on a mathematical model developed along with experimental results, a study would be conducted to provide a complete package of information for an engineer to design a desulfurization unit for integration with coal gasifier, primary desulfurization, and fuel cell or other applications such as combined cycle power plants.

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