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REMOVAL OF H₂S FROM GEOTHERMAL STEAM

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by

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I. Summary

The program objective is to identify and evaluate a technique to remove hydrogen sulfide from geothermal steam before it is used for power generation. The study was officially initiated on April 1, 1975.

The last six months were spent in the literature search, sorbent preparation and evaluation, and construction of an experimental apparatus. ZnO, mentioned in our original proposal as a good candidate for H₂S adsorption, was verified as such by the literature search and laboratory experiments. However, regeneration of sulfided sorbent proved to be difficult. Our interests were, then, switched to formulating sorbents made of mixtures of different kinds of metal oxides. At present, we have formulated two sorbents which, when evaluated with a gas adsorption apparatus in our laboratory, possess better H₂S adsorption-regeneration capabilities than ZnO or sorbents obtained from catalyst manufacturers. Large-scale gas adsorption equipment for use with simulated geothermal steam has been designed, built and shakedown operation of the equipment is in progress.

II. Introduction

Use of many geothermal energy sources is hampered by the fact that the steam from the source contains impurities. Hydrogen sulfide is present in virtually all geothermal steam, therefore, direct use of the steam for power generation is both harmful to the turbine blades and offensive to the environment. For these reasons, geothermal steam must be purged of hydrogen sulfide before the steam is fed to a turbine.

The present project is a three-phase research program having the objective to identify and evaluate a process for removing hydrogen sulfide from geothermal steam before its use for power generation. The proposed process involves contacting the steam with a sorbent to remove hydrogen sulfide, and regeneration of the sorbent to recover elemental sulfur or stable sulfur compounds.

This program was officially initiated on April 1, 1975. Work has been carried out in the following three areas:

1) Literature search and solid sorbent inquiry.

Available processes for H_2S removal from gas streams have been searched through the literature. Thermodynamic studies on some potential metal oxide sorbents have been conducted. Commercially available sorbents, though not specially designed for the present purpose, have been requested from catalyst manufacturers.

2) Sorbent evaluation.

A simple gas uptake apparatus, to be used for sorbent evaluation, has been constructed. Some sorbents have been prepared in our laboratory, and they have been evaluated, along with those requested from manufacturers, for their H_2S sorption-regeneration performance.

3) Construction of large-scale laboratory gas sorption apparatus.

A large-scale laboratory gas sorption apparatus capable of using a simulated geothermal stream has been designed and built in our laboratory.

Details of these activities are given in the following sections.

III. Literature Search and Solid Sorbent Inquiry

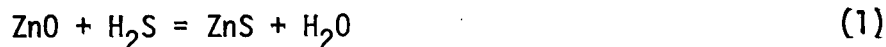
A search of literature related to the present project shows that up to now, no commercial H_2S removal processes have been specifically designed for geothermal steam scrubbing. Most H_2S removal processes are designed to scrub gas or liquid products of petroleum refining: natural gas, coke oven gas, producer gas, and synthetic natural gas.

Water vapor is only a minor constituent of these media, however, water vapor is the principal component of geothermal steam. Therefore, direct application of current processes is difficult. Wet methods, using aqueous or non-aqueous solutions of various kinds of chemicals (excluding molten salt processes) could cause condensation of steam, and thus are not suitable. Dry processes using solid sorbents which either physically adsorb or chemically react with H_2S may or may not work with steam; however, sorbents used in dry processes are good trial materials.

The most commonly used sorbents in dry processes are zinc oxide, iron oxide and activated carbon. These sorbents, in various forms, can be obtained from most catalyst manufacturers. The process recently developed by the

Bureau of Mines in Morgantown, West Virginia, using iron oxide and fly ash is a typical dry process. (1)

Since most solid sorbents for H_2S removal are essentially metal oxides in nature, thermodynamic studies on the potential metal oxides have been conducted. Metal oxides studied include ZnO , FeO , Fe_2O_3 , Fe_3O_4 , SnO , SnO_2 , AgO , Al_2O_3 , BaO , Bi_2O_3 , CaO , CdO , CoO , CO_2O_3 , CuO , Cu_2O , K_2O , K_2O_3 , MgO , MoO_2 , MoO_3 , Na_2O , NiO , Sb_2O_3 , Sb_2O_5 , SiO_2 , SnO , SnO_2 . The calculated free energy change for reaction of these metal oxides with H_2S are given in Appendix I. Special emphasis has been placed on $ZnO-H_2S$ adsorption and regeneration. Typical chemical reactions involved in this sorption-regeneration cycle are:



Free energy change of reactions, heat of reactions, and equilibrium constants at various temperature of these reactions have been calculated and are shown in Table 1 and Figure 1. The equilibrium H_2S concentration, based on a typical geothermal steam with 200 ppm of H_2S as a feedstock, is 0.029 ppm, which is much lower than the allowable H_2S concentration for steam-turbine electric generators. Thus, using ZnO as a sorbent to remove H_2S from geothermal steam is thermodynamically feasible. However, as shown in Figure 1, the formation of $ZnSO_4$ is favored over formation of ZnO when ZnS is regenerated with oxygen or air at low temperatures. Temperatures higher than $1200^\circ C$ are required for regeneration in accordance with reaction (2). At these temperatures, the absorbent rapidly loses its capacity to absorb H_2S (the loss of activity of ZnO in regeneration has been observed in laboratory experiments and will be discussed later).

Other metal oxides studied possess the same characteristics as ZnO . No significant problems exist in adsorption of H_2S , but complete regeneration is difficult. Difficulties in restoring sorption capacities may be thermodynamically attributed to the preferential formation of sulfates rather than oxides.

It is postulated that calcined mixtures of metal oxides may provide crystal stability sufficient for repeated sorption-regeneration cycles.

Heat of Reaction, Free Energy Change and Equilibrium
Constants of Reactions for ZrO-H₂S Sorption and Regeneration

		Reaction		
		1	2	3
ΔH_{298}^+ , Cal/Mole:		-18,305	-105,630	-185,380
ΔG_{298}^f , Cal/Mole		-18,295	-100,440	-160,910
Equilibrium Constant, K_p	25°C	1.8733×10^{13}	4.5712×10^{73}	$>10^{99}$
	50°C			
	100°C	3.8088×10^{10}	6.6777×10^{56}	4.4710×10^{90}
	150°C	2.0921×10^9		
	175°C	6.2626×10^8		
	200°C		5.957×10^{43}	4.6559×10^{67}
	300°C		1.4862×10^{35}	5.0952×10^{52}
	400°C		1.4505×10^{29}	1.5841×10^{42}
	500°C		5.1029×10^{24}	
	600°C		1.8614×10^{21}	
	700°C		3.4723×10^{18}	5.0439×10^{23}
	800°C		2.0856×10^{16}	7.3126×10^{19}
	900°C		2.9952×10^{14}	4.9636×10^{16}
1000°C		8.3756×10^{12}	1.0995×10^{14}	
1100°C		3.9416×10^{11}	6.1558×10^{11}	
1200°C		2.8074×10^{10}	7.2237×10^9	

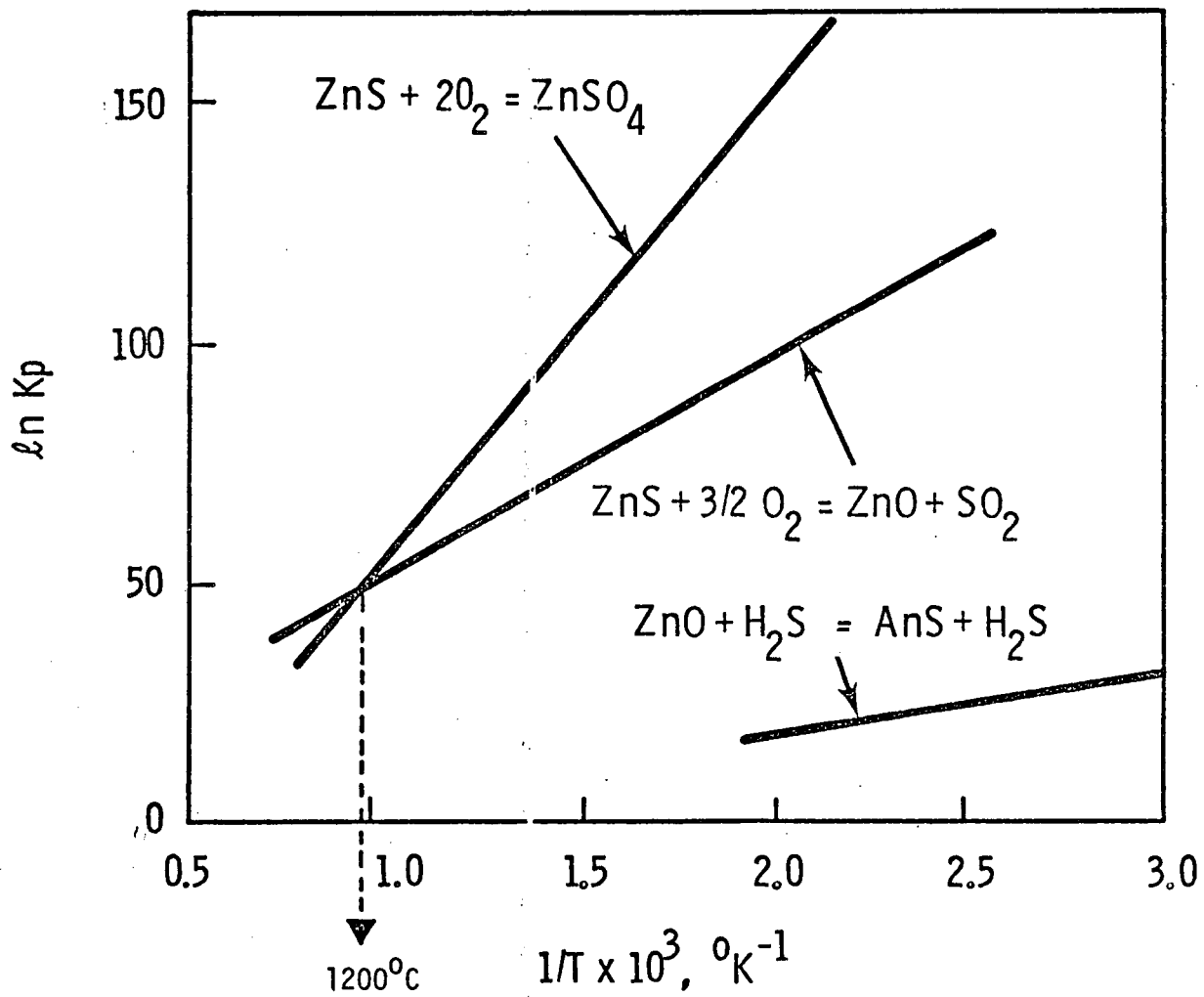


FIGURE 1. $\ln K$ vs $\frac{1}{T}$ of Reactions for ZnO-H₂S Sorption and Regeneration

Metal oxide mixtures in extruded forms were tried for H₂S removal purposes. Preparation and evaluation of H₂S sorption-regeneration capacities of metal oxide mixtures are, therefore, an important part of this study.

During the patent search, it was noted that sulfided zinc oxide could be regenerated by limiting reaction temperature and rate by careful control of oxygen concentration. The reaction was starved for oxygen in the early stage of regeneration. The oxygen was gradually increased to complete the reaction. This procedure will be tested.

As mentioned previously, many different kinds of commercially available sorbents are produced by catalyst manufacturers. For the present research, sorbents listed in Table 2 were obtained from Harshaw Chemical Company and Girdler Chemicals, Inc. They have been evaluated for their H₂S sorption and regeneration capabilities:

Table 2. Commercial Sorbents

Harshaw

Zn-0401E (ZnO)	3/16" tablets
A1-0104T	3/16" tablets
A1-0104T	1/4" tablets

Girdler

G-72 (ZnO)	1/8" tablets
G-72C (ZnO)	3/16" sphere
G-72D (ZnO)	3/16" extrusion
G-32J (activated carbon)	4 x 8 mesh, granular

IV. Sorbent Evaluation

A simple procedure for rapid screening of absorbents has been devised. The commercially available sorbents (shown in Table 2) have been compared with sorbents prepared in the laboratory. Methods of sorbent preparation and testing and the results obtained are described below:

A. Preparation of Sorbents

A general procedure for sorbent preparation is shown in Figure 2. Metal salts, either metal nitrates or sulfates, were weighed and dissolved

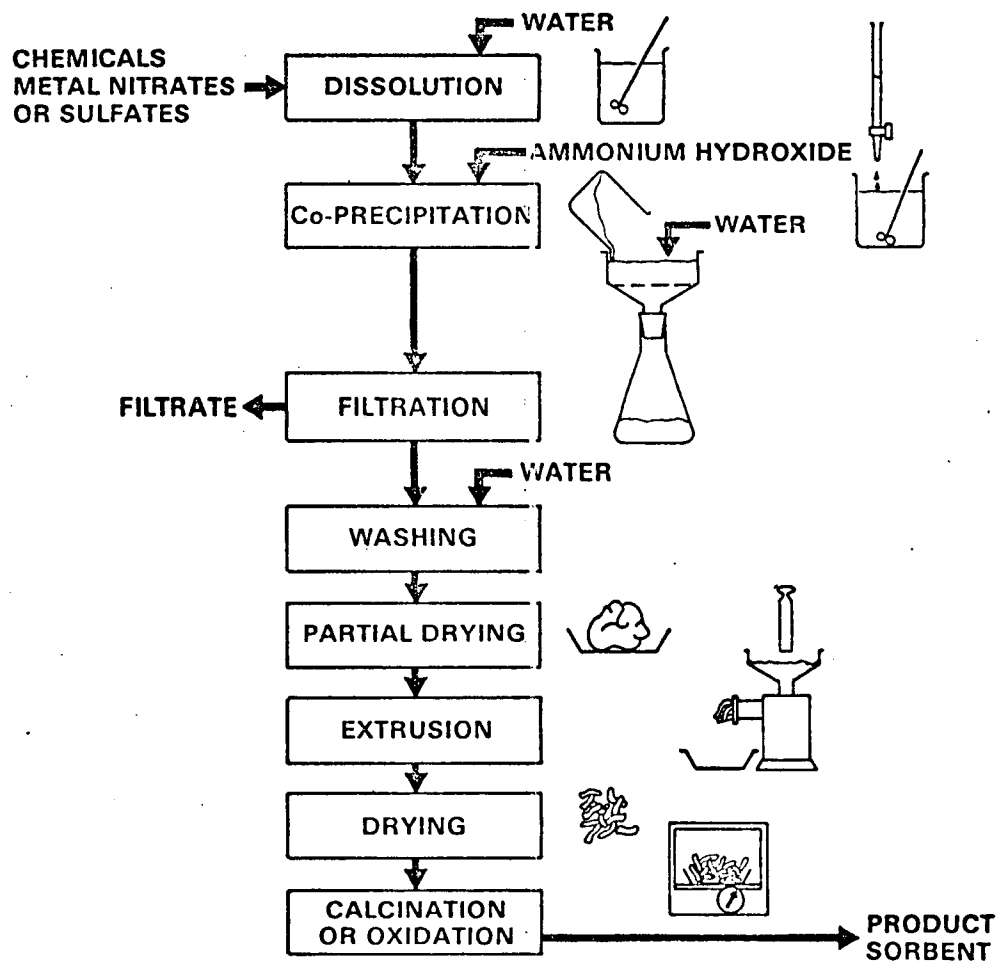


FIGURE 2. Procedure for Sorbent Preparation

in water. Metal hydroxides were precipitated by titrating the solution with ammonium hydroxide. The precipitated metal hydroxides were collected in a Buchner funnel by the vacuum filtration method. The wet cake was partially dried in a vacuum oven. By use of an extruder (a meat grinder was used in our laboratory), the partially dried cake was pelletized to form cylindrical particles. These particles were dried in an oven and then calcined in a muffle furnace at 800°C overnight. After having cooled in a desiccator the sorbent was ready for evaluation.

B. Method of Sorbent Evaluation

1. Apparatus: A simple gas absorption apparatus was assembled. A sketch of this apparatus is shown in Figure 3. The apparatus consists of a gas sorption column, condenser, product water collector, gas sample reservoir, gas circulating pump and manometer. Reaction of H₂S with a weighed quantity of sorbent at room temperature can be followed by monitoring the pressure changes during the reaction.
2. Procedure: The gas sample reservoir (Figure 3) was evacuated and then re-filled to 1.0 atmosphere pressure with pure H₂S. The gas circulation pump was then started and the gas circulated through a small column of sorbent. The pressure was measured at intervals and gas circulation maintained until the pressure approached a constant value. Water, a by-product of the reaction, was condensed out; however, it must be assumed that the gas was saturated (25°C) with respect to water vapor and the pressure readings corrected accordingly. The rate of change of pressure with time was considered proportional to the rate of H₂S absorption.

The weight increase of the sorbent was determined after drying 2 hours at 100°C. This weight gain was due to chemisorbed H₂S. Finally, the sorbent was regenerated by heating at 800°C in a muffle furnace overnight (16-18 hours). The loss in weight represents the conversion back to oxide and loss of chemisorbed H₂S. A given sample of sorbent can be cycled repeatedly through the sequence of absorption, drying and regeneration steps.

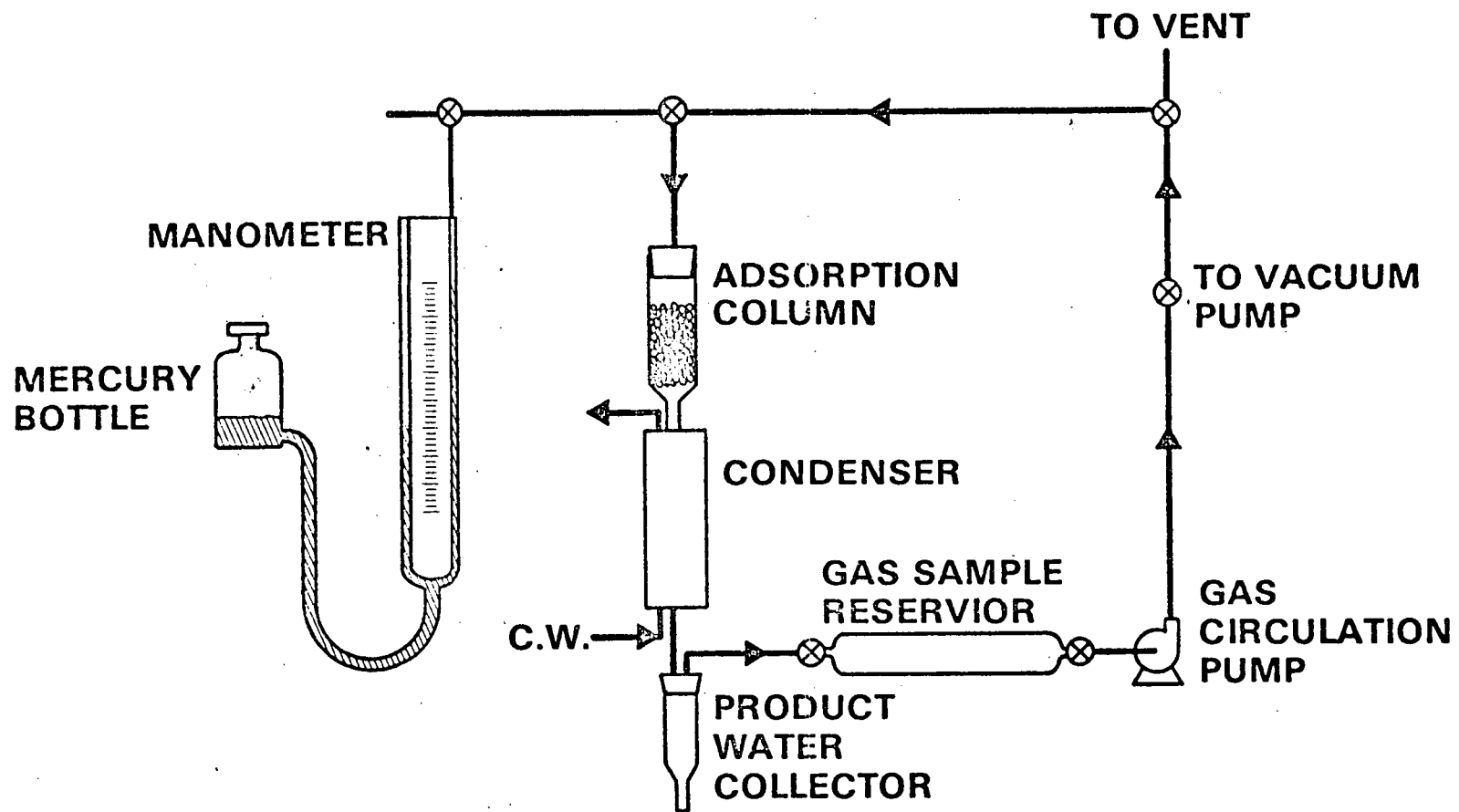


FIGURE 3. Apparatus for Sorbent Evaluation

C. Results of Absorption Screening Tests

Curves illustrating the absorption of H_2S by two commercial catalysts are shown in Figures 4-a and 4-b. The initial high rate of absorption decreases sharply after 10 minutes and has nearly ceased after 40-60 minutes. Following regeneration (Runs 190 and 194), the absorption capacity of these absorbents is sharply reduced.....to about 1/3 to 1/4 of the initial value.

The Girdler G-72C catalyst is a pure pelletized ZnO of high surface designed for removal of the H_2S from fuel gases at modest temperatures. This pure ZnO sorbent suffers a greater loss of sorption capacity than does the Harshaw ZnO-312 sorbent. This latter is a methanol catalyst containing 22% chromic oxide (Cr_2O_3) in addition to ZnO. The chromic oxide is presumed to stabilize the ZnO lattice in the same manner that MgO stabilizes the dolomite structure through repeated cycles of sulfidation and regeneration⁽²⁾. Run 190 shows that Cr_2O_3 is relatively ineffective for this purpose though a slight effect may be noted.

Figure 5 shows results of H_2S absorption on a sorbent prepared in this laboratory which consists of the mixed oxides of Al, Fe and Zn (Formula XI, Appendix III). In Run 181, the freshly prepared sorbent was used. Runs 183, 186 and 192 were made with consecutively regenerated sorbent. Though this formulation does not exhibit the initial rapid absorption exhibited by the commercial sorbents, its ultimate capacity appears nearly as great and both the rate and capacity for absorption are degraded more slowly by regeneration at $800^{\circ}C$.

In Figure 6, results of H_2S absorption experiments are illustrated using a slightly different formulation of the Fe, Al, Zn mixed oxide sorbent (Formula X, Appendix III). Extrusions of this mixture tended to disintegrate to a powder on calcination. This, and the consequent higher surface, may explain why this sorbent exhibits a higher rate of reaction than that of Formula XI. These curves exhibit slight irregularity in shape indicative of irregular changes in reaction rate for which no satisfactory explanation is evident. As with preparation XI, this material shows no tendency to lose extraction capacity following three regeneration cycles.

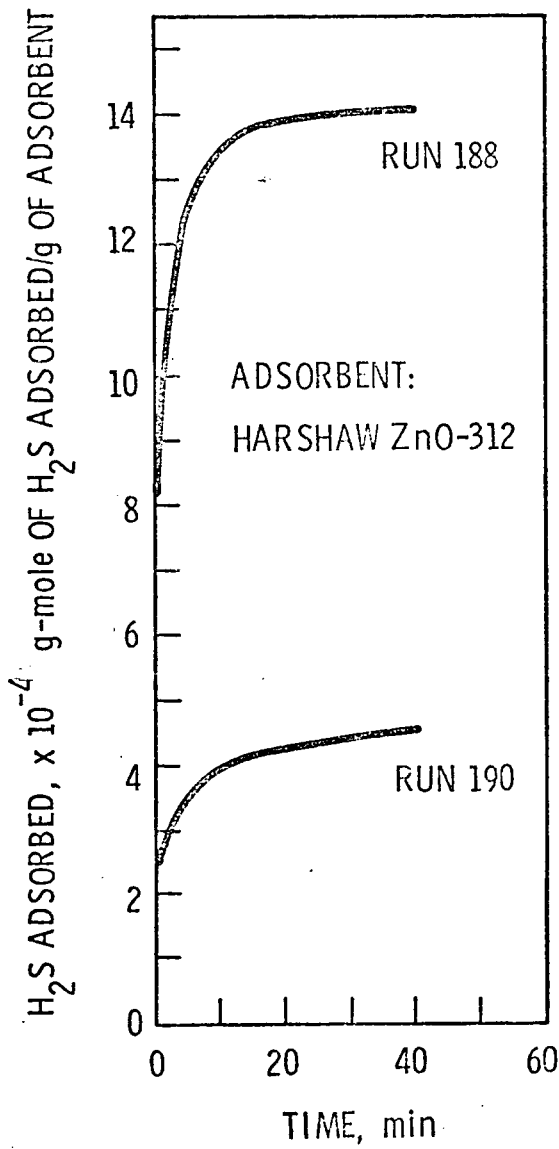


FIGURE 4-a. Gas Uptake vs Time for Harshaw ZnO-312

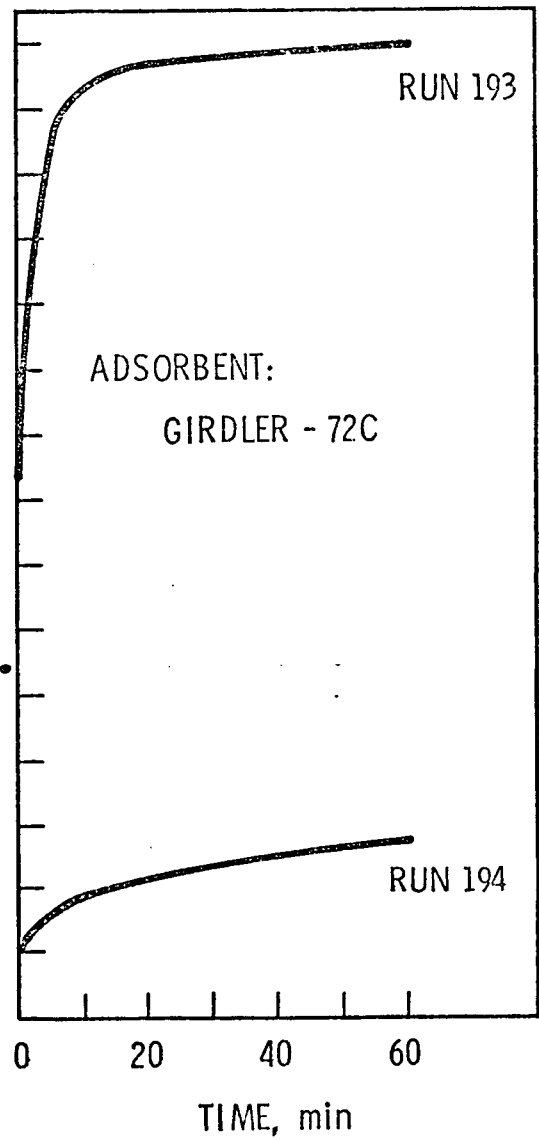


FIGURE 4-b. Gas Uptake vs Time for Girdler G-72C

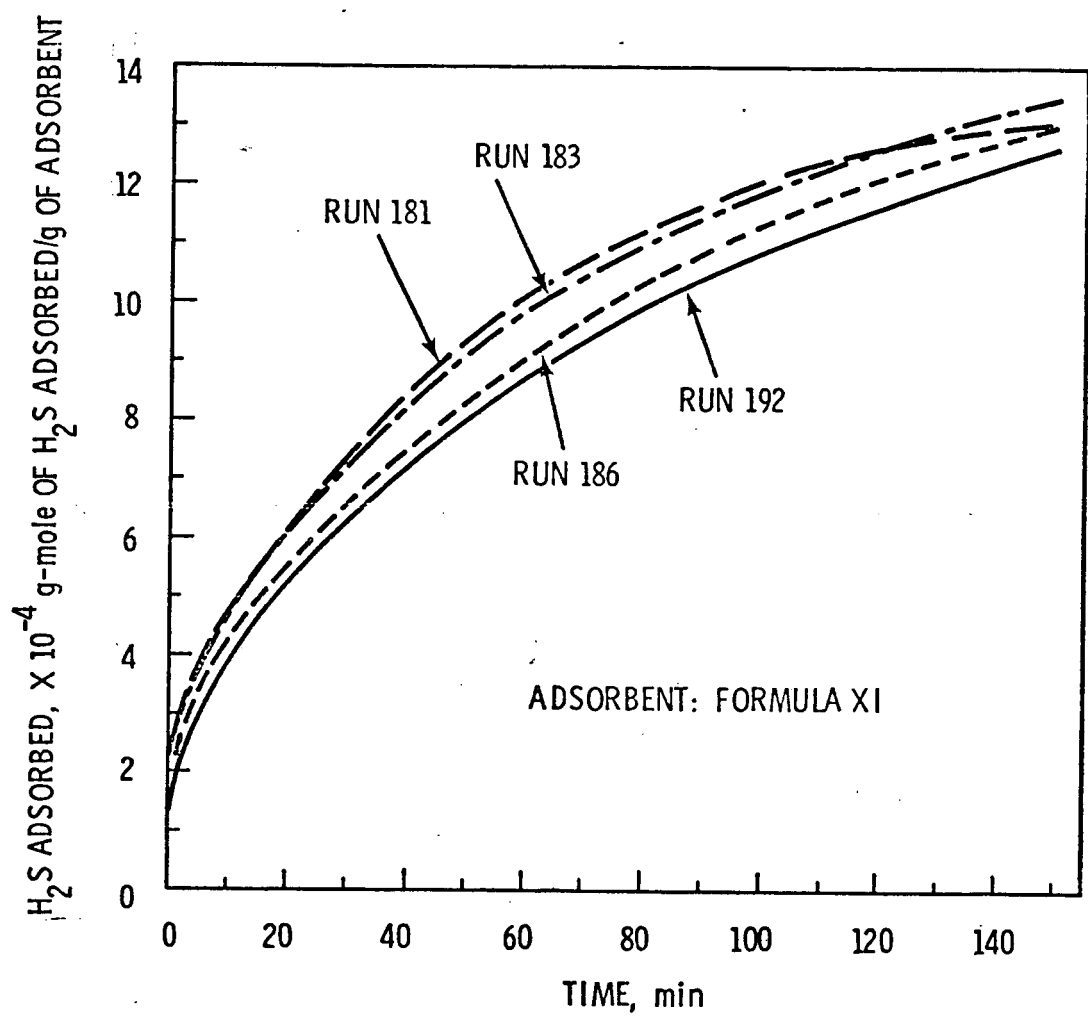


FIGURE 5. Gas Uptake vs Time for Sorbent Prepared from Formula XI

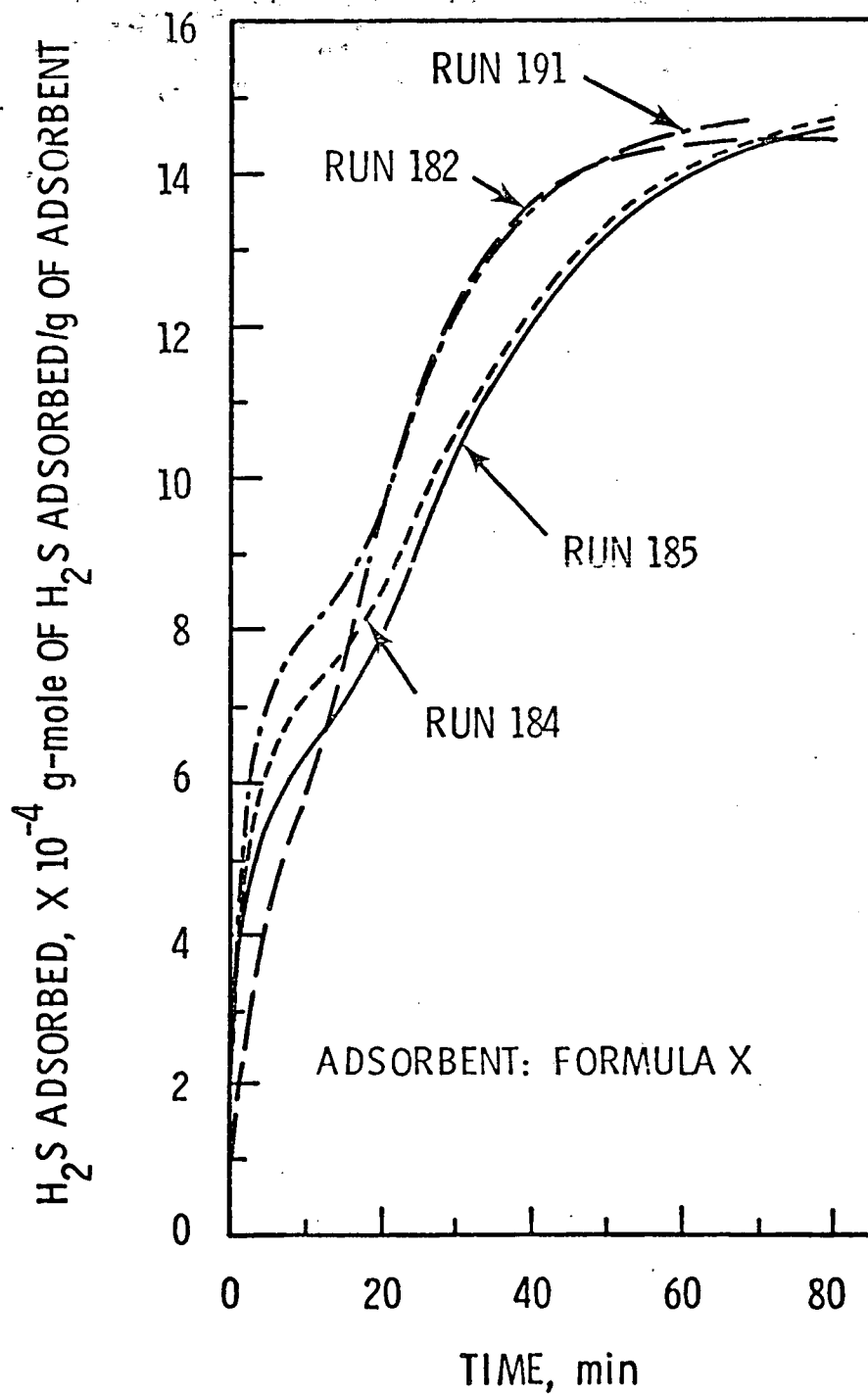


FIGURE 6. Gas Uptake vs Time for Sorbent Prepared from Formula X

It must be noted that the gas used in these screening tests contained only H₂S and air, whereas with geothermal steam, about 99.5% of the gas is steam. Extraction results with geothermal steam may not be predictable from these data. On the other hand, the regeneration conditions will not differ too significantly from those used here, so the evidence that the mixed oxide sorbents can be regenerated to full capacity is a significant advance. Confirmation that the mixed oxide sorbents are practical must await experiments in a laboratory scale process demonstration unit now nearing completion

V. Large-Scale Laboratory Gas Sorption Set-Up

In order to simulate the geothermal steam more closely, a large-scale laboratory gas sorption apparatus has been constructed. The flow diagram of this apparatus is shown in Figure 7. Main components of the system are: a steam generator, a gas sorption column, a back pressure regulator, a steam condenser, a condensate catch pot, and a non-condensable gas mixing station. Instruments monitoring various operating parameters include a wet testmeter, pressure gauges, thermocouples, rotameters, and, for analysis, gas chromatographs.

Water through a gear pump (Tweed, Model 1P741WE) is charged into a steam generator (Chromalox-Electric steam boiler CHPE-18). Water is metered before it goes to the pump. Steam generated from the boiler goes to the gas sorption system through a heating tape-traced and Kaowool-Insulated 1/2 in. stainless steel pipe. Before steam enters the gas sorption column, it is mixed with the non-condensable gas, including CO_2 , H_2S , NH_3 , and CH_4 , coming from the gas mixing station. The gas sorption column is made of a piece of 1 in. stainless steel pipe (24 in. length) with sorbent, spacers, and gas distributors fitted inside the pipe. The detailed design of this column is shown in Figure 8. A 2 in. pipe gas sorption column was also fabricated for the future work. Figure 8 shows thermocouples to measure the sorbent bed temperatures. Scrubbed steam-gas mixture passes through a back pressure regulator (Tower Equipment, Model 123-6), which keeps the system pressure at a desired pressure of 100 psig. Steam is condensed and collected in a condensate catch pot. In the catch pot, the un-adsorbed non-condensable gas is separated from liquid water and flows to a wet test meter for the gas volume measurement. The effluent gas from the wet test meter is vented to the building ventilation system. Gas samples are taken at the gas mixing station, before steam-gas mixtures enter the gas sorption column, after scrubbing, and after passing through the condensate catch pot. These gas samples are directly piped to the gas chromatograph (Hewlett Packard 5710A and 7620A Research Chromatograph) for gas analyses.

The equipment has been assembled in our energy research laboratory. Major work on equipment construction and the industrial safety inspection have been finished. System shakedown and calibration of instruments is in progress.

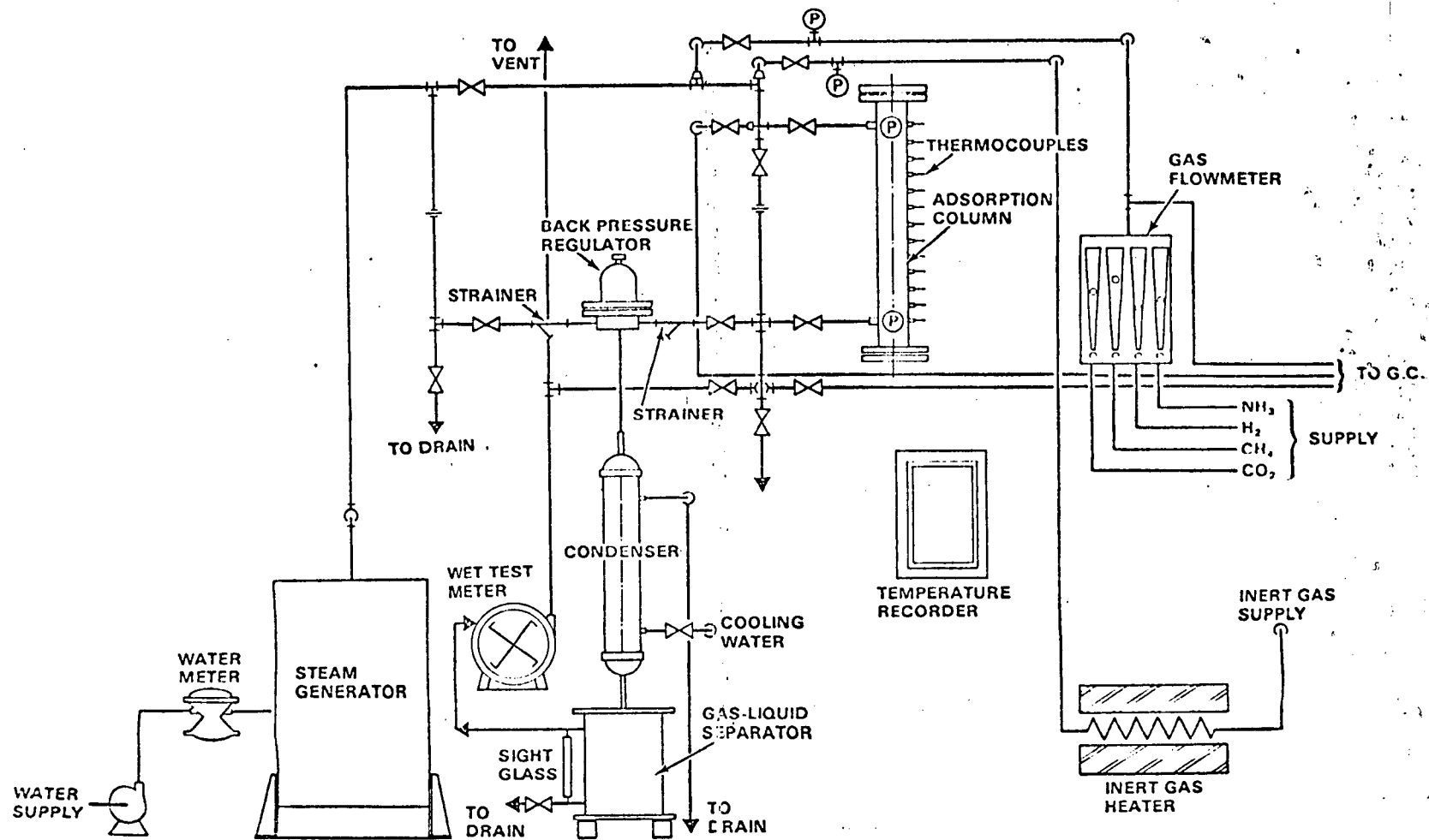


FIGURE 7. Flowchart for Removal of H_2S from Geothermal Steam Experiments

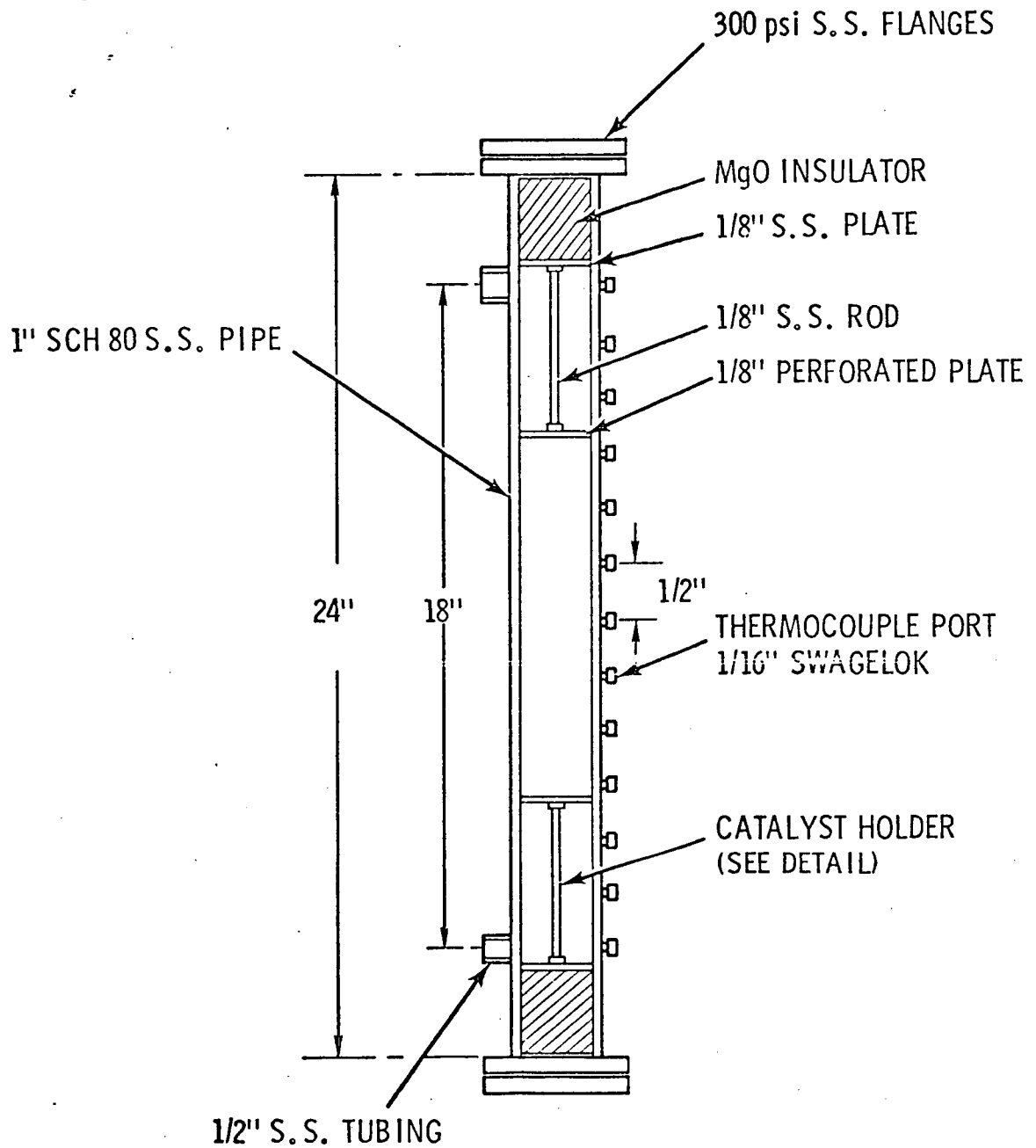


FIGURE 8. Gas Sorption Column

Appendix

Change of Free Energy of Reaction of Candidate Sorbent
with Hydrogen Sulfide @ 176°C

<u>Sorbent</u>	<u>Sorbent Product</u>	<u>ΔG</u>
ZnO	ZnS	-17.5
Fe	FeS	-14.17
Fe	FeS ₂	-13.9
FeO	FeS	-11.5
FeO	FeS ₂	-81.1
Fe ₂ O ₃	FeS, FeS ₂	-162.2
SnO	SnS	-5.89
Ag	Ag ₂ S	-1.19
Ag ₂ O	Ag ₂ S	-54.02
Al	Al ₂ S ₃	-87.26
Al ₂ O ₃	Al ₂ S ₃	+119.16
Ba	BaS	-32.96
BaO	BaS	-15.41
Bi	Bi ₂ S ₃	-8.87
Bi ₂ O ₃	Bi ₂ S ₃	-58.99
Ca	CaS	-94.09
CaO	CaS	-16.81
CaCO ₃	CaS	-96.1
Cd	CdS	-23.75
CdO	CdS	-26.56
Co	COS	+12.50
CoO	COS	-9.47
Co ₂ O ₃	Co ₂ S ₃	--
Cu	CuS	-63.37
CuO	CuS	-28.13
Cu ₂ O	Cu ₂ S	-32.48
Cu (with CS ₂)	Cu ₂ S	-109.60
K	K ₂ S	-73.53
K ₂ O	K ₂ S	-64.77
Li	Li ₂ S	--

Appendix 1 (cont'd)

Mg	MgS	-66.67
MgO	MgS	-3.18
Mo	MoS ₂	-33.50
MoO ₂	MoS ₂	-34.61
MoO ₃	Mo ₂ S ₃	-24.78
Na	Na ₂ S	-65.42
Na ₂ O	Na ₂ S	-33.18
Nb	Nb ₂ S ₃	--
Ni	NiS	-1.42
Ni	Ni ₃ S ₂	-8.02
NiO	NiS	-6.14
Sb	Sb ₂ S ₃	+4.47
Sb ₂ O ₃	Sb ₂ S ₃	-30.49
Si	SiS	+19.50
Si	SiS ₂	-30.00
SiO ₂	SiS ₂	+56.15
Ta	Ta ₂ S ₄	--

-- Thermodynamic data insufficient to permit calculation.

Appendix II

Typical Formulas for Sorbents Prepared in Laboratory

Formula X

$Al(NO_3)_3 \cdot 9 H_2O$	100g
$Zn(NO_3)_2 \cdot 6 H_2O$	76.8g
$Fe(NO_3)_3 \cdot 9 H_2O$	108g
Water	1000 Ml
NH_4OH (28%)	245 Ml

Formula XI

$Al(NO_3)_3 \cdot 9 H_2O$	100g
$Zn(NO_3)_2 \cdot 6 H_2O$	76.8g
$Fe(NO_3)_3 \cdot 9 H_2O$	25g
$Fe_2(SO_4)_3 \cdot X H_2O$	75g
Water	1000 Ml
NH_4OH (28%)	287 Ml

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