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FINAL REPORT

REMOVAL OF H_2S FROM GEOTHERMAL STEAM

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I. SUMMARY

The program objective was to identify and evaluate the use of solid sorbents to remove hydrogen sulfide from geothermal steam. The program was initiated on April 1, 1975.

The program was organized as a series of tasks consisting of a literature review, thermodynamic study of candidate sorbents, preparation of sorbents, obtaining sorbents from commercial sources, setting up sorbent screening and evaluation apparatus, screening of candidate sorbents and evaluation of screened sorbents under simulated geothermal steam conditions.

No process, so far, has been developed commercially to remove H_2S from steam. Zinc oxide was verified as a good candidate by literature search and laboratory experiments. However, regeneration of sulfided sorbent proved to be difficult. Mixed metal oxide sorbents were prepared. Some of these sorbents reacted with hydrogen sulfide in a H_2S-air system; however, they show no activity to hydrogen sulfide in steam. Impregnation of catalyst support with organic compounds, such as diethanolamine was attempted. Diethanolamine was leached out of the impregnated sorbent upon contact with steam, and the sorbent failed to remove H_2S from steam. Solid organic sorbents were evaluated; one of these sorbents, Sorbent-0091* showed good potential. The sorbent reacted with H_2S under simulated geothermal conditions and could be regenerated easily by purging the spent sorbent with superheated steam. The high pressure drop through packed beds and excessive steam required for regeneration are major problems in the practical application of this particular material.

The following conclusions were drawn from this study:

- Zinc oxide is a good sorbent for removing H_2S from geothermal steam; however, regeneration of sulfided sorbent is difficult.
- Some laboratory prepared mixed oxide sorbents showed good H_2S uptake capacity and regenerability with dry H_2S. However, under simulated geothermal steam conditions these sorbents failed to react with H_2S.

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* Generic description of the sorbents are given in Appendix II.

- Sorbents prepared by exchanging multivalent metal ions for the original monovalent cations present in molecular sieves were found to be inactive to H_2S.
- The polymeric sorbent, Sorbent-0091, reacted with H_2S under simulated geothermal steam conditions, and regeneration could be accomplished by passing super-heated steam through the spent sorbent. However, due to the small particle size of this sorbent the pressure drop through the sorption bed was high, and an unreasonably large quantity of super-heated steam was required for regeneration.
- Sorbents prepared by impregnating inert substrates with organic compounds having high basicities were prepared and evaluated. These materials were not stable in steam due to leaching of the active constituents.
- The amount of solid sorbent required for H_2S removal in a geothermal power generation system is large. Therefore, selection of the gas-solid contactor is critical especially because of capital costs. Use of a continuous regenerating contactor, such as a fluidized bed or a moving bed, will reduce the amount of solid sorbent required.
- The use of expendable metal oxide sorbents, for example ZnO, is expensive even with credit from recovery metal by a commercial smelting.

Although the search for suitable solid sorbents for removal of H_2S from geothermal steam was not exhaustive, our laboratory work has indicated that the use of this type of sorbent is economically infeasible. Therefore, further work on such sorbents is not recommended.

REMOVAL OF H_2S FROM GEOTHERMAL STEAM

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II. INTRODUCTION

Geothermal energy has been used to generate electricity since 1904 when Italy started a 250 kW plant in Larderello. Today, slightly over 1,000 MWe of electricity is being generated by countries including New Zealand, Japan, the United States, Russia, Mexico and Italy. Estimates as high as 30,000 MWe have been made for potential geothermal energy by 1985.[1]

Use of many geothermal energy sources is hampered because steam from the source contains impurities. Hydrogen sulfide (H_2S) 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. Hydrogen sulfide concentration varies from well to well. Hydrogen sulfide concentrations as high as 1,600 ppm have been reported at Geysers;[2] however, the H_2S concentration in geothermal steam usually ranges from 60 to 1,000 ppm.

The serious drawback to using geothermal steam for power generation can be seen in the following situation. A geothermal power plant with a capacity of 1,000 MWe requires 430 million pounds of steam per day.[3] If the H_2S concentration in the steam is 225 ppm (the average value of steam produced at the Geysers) the total H_2S carried by the steam to the surface is 48.4 tons/day. Aside from this potential environmental insult, the corrosion of power generating equipment and transmission lines due to the release of H_2S to the atmosphere cannot be ignored. For these reasons the removal of H_2S before geothermal steam is fed to a turbine is advantageous.

III. LITERATURE SEARCH AND SOLID SORBENT INQUIRY

1. Composition of Geothermal Steam

Hydrogen sulfide is present in virtually all geothermal steam, whether the steam is natural or flashed from hot water. Table 1 illustrates typical chemical compositions of geothermal steam from various sites.[4]

TABLE 1. Chemical Composition of Geothermal Steam

	Geysers (USA)	Larderello (Italy)	Krysuvik (Iceland)	Wairakei (New Zealand)
Wellhead Temperature, °F	347	374	320	383
Total Noncondensable Gas Content of Steam (wt%)	0.7	4.5	1.3	0.5 (max)
Noncondensable Gases in Steam (ppm by weight)				
CO_2	6,210	43,000	11,800	1,900
H_2	52	30	35	--
H_2S	208	903	1,048	60
CH_4	385	170	5	6
NH_3	55	307	--	--
N_2	91	178	80	20
Residuals	--	262	--	--

Though H_2S concentrations as high as 1,600 ppm have been reported at the Geysers,[2] the H_2S concentration in geothermal steam generally ranges from 60 to 1,000 ppm. For the present study an H_2S concentration of 200 ppm was chosen as typical of geothermal steam; the geothermal steam simulated in the laboratory was set in this range of concentration.

2. Status of Present H_2S Removal Processes

No commercial H_2S removal processes have yet been specifically designed for steam. Most H_2S removal processes including liquid scrubbing, dry adsorption, and molten salt processes, are designed to remove gas or liquid products from petroleum refining or natural gas, coke oven gas, producer gas, and synthetic natural gas.

The difficulties of removing H_2S from geothermal steam before its use for power generation are that an enormous volume of steam is involved, and that only a limited sacrifice of steam quality is tolerable. Minimal pressure drop and heat loss are allowable for the process we are seeking. Though the average concentration of H_2S in geothermal steam produced in the Geysers area is 200 ppm, the total H_2S to be removed from the steam for a typical 110 MWe power plant is about 4.8 ton/day. This requires recycling the sorbent used to capture H_2S, unless the sorbent in question is cheap and after capturing hydrogen sulfide it can be disposed of in an environmentally acceptable manner.

3. Criteria for H_2S Removal Processes for Geothermal Steam

The following criteria must be met to evolve a commercially viable regenerative H_2S removal process for a geothermal steam power plant:

i) Minimum Degradation of Steam

The H_2S removal process in question removes only non-condensable gases, specifically H_2S, from the steam and causes little or no degradation of the steam quality. The purpose of this project, as mentioned before, is to remove H_2S before the steam enters the power generator; therefore, any pressure drop and heat loss due to the removal process must be minimal. Sacrifice caused by the addition of the H_2S removal unit of the amount of power which can be generated must be low so that the process is economically feasible.

ii) Regenerable Sorbent

An enormous amount of steam will be treated in the H_2S removal process before entering the power generator. Thus, a once-through sorbent, unless its cost is very low, will not be practical. Besides, the disposal of large amounts of

used sorbent will create other environmental problems.

The sorbent used must be physically and chemically stable. The H_2S sorption capacity of the sorbent in question should not decrease significantly during the subsequent sorption-regeneration cycles.

iii) Reasonably High Sorption Capacity

The amount of H_2S which can be removed when breakthrough occurs should be high; otherwise, a large quantity of sorbent will be required, and costs of sorbent and equipment for H_2S removal will be high. A sorbent with large sorption capacity will also reduce the frequency of regeneration needed, and thus reduce operating costs.

iv) Simple Regeneration Process

The regeneration process should be a continuous process (as in wet scrubbing systems) or an *in situ* process (as in solid sorbent systems). The spent sorbent is regenerated in the sorption column by either gaseous or liquid reactants. Severe conditions, such as high temperature and pressure must be avoided for regeneration, so as to minimize the energy and capital costs of steam cleanup.

v) Quick Regeneration

If the time required for regenerating a batch of spent sorbent exceeds that of breakthrough, then an extra set of gas removal equipment, namely the sorption column, will be required. This would mean that extra capital investment is necessary.

vi) Stable or Useful By-product of Regeneration

The sulfur content of the regeneration process effluent must be such that sulfur can be recovered or converted to other useful or stable compounds by commercially available processes. Elemental sulfur is quite stable and is not a significant environmental problem. This recovery of H_2S as elemental sulfur is desirable. On the other hand, if H_2S is converted to other useful chemicals, such as sulfuric acid, which have

market value, then the credit from the selling of the useful by-product will certainly reduce the cost of H_2S removal.

Conventional wet processes (hot potash process, mono- or diethanolamine process) which use aqueous or non-aqueous solutions of various chemicals could cause condensation of steam or loss of liquid sorbent. Unless very sophisticated temperature and flow controls balance the vapor pressure of sorbent solution and the steam, the wet processes for removal of H_2S will be very difficult to operate. The pressure drop in wet processes is usually high compared to dry processes; therefore, the practicality of wet processes is questionable.

Molten salt processes use molten salts of alkaline metals, either in carbonate or nitrate, or the combined forms. They are essentially a wet process, except the operating temperature is higher than that of regular wet processes. Thus, the temperature, pressure drop, and freezing of salt in the sorption column are some of the problems which limit the application of molten salt processes to steam cleanup. Corrosion problems due to the use of molten salts will be difficult to overcome, especially if entrained salt enters the turbine.

Dry processes, which use solid sorbents in pellet, spherical or cylindrical form, packed in sorption columns, are quite common in removing H_2S from gas streams. Solid sorbents, which either physically adsorb or chemically react with H_2S, are usually regenerated by oxidation or heating at the end of the sorption cycle. The regenerated sorbent is re-used in the process. Sorbents used to remove H_2S from gas streams are usually composed of metal oxides promoted or stabilized with small amounts of other chemicals. The reaction of metal oxides with H_2S can be described by the following equation:

$$MO + H_2S = MS + H_2O \qquad (1)$$

where MO and MS are metal oxide and metal sulfide respectively.

As can be seen from equation (1) the products of H_2S removal are metal sulfides and water. In removing H_2S from a gas stream, such as natural gas,

producer gas or synthetic natural gas, the presence of small amounts of reaction by-products, namely water vapor, does not seriously hamper gas cleaning operation. However, water vapor is the principle component of geothermal steam, and thus the direct use of current dry H_2S removal processes is difficult.

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 manufacturers. The processes developed by the Bureau of Mines in Morgantown, West Virginia,[5] using iron oxide and fly ash, and by Squires[6] using half-calcined dolomite are typical.

4. Thermodynamic Study of Metal Oxide Sorbents

Since most solid sorbents for H_2S removal are essentially metal oxides, thermodynamic studies of potential metal oxides have been conducted. Metal oxides studied include ZnO, FeO, Fe_2O_3, Fe_3O_4, 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 changes for reaction of these metal oxides with H_2S are given in Appendix I-A and I-B. Special emphasis has been placed on ZnO-H_2S adsorption and regeneration. Typical chemical reactions involved in this sorption-regeneration cycle are:

$$ZnO + H_2S = ZnS + H_2O \qquad (2)$$

$$ZnS + 3/2\ O_2 = ZnO + SO_2 \qquad (3)$$

$$ZnS + 2O_2 = ZnSO_4 \qquad (4)$$

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 2 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. 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 above 1200°C are

TABLE 2. Heat of Reaction, Free Energy Change and Equilibrium Constants of Reactions for $ZnO-H_2S$ Sorption and Regeneration

		Reaction 2	Reaction 3	Reaction 4
ΔH^f_{298}, Cal/Mole		-18,305	-105,630	-185,380
ΔG^f_{298}, 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}

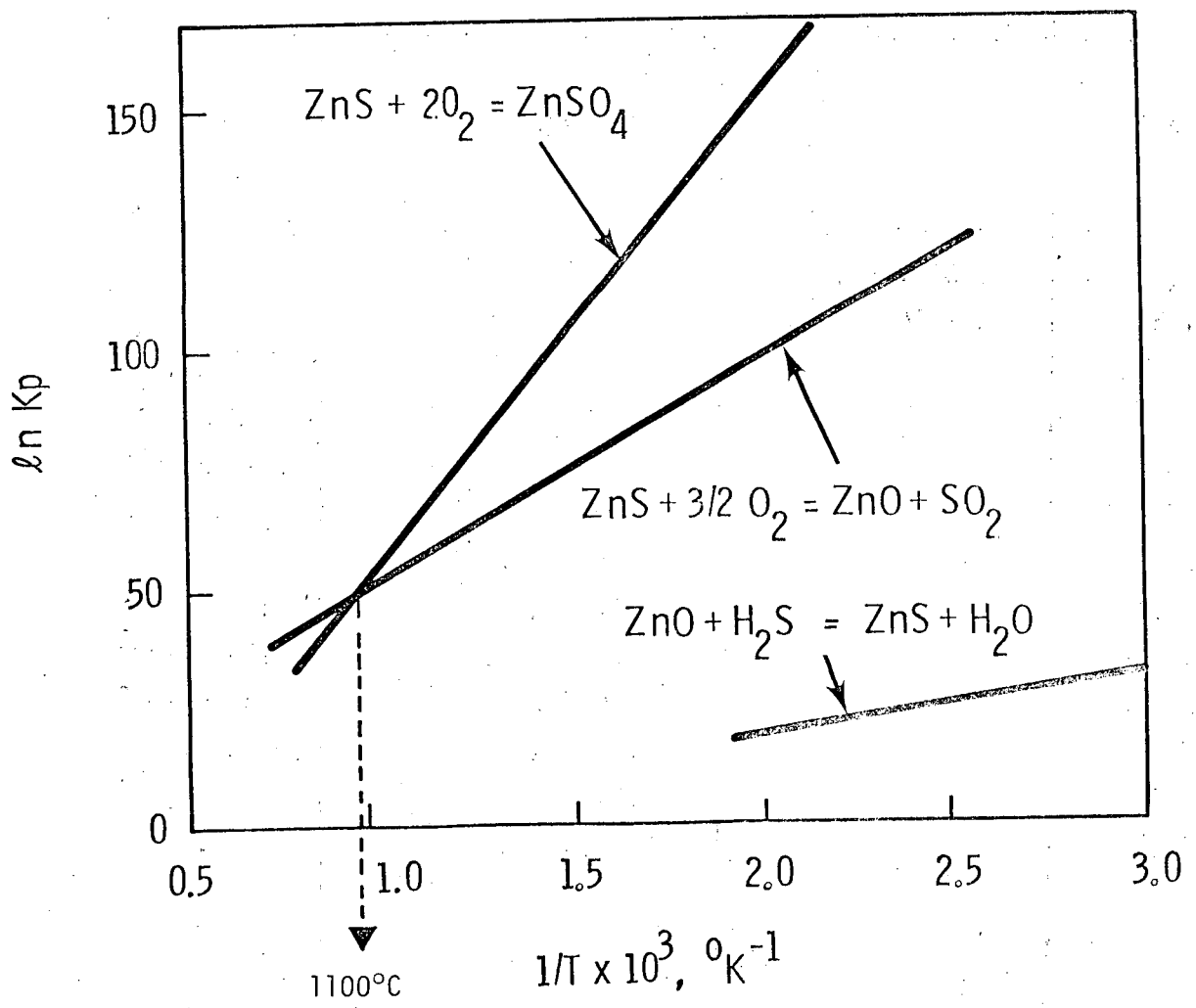


FIGURE 1. $\ell n K$ vs $\frac{1}{T}$ of Reactions for $ZnO-H_2S$ Sorption and Regeneration

required for regeneration in accordance with reaction (3). At these temperatures, the absorbent rapidly loses its capacity to react with 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 sorption 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 was postulated that calcined mixtures of metal oxides may have sufficient crystal stability for repeated sorption-regeneration cycles. Metal oxide mixtures in extruded forms were tested for H_2S removal purposes. Preparation and evaluation of H_2S sorption-regeneration capacities of metal oxide mixtures were an important part of this study.

During the patent search, it was noted that sulfided ZnO could be regenerated by limiting reaction temperature and rate through 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.

5. Solid Organic Sorbents

Solid organic sorbents made of heat resistant polymeric material are potential H_2S sorbents. In the conventional amine process for removing H_2S from synthesis gas, the amine group is the main component. It reacts with H_2S in the gas stream according to the following reaction:

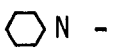
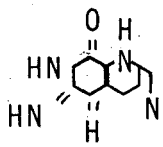
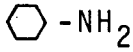
$$R'R''R'''N + H_2S \rightleftarrows [R'R''R'''NH]\ HS \qquad (5)$$

or $$B: + H_2S \rightleftarrows BH^+HS^-$$

where R' is $HO(CH_2)_2$- and R", R'" can be either H, or $HO(CH_2)_2$- depending upon whether di- or tri-ethanolamine is used. B: is a basic substrate. If "R" groups in the above reaction are replaced by some polymeric

functional groups, the resulting resin with active amine groups attached to its backbone may be able to react with H_2S. Various amine compounds could be used as starting materials. To select suitable amine compounds for evaluation, basicities of a group of amine compounds have been calculated. These are shown in Table 3. K_b in the table is defined as $K_b = [BH^+HS^-]/[B:][H_2S]$.

TABLE 3. Basicity of Various Compounds

Compound	Formula	K_b
Biguanide	$H_2N - \overset{\overset{\displaystyle NH}{\|}}{C}HNH\overset{\overset{\displaystyle NH}{\|}}{C}H - NH_2$	6.3×10^{-2}
Quanidine	$NH = C(NH_2)_2$	2×10^{-11}, 2×10^{-5}, 2×10^{-2}
Piperidine		1.6×10^{-3}
Diethylamine	$(CH_3CH_2)_2NH$	9.6×10^{-4}
Hexamethylenediamine	$H_2N(CH_2)_6NH_2$	6.7×10^{-5}, 8.5×10^{-4}
Guanine		6×10^{-4}
Cyclohexylamine		4.4×10^{-4}
Ethylenediamine	$H_2N(CH_2)_2NH_2$	7.1×10^{-8}, 8.5×10^{-5}
Ethanolamine	$HOCH_2CH_2NH_2$	3.2×10^{-5}
Diethanolamine	$(HOCH_2CH_2)_2NH$	7.6×10^{-6}
Pyridine		1.7×10^{-7}
Analine		3.8×10^{-10}
Acetamide	$CH_3\overset{\overset{\displaystyle O}{\|}}{C} - NH_2$	2.5×10^{-13}

The above values are calculated from pKa for proton transfer

reactions.[7] The larger the K_b value the more H_2S can react with the amine compound. Thus, compounds, such as bignanide, guanidine, and guanine are good candidates for H_2S removal. These materials can be either incorporated with polymeric materials or impregnated on the surface of proper inert substrates such as silica gel or alumina.

Recent developments of organometallic catalysts are also of interest. Metals or metallic oxides bonded to rigid polymeric materials have been used as catalystsin hydrogenation, hydrosilation and hydromylation.[8] Organometallic compounds are also be examined in this work.

6. Sorbent Inquiry

Many different kinds of commercially available sorbents produced by catalyst manufacturers have been requested. Although they are designed to work under dry gas stream (or gas with low moisture content), these sorbents will be evaluated as trial materials. Sorbents obtained from the manufacturers are listed in Appendix II by generic type.

IV. SORBENT PREPARATION AND EVALUATION

1. Sorbent Preparation

Through thermodynamic calculations done during the literature search, some potential metal oxides were selected and sorbents based on these oxides were prepared in our laboratory.

i) Sorbents Prepared from Metal Salts:

A general procedure for metal oxide-based sorbents is shown in Figure 2. Metal salts, either metal nitrates or sulfates, were weighed and dissolved in distilled water. Metal hydroxides were precipitated by slowly adding ammonium hydroxide to the thoroughly agitated metal salt solution. The precipitated metal hydroxides were collected and washed with distilled water in a Buchner funnel by vacuum filtration. 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. The particles were dried in an oven and then calcined

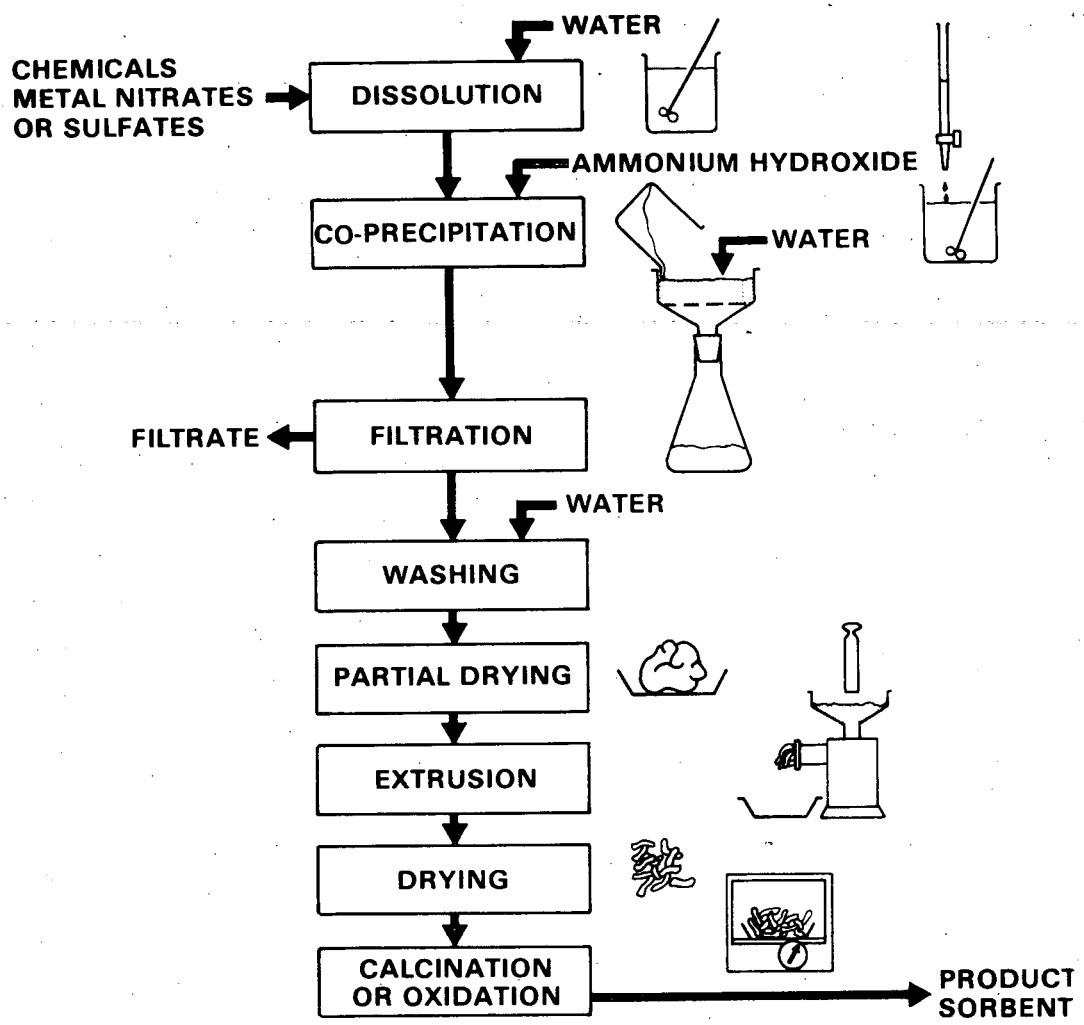


FIGURE 2. Flowsheet for Sorbent Preparation

in a muffle furnace at 800°C overnight. The calcined material was cooled in a desiccator and the sorbent was ready for evaluation.

ii) Sorbent Prepared from Metal Oxides or Metal Carbonates with Sodium Silicate:

A. When a metal oxide or carbonate was used as a starting material the following method of sorbent preparation was adopted. A known amount of oxide or carbonate was suspended into a beaker filled with aqueous sodium silicate. Diluted hydrochloric acid was added until a gel formed. This gel was dried in an vacuum oven and then fired in a muffle furnace. Depending on the starting material various firing temperatures were used. The products of firing were irregular flaky shaped materials.

B. With glass frit: Metal oxides were properly mixed according to the ratio of some natural or man-made spinels. The mixture was then fired at the fusion temperature of the material. After cooling, the material was ground into powder. This powder was then mixed with glass frit and pelletized in a tumbling table pelletizer. The particles were dried and heated to the frit fusion temperature which was lower than the first temperature used for firing.

iii) Sorbent Prepared from Molecular Sieves

It is known that molecular sieves usually adsorb water vapor preferentially to gases such as H_2S and CO_2. Therefore, the direct use of such materials in a H_2S-steam system for H_2S removal is impractical. However, molecular sieves can be modified by substituting higher valent cations for the monovalent ions present in such materials. Zn^{+2}, Fe^{+2} and Fe^{+3} are desirable cations because they can be converted to oxides which are known to be active to H_2S. Commercially available molecular sieves* were modified along the above lines in accordance with the supplier's

* Commercial molecular sieve type 5A.

recommendations: degassing by vacuum treatment followed by immersion in zinc nitrate, zinc acetate, or ferric nitrate solution and subsequent clacining at 800 to 1000°C. The resulting material was in pellet form and suitable for subsequent sorbent screening tests.

iv) Sorbents Prepared from Organic Material:

To test the concept of using organic solid sorbents two kinds of organic sorbents were prepared:

A. Aniline-lignin sorbent:[9] Two parts of lignin and one part of aniline were heated at 150°C for one hour, and the resulting dark brown, hard and brittle resin was crushed. The resin chips were evaluated for sorbent ability.

B. Melamine-Formaldehyde: One mole of melamine and three moles of formaldehyde were refluxed in a flask for 40 minutes. The solution was distilled to about 70 percent solids. The resulting syrup was solidified in an oven at 150°C. The clear, hard product was crushed to between 12 and 100 mesh. The sorbent was then ready for evaluation.

2. Sorbent Evaluation

i) Purpose:

The purpose of the evaluation is to quickly identify potentially effective sorbents from the large numbers of those available. Because the number of available sorbents is so large, the evaluation method must be simple, and the test results must indicate the sorbent's activity to H_2S. In this study, sorbents are put into an atmosphere of H_2S-air (not including steam) and the H_2S up-take by the sorbent is monitored. The sulfided sorbent is regenerated in a muffle furnace. The resulting regenerated sorbent is subjected to the same gas up-take test. Due to the absence of steam in the system, the test results only indicate that if a sorbent passes the test (reacts with H_2S at a reasonable rate), the sorbent may remove H_2S from geothermal steam.

ii) Apparatus:

A simple apparatus for the sorbent evaluation was assembled. A sketch of this apparatus is shown in Figure 3. It consists of a gas sorption column (15 ml Buchner funnel with coarse frit), condenser, product water collector, gas sample reservoir (180 ml), gas circulating pump (Cole-Parmer) and mercury manometer. With this simple arrangement the reaction of H_2S with a weighed quantity of sorbent at room temperature can be followed by monitoring the pressure in the gas up-take system during the reaction.

iii) Procedure:

About five grams of sorbent are weighed and charged into the gas sorption column. The gas reservoir is partially evacuated (or pressurized) and the pressure of gas in the reservoir is recorded. The gas reservoir is then connected to the sorption system. The valves of the reservoir are opened, and the overall system pressure is measured. Using volume and pressure of the gas reservoir, the overall system pressure and applying the ideal gas law the total volume of the system can be calculated. The gas sample reservoir is then evacuated by a vacuum pump and refilled to 1.0 atmosphere pressure with H_2S. The reservoir containing H_2S is then connected to the system. The gas circulation pump is started; H_2S circulates in the system and continuously reacts with sorbent in the column. The pressure of the system is recorded along the progress of the gas uptake reaction. The gas circulation is maintained until the pressure approaches a constant value. The rate of change of pressure with time was considered proportional to the rate of H_2S adsorption. The amount of actual H_2S uptake can be calculated from the system pressure, volume, and amount of H_2S charged into the system. The detailed equations derived for H_2S gas uptake calculation are in Appendix III. The weight increase of the sorbent due to the gas uptake is determined after drying 2 hours at 100°C

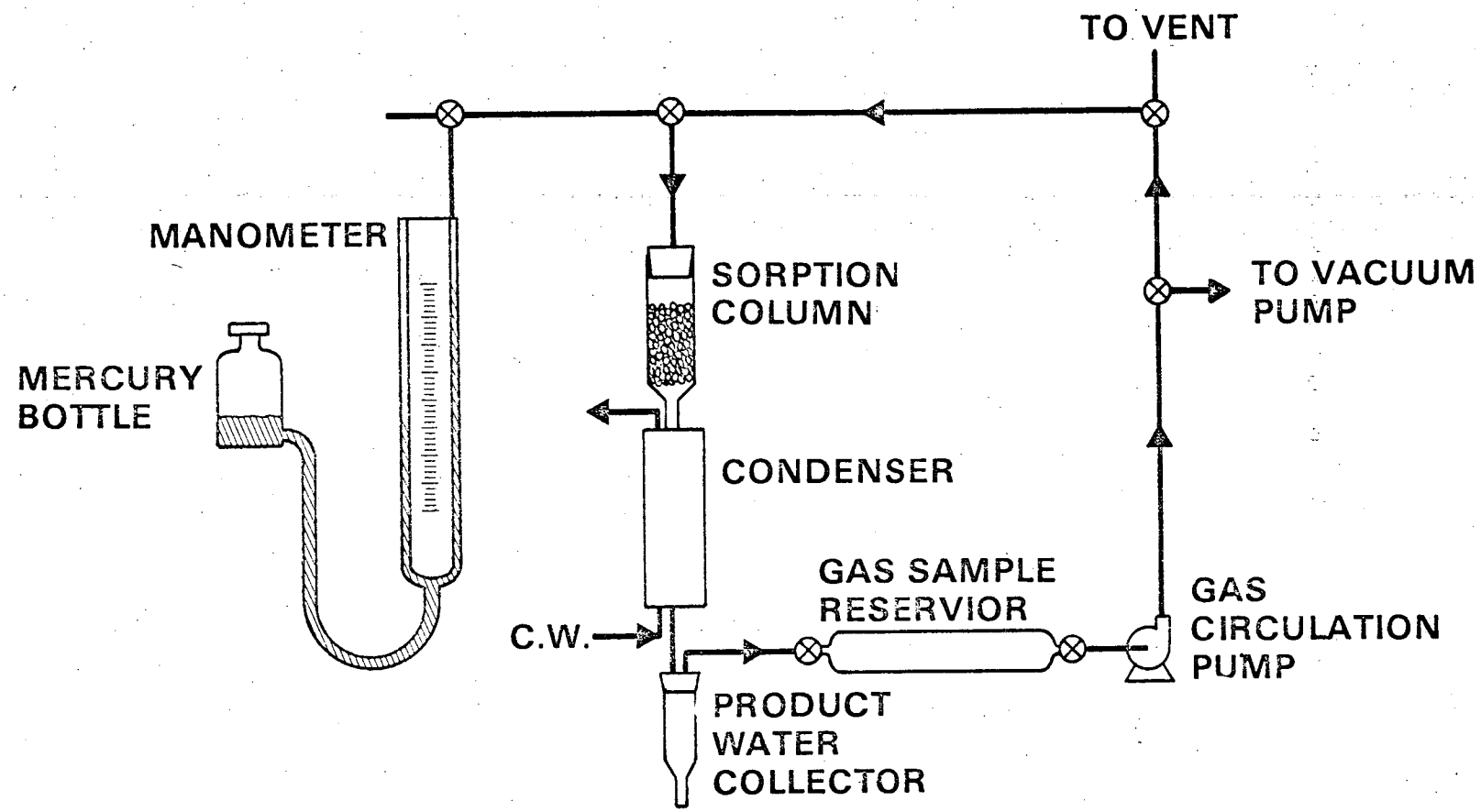


FIGURE 3. Apparatus for Sorbent Evaluation

To eliminate the moisture adsorbed on the sorbent during the test. The weight gained is considered as chemisorbed H_2S. Finally, the sorbent is regenerated by heating the sulfided sorbent in a muffle furnace overnight (16-18 hours). The change in weight represents the conversion of sulfide to oxide, sulfate or other compounds of the metal. A given sample of sorbent can be cycled repeatedly through the sequence of adsorption, drying and regeneration steps.

IV. RESULTS OF SORPTION SCREENING TESTS

A summary of results of sorption screening tests is given in Appendix V. In this section some special cases will be discussed.

Curves illustrating the sorption of H_2S by two commercial materials are shown in Figures 4-a and 4-b. The initial high rate of absorption decreases sharply after 10 minutes and nearly ceases after 40-60 minutes. Following regeneration (Runs 190 and 194), the sorption capacity of these sorbents reduces sharply to 1/3 to 1/4 of the initial value.

The Sorbent-3002 material is a pure pelletized ZnO of high surface area (23 cm^2/g), designed to remove H_2S from fuel gases at modest temperatures. This pure ZnO sorbent suffers a greater loss of sorption capacity than does the Sorbent-3012 which is a methanol catalyst containing 22 percent chromic oxide (Cr_2O_3) in addition to ZnO. Chromic oxide is presumed to stablize the ZnO lattice in the same manner that MgO stabilizes the dolomite structure through repeated cycles of sulfidation and regeneration. Run 190 shows that Cr_2O_3 is relatively ineffective for this purpose though it has a slight effect.

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

Figure 6 illustrates results of H_2S absorption experiments using a slightly different formula of the Fe, Al, Zn mixed oxide sorbent (Formula X, Appendix IV). Extrusions of this mixture tended to disintegrate to a powder on calcination. This, and the consequent higher surface area, may explain why this sorbent exhibits a higher rate of reaction than Formula XI. These curves are slightly irregular in shape, indicating irregular reaction rates for which no satisfactory explanation is evident. As with Formula XI, this material shows no tendency to lose sorption capacity following three regeneration cycles.

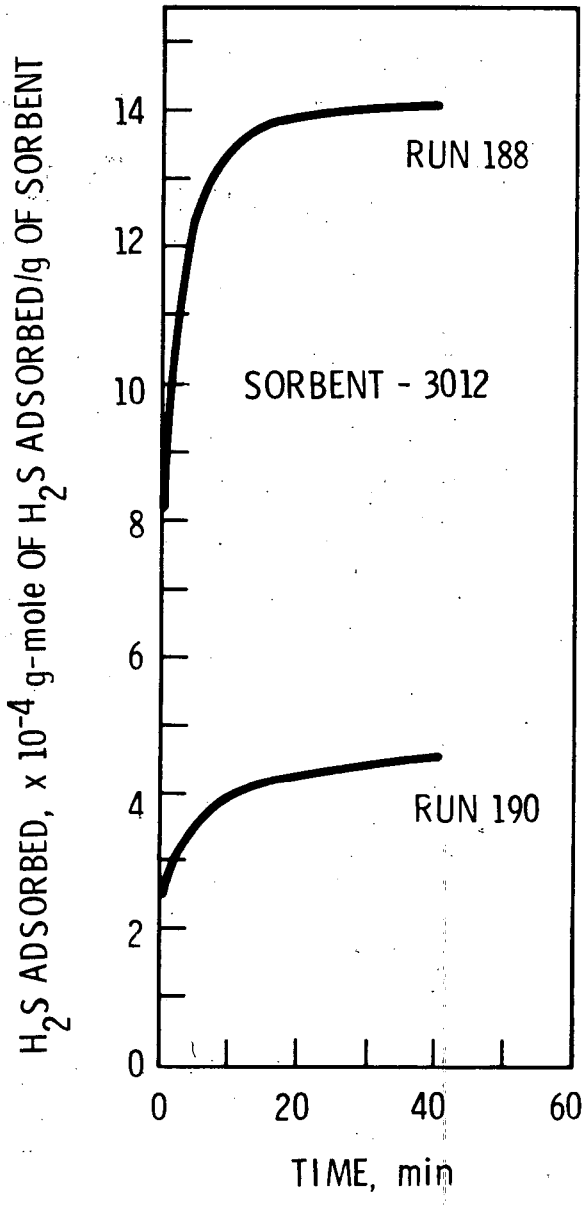


FIGURE 4-a. Gas Uptake vs Time for Sorbent-3012

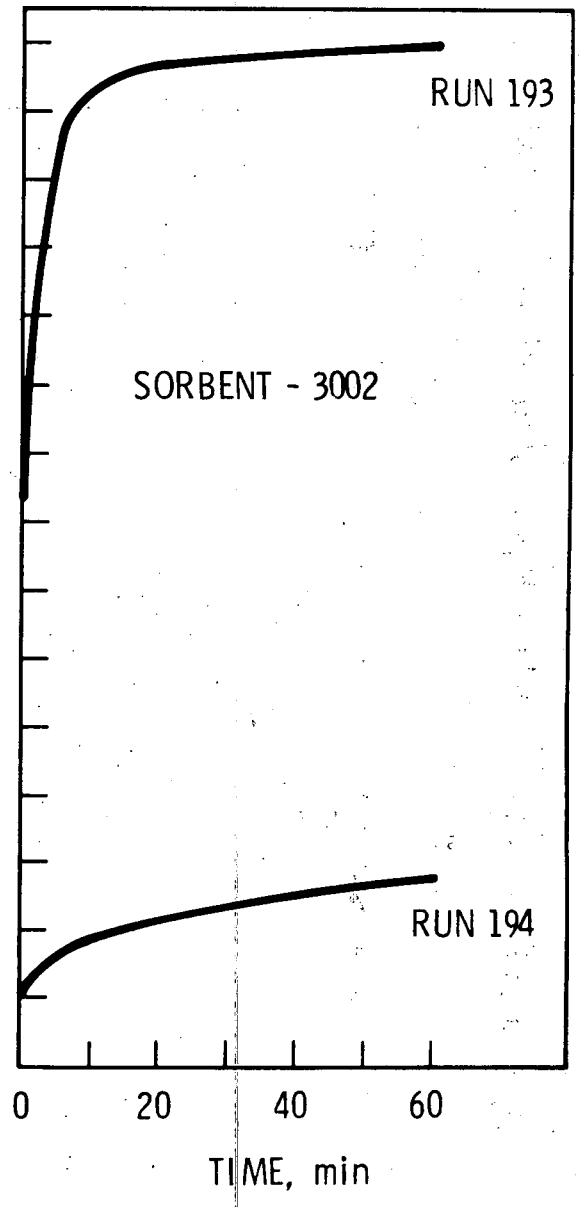


FIGURE 4-b. Gas Uptake vs Time for Sorbent-3002

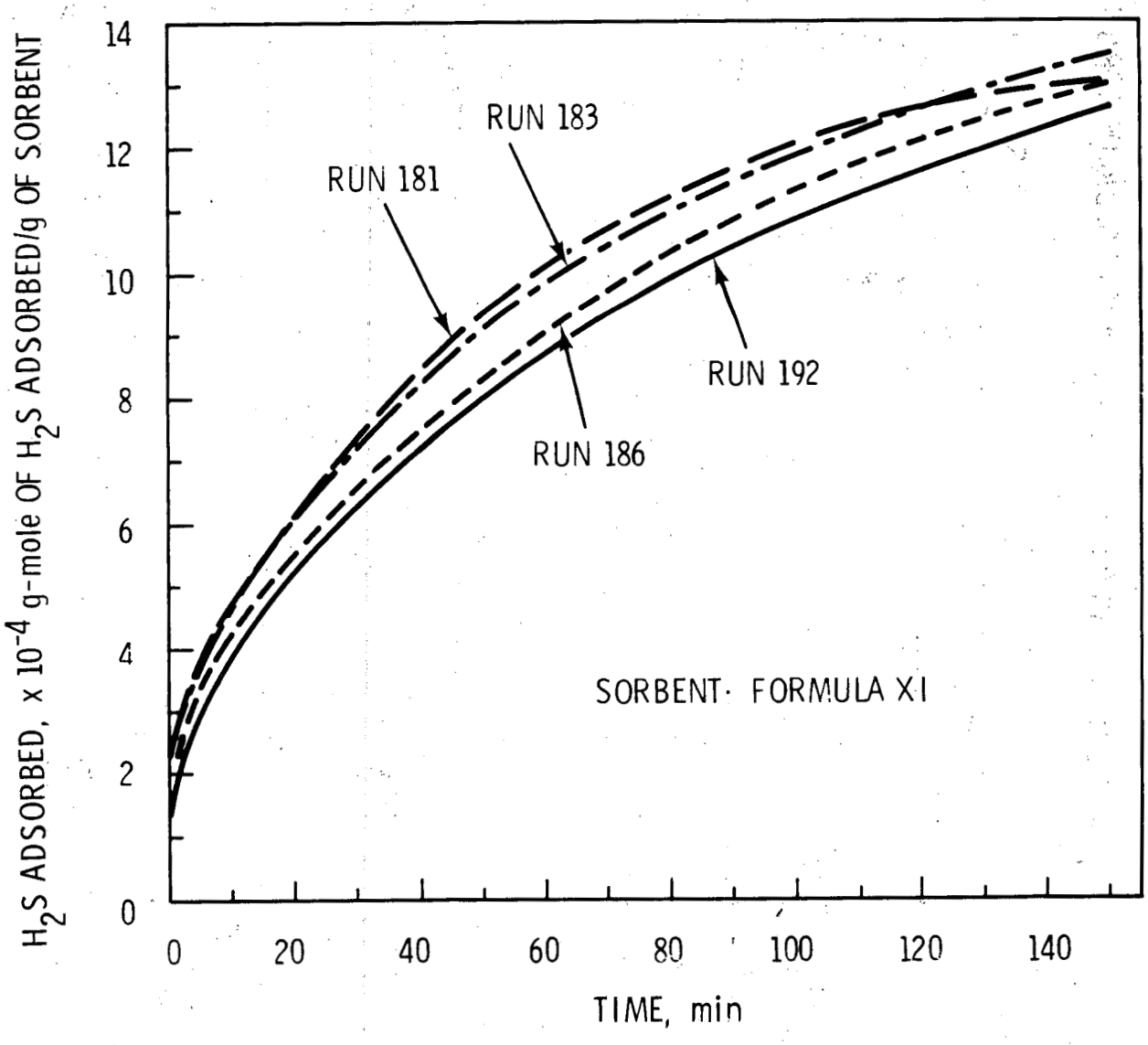


FIGURE 5. Gas Uptake vs Time for Sorbent Prepared from Formula XI

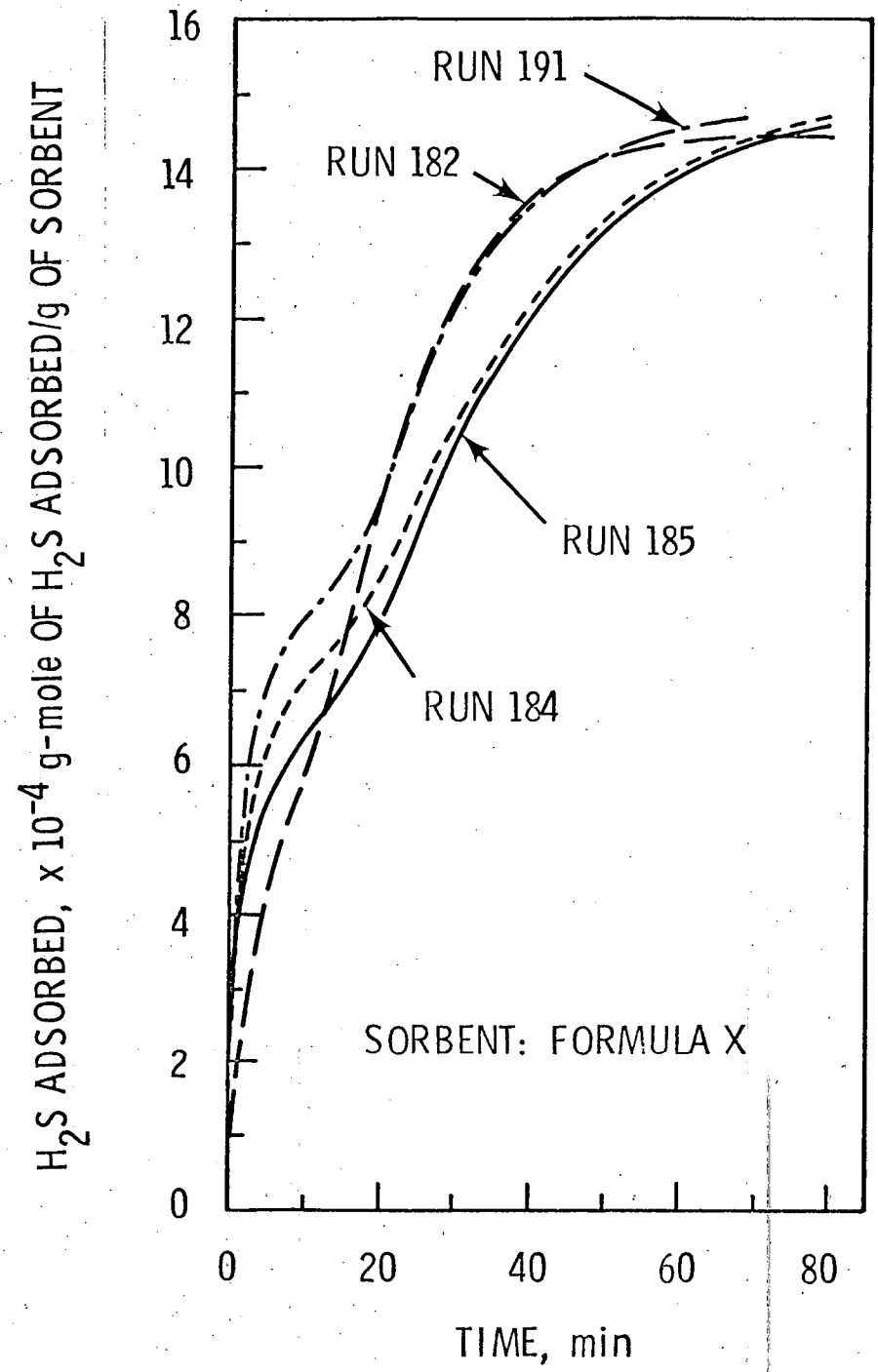


FIGURE 6. Gas Uptake vs Time for Sorbent Prepared from Formula X

Figure 7 shows the hydrogen sulfide up-take curves of a fresh and a steam regenerated Sorbent-0091. As described by the supplier, this is a polymeric sorbent which will react with hydrogen sulfide. It can be regenerated by heating or passing superheated steam through a bed of spent sorbent. The sorbent is formed in spherical beads of about 40 mesh. This material must be preconditioned by passing H_2S and steam alternatively through the bed packed with the sorbent for several cycles before the sorbent develops its full capacity to adsorb H_2S. The gas up-take curves in Figure 7 show that both rate and capacity of the sorbent are comparable to the commercially available zinc oxide (see Figures 4-a and 4-b). The gas up-take curve of steam (100 psig, 280-350°C) regenerated sorbent shows that the capacity and rate of the regenerated sorbent are not harmed by the steam regeneration process. On the contrary, steam does help the sorbent to develop its full gas up-take capacity.

Sorbent prepared from metal oxide using glass frit as a binding agent did not react with H_2S under the sorbent evaluating conditions. It was found later in an X-ray diffraction analysis that during the last step of sorbent preparation, where metal oxide-glass frit pellets were fired at temperature above the frit fusion point, the metal oxide reacted with the frit to form compounds of silicate and lost its activity.

Molecular sieve based sorbents were also subjected to the above sorbent screening tests. Results of these tests showed that sorbents so prepared were not active to H_2S. Possible reasons are that the activity of metal oxides is diminished by spatial effects within the sieve matrix, that water formed during sulfide formation was adsorbed on the molecular sieve and partially blocked available sites for sulfidization, or that the number of metal oxide sites incorporated into the molecular sieve was small.

Organic sorbents, such as aniline-lignin and melamine-formaldehyde prepared in our laboratory, showed only very small H_2S up-take capacities. Surface areas of these sorbents are low compared to ZnO pellets obtained from Catalyst Manufacturers.

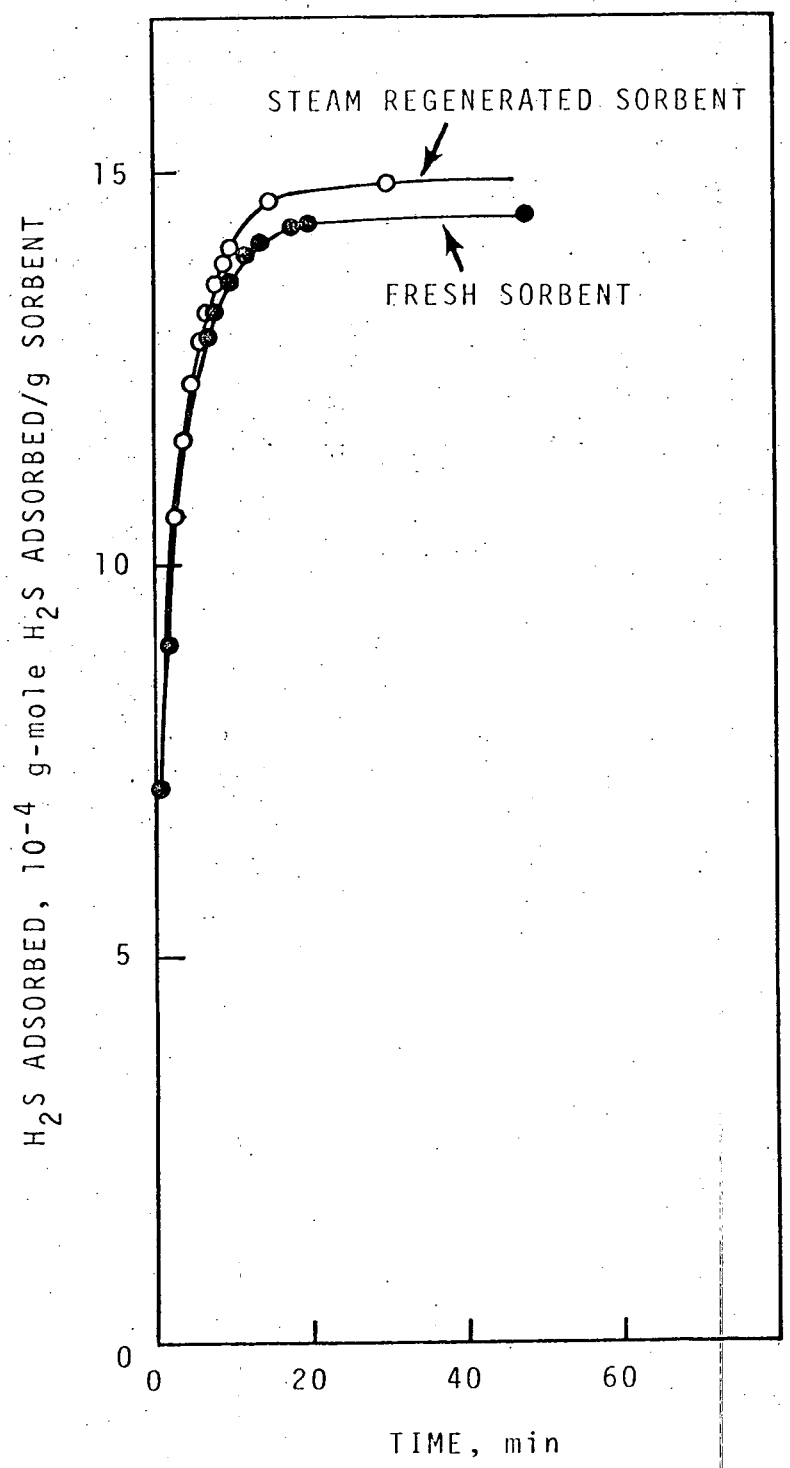


FIGURE 7. Gas Uptake vs Time for Sorbent-0091

The gas used in these screening tests contains only H_2S and air, whereas geothermal steam is sbout 99.3 percent steam. Therefore, the direct application of data obtained from sorbent screening tests to geothermal steam cases is limited. The screening tests only show that a sorbent which reacts with H_2S in the H_2S-air system could work, but is not guaranteed to remove hydrogen sulfide from steam. Those which fail to pass this test cannot work in geothermal steam. However, the regeneration conditions used for these tests are representative. The evidence that the mixed oxide sorbents and polymeric sorbent, Sorbent-0091, can be regenerated to near their full capacity is a significant finding.

V. LABORATORY SCALE GAS SORPTION TESTS

1. Equipment Setup

To simulate geothermal steam a laboratory-scale gas sorption apparatus has been constructed. A schematic flow diagram of this apparatus is shown in Figure 8. Main components of the system are: a boiler feed water pump, a steam generator, a steam superheater, a gas sorption column, a back pressure regulator, a steam condenser, a condensate catch pot, and a noncondensable gas mixing station. Instruments monitoring various operating parameters include a wet testmeter, a watermeter, a temperature recorder, thermocouples, rotameters, and gas chromatographs for analysis. All parts contacting the simulated geothermal steam are stainless steel.

Water is charged into the steam generator* through the watermeter and the gear pump.** The boiler is operated at 210 psig. Steam generated from the generator goes to the steam superheater where it is superheated to a temperature which will allow the steam to be 175°C at the inlet of the sorption column. The steam superheater is a one-inch schedule 80, 11-inch long stainless steel pipe. The pipe is packed with aluminum pellets (3/16" x 3/16"), and its outer surface is coiled with a 76-inch tubular heater.*** The temperature to which the steam is superheated can be controlled by a variac connected to the heater.

The superheated steam flows to the gas sorption system through a 1/2-inch stainless steel pipe traced with heating tape and insulated with Kaowool. Before entering the gas sorption column, steam is mixed with the noncondensable gas (H_2S and N_2) coming from the gas mixing station.

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* Chromalox - Electric Steam Boiler (CHPE-18).
** Tweed, Model 1P741WE.
*** Chromalox TRL7612.

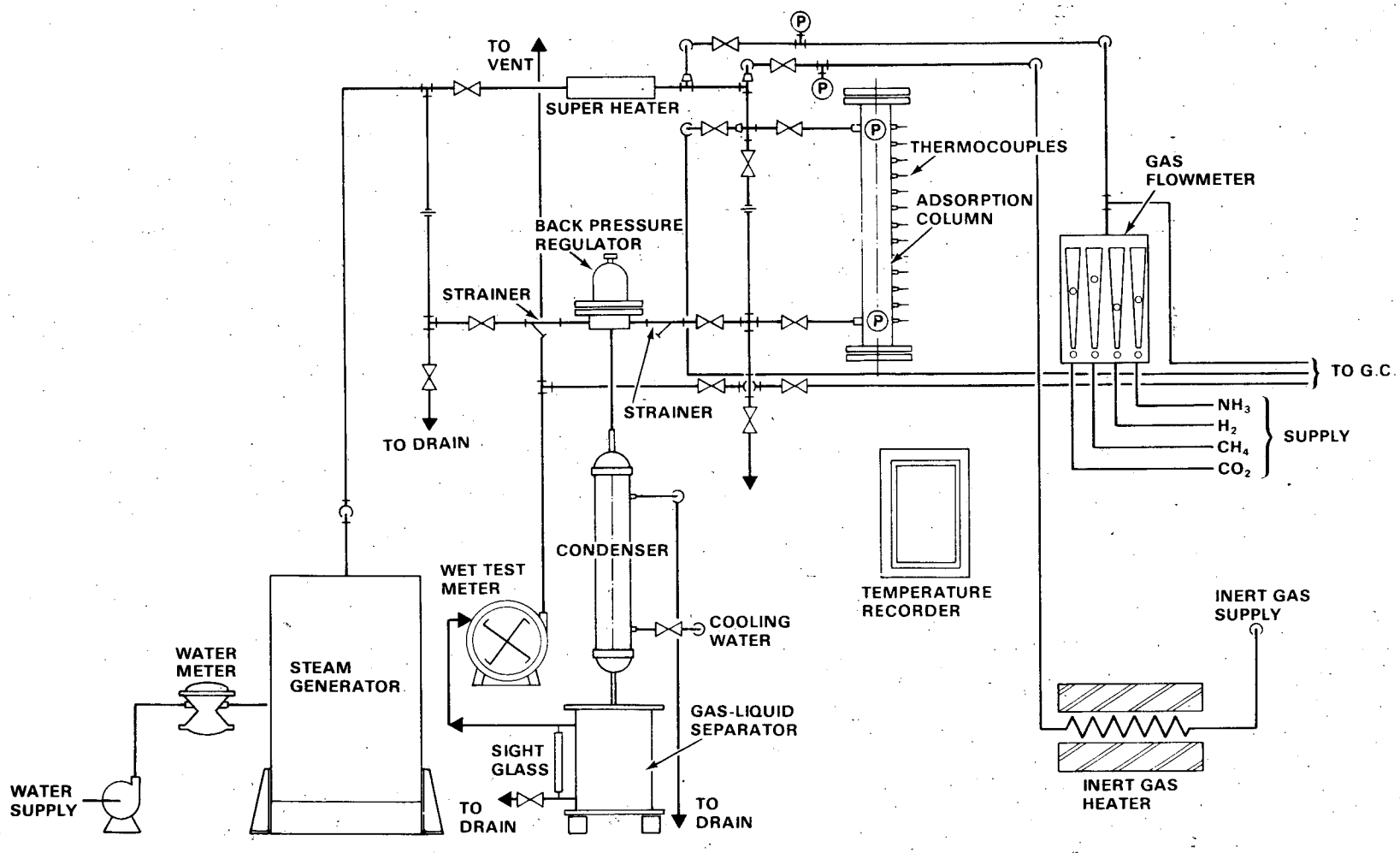


FIGURE 8. Flowchart for Removal of H_2S from Geothermal Steam Experiments

The gas sorption column is a piece of one-inch schedule 80 stainless steel pipe (24 inches long) with spacers to hold sorbent in the column and gas distributors fitted inside the pipe. The detailed design of this column is shown in Figure 9. Figure 9 also shows locations of thermocouples for measurement of sorbent bed temperatures. When the simulated geothermal steam passes through the sorbent packed column, H_2S is retained in the column until the sorbent is loaded with H_2S and breakthrough occurs. The processed steam-gas mixture coming from the column passes through the back pressure regulator,* which maintains the system at the desired pressure of 100 psig. Steam from the regulator, after being reduced to one atmosphere pressure, is condensed in the steam condenser and collected in the condensate catch pot. The unadsorbed noncondensable gas, such as nitrogen, is separated from condensate in the condensate catch pot and flows to a wet testmeter where the volume of the gas is measured. The effluent of the wet testmeter is vented to a building ventilation system. Gas samples are taken from four different places: the gas mixing station; the entrance to the gas sorption column; the exit of the gas sorption column; and the downstream of the wet testmeter. These gas samples are piped directly to gas chromatographs for analysis.

Gas chromatographs used for this project are the Hewlett Packard 5710A and 7620A research chromatographs. The Hewlett Packard 5710A with porapak N column and a flame photometric sensor is used for detecting H_2S in steam, and the 7620A with porapak Q column and a thermal conductivity cell is used for analyzing other noncondensable gases. To double check results obtained from gas chromatographic analyses a wet chemical analytical method for determining H_2S has also been established.

* Tower Equipment, Model 123-6.

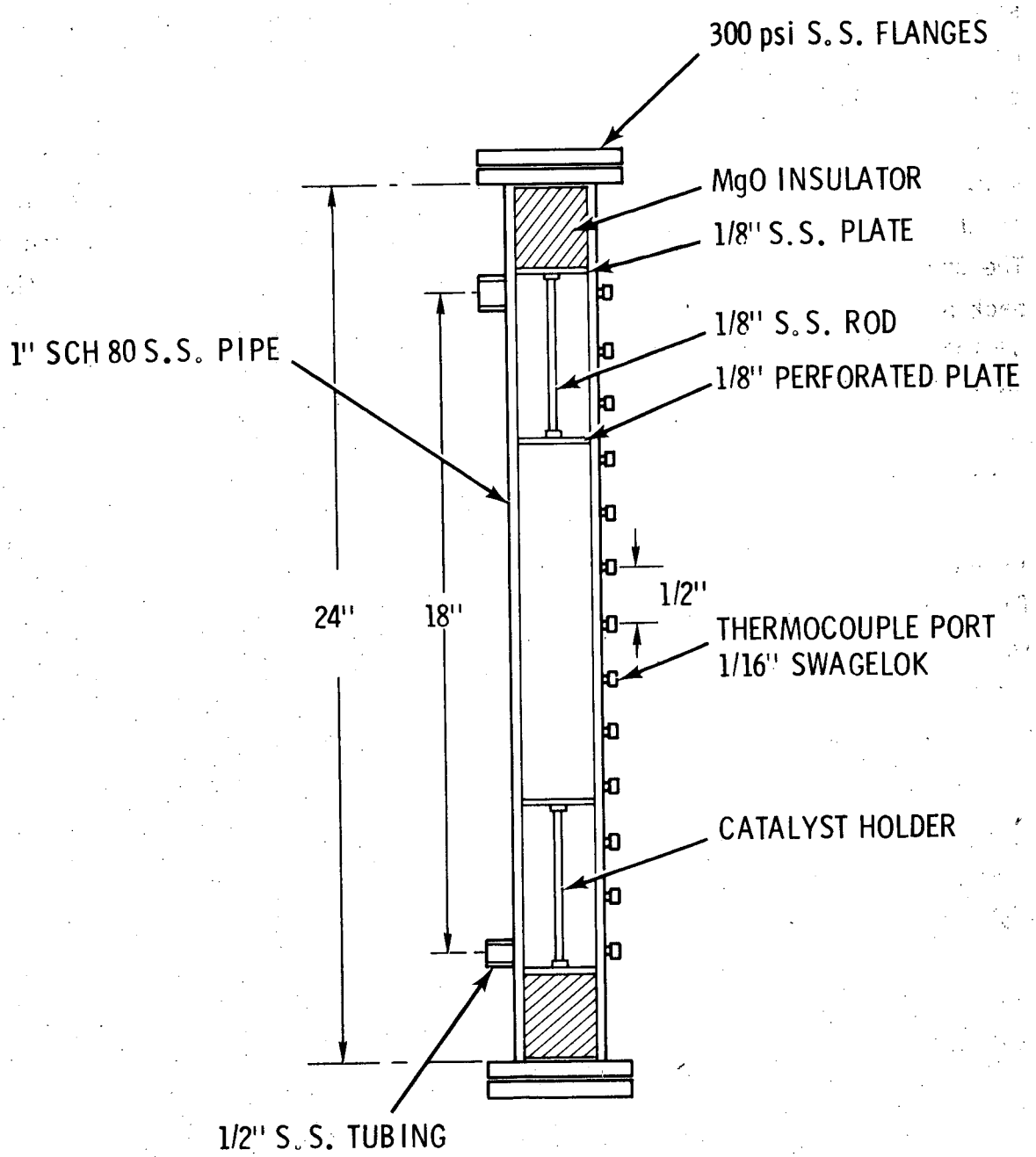


FIGURE 9. Gas Sorption Column

Samples for the wet chemical analysis are collected by passing the simulated geothermal steam or processed steam through a condenser. The condensate containing dissolved H_2S is collected in an Erlenmeyer flask attached to the bottom of the vertical condenser. Zinc acetate solution in the flask reacts immediately with the dissolved H_2S to form white zinc sulfide precipitates. The noncondensable gas in the condenser is introduced to a gas bubbling bottle also containing zinc acetate solution. The sampling apparatus is shown in Figure 10. At the end of each sampling operation the whole sampling system is purged with nitrogen introduced from the top of the condenser. The weight increase of Erlenmeyer flask due to the collection of condensate is considered to be the size of the sample. White zinc sulfide precipitate solutions, both in the Erlenmeyer flask and bubbling bottle are combined and then reacted with a known amount of acidified standard iodine solution. An iodometric method using back titration with a standard sodium thiosulfate solution is then used to determine H_2S concentration of the sample.

2. Operating Procedure

To operate the gas sorption system, the steam generator is first filled with water and the power supply switch of the generator is turned on. The pressure of the generator increases gradually to the operating pressure of 210 psig. The superheater power supply switch is turned on next. The steam rate is controlled by throttling steam through the superheater inlet valve. The noncondensable gases, H_2S and nitrogen, are blended to the desired H_2S concentration in the steam by adjusting needle valves on rotameters at the gas mixing station. The steam-H_2S mixture bypasses the sorption column until the system is ready to run. A known amount of sorbent usually in a range of 100 to 200 grams, is charged to the column. To prevent the occurrence of steam condensation, the sorption column is heated with heating tapes to a temperature slightly above that of steam before it enters the column.

Pipes carrying steam are all heated with heating tapes. The pressure of the system is kept at 100 psig by controlling the back pressure regulator. When the flow rate of steam and H_2S concentration reach a steady state, the bypass valve is shut off, steam is introduced to the sorption column, the outlet valve of the condensate catch pot is closed, and the

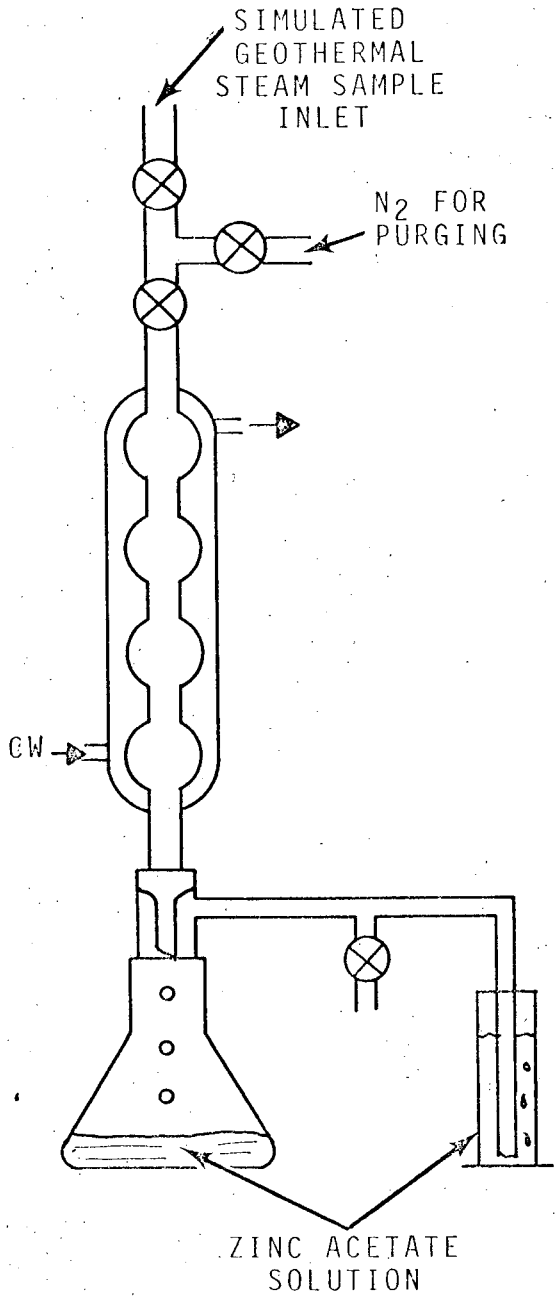


FIGURE 10. Apparatus for Collecting Geothermal Steam Sample

effluent gas line from the catch pot is connected to the wet testmeter. During the experiment, steam flow rate, pressure, temperature, and H_2S concentration at the inlet and outlet of the sorption column are monitored. At the end of the experiment, sorbent is discharged from the column and the weight increase of the sorbent is determined. Sulfur content of the spent sorbent is determined by a chemical analysis.

Two types of regeneration methods are used for reviving the spent sorbent. With metal oxide sorbents, regeneration is usually carried out in a separate reactor. Details of regeneration will be discussed later. When a polymeric sorbent, such as the Sorbent-0091, is used, the regeneration is carried out in the sorption column. Steam from steam generator is first heated to 280°C-350°C in the superheater. The superheated steam is introduced to the column packed with spent sorbent. The regeneration continues until the H_2S concentration in the column outlet stream is low (near the detectable limit). Instead of using steam, regeneration can also be done using an inert gas such as nitrogen. The regenerated sorbent, after being cooled to a temperature near that of simulated geothermal steam (175°C) is ready for another gas sorption cycle.

3. Results of Laboratory Scale Gas Sorption Experiments

Sixty-four runs have been performed with the simulated geothermal steam in the laboratory scale gas sorption unit. Sorbents used for these runs include those shown active to H_2S in the air-H_2S system. Sorbents used for these experiments are listed in Appendix II. Generally, experiments were carried out at steam pressure of 100 psig and temperature of 160° to 185° at the inlet of the gas sorption column. Water rate, which equaled the amount of steam passing through the sorption column expressed as the amount of condensate collected in the condensate catch pot was about 90 to 100 ml/min. Although the H_2S concentration in simulated geothermal steam was set at 200 ppm in the laboratory, due to control problems, the H_2S concentration varied from 140 ppm to 250 ppm. The amount of sorbent charged into the column and the depth of the bed varied depending upon the density of sorbent; this ranged from 65 to 200 grams or 8 to 13 in. respectively. The breakthrough point is defined as the time when H_2S concentration in the outlet stream of the sorption column reaches 10 percent of that of the inlet, or in

our case 20 ppm. Some runs lasted for hours but for most of them the breakthrough occurred a few minutes after the experiments began. As expected, some sorbents showed good activities to H_2S in the H_2S-air system of the sorbent evaluation tests but did not react with hydrogen sulfide under simulated geothermal conditions.

A summary of laboratory-scale gas-sorption experiments using the simulated geothermal steam is given in Appendix VI and results of a few typical runs follow.

Run 7 used Sorbent-3002. This sorbent, as described by the supplier, is a kind of zinc oxide catalyst used for desulfurization of various gas streams. It is in the form of spherical particles of 1/8- to 3/16-inch diameter with a bulk density of approximately 70 lb/ft^3. A total of 200 grams of sorbent corresponding to a bed height of 15 in. was charged into the one-inch gas sorption column. The simulated geothermal steam with 239 ppm of H_2S, 100 psig and 160°C was used for this run. The space velocity was calculated as 3.2/sec, and the total run time was four hours and twenty minutes. The operating conditions are summarized in Table 4, and the breakthrough curve (or time versus H_2S concentration of the gas sorption column effluent) is shown in Figure 11. The H_2S concentration at the outlet of the column reached 20 ppm after 80 minutes; it increased gradually to about 100 ppm at 200 minutes. The slope of breakthrough curve while the breakthrough occurred was quite steep indicating that diffusion of gas through the bed was not an important factor.

Run 9 used the same sorbent as in Run 7. However, the steam flow rate was reduced to about half of that of Run 7 and the H_2S in the inlet stream was 226 ppm. The total run time was twelve hours and thirty minutes. The space velocity was calculated as 1.7/sec, and weight increase of sorbent due to the reaction of zinc oxide and H_2S was 3.5 percent of the zinc oxide initially charged. The operating conditions are summarized in Table 5, and a material balance and the breakthrough curve are shown in Figures 12 and 13 respectively.

TABLE 4. Operating Conditions for Run 7

Run number:	7
Date:	1/16/75
Sorbent:	Sorbent-3002
Amount of sorbent charged:	200 grams
Bed height:	15 in.
Total run time:	260 minutes
Steam pressure:	100 psig
Temperature:	160°C
H_2S concentration at inlet:	238.7 ppm
Sorbent weight increase at end of experiment:	Not available
Gas measured in wet testmeter	156 ℓ

TABLE 5. Operating Conditions for Run 9

Run number:	9
Date:	1/21/76
Sorbent:	Sorbent-3002
Amount of sorbent charged:	200 grams
Bed height:	15 in.
Total run time:	12 hrs. 30 min.
Steam pressure:	102 psig (average)
Temperature:	165 - 170°C
H_2S concentration at inlet:	226 ppm
Sorbent weight increase at the end of experiment:	3.5%
Gas measured in wet testmeter:	615 ℓ

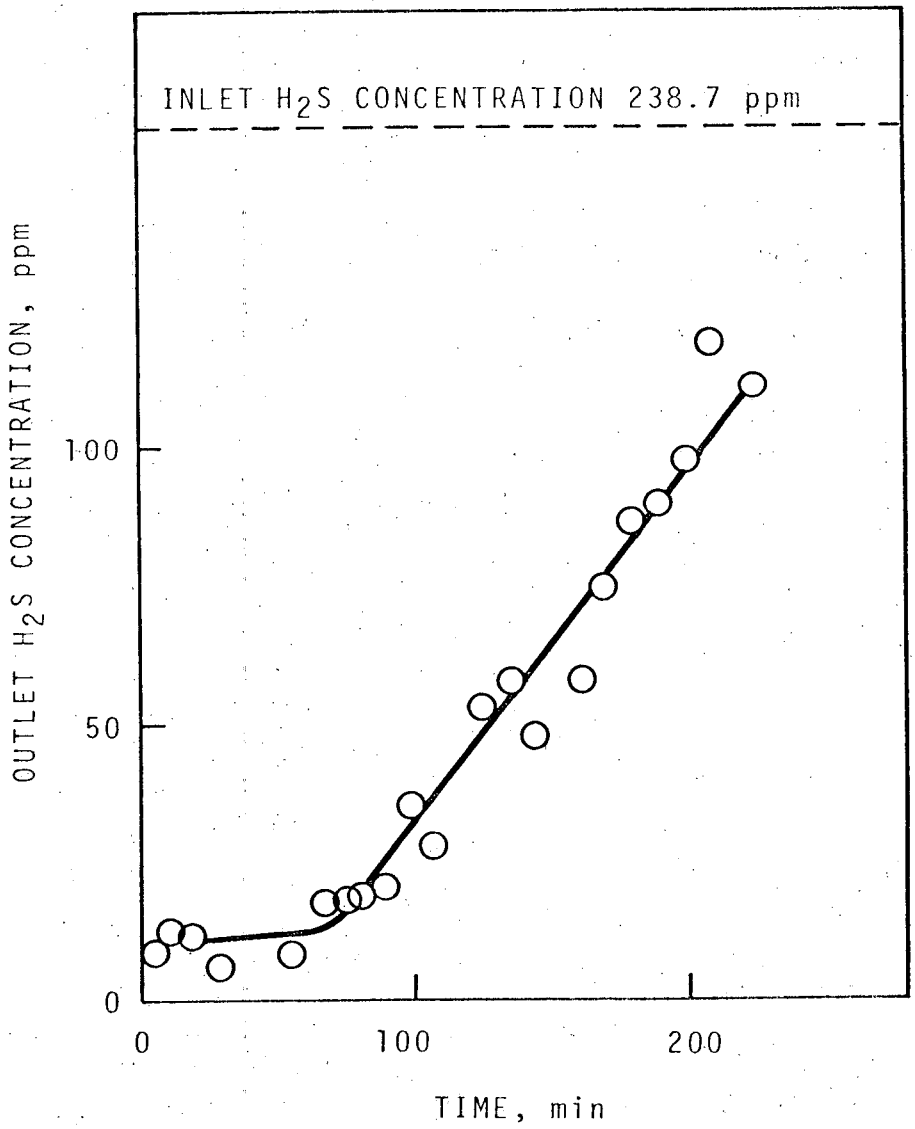
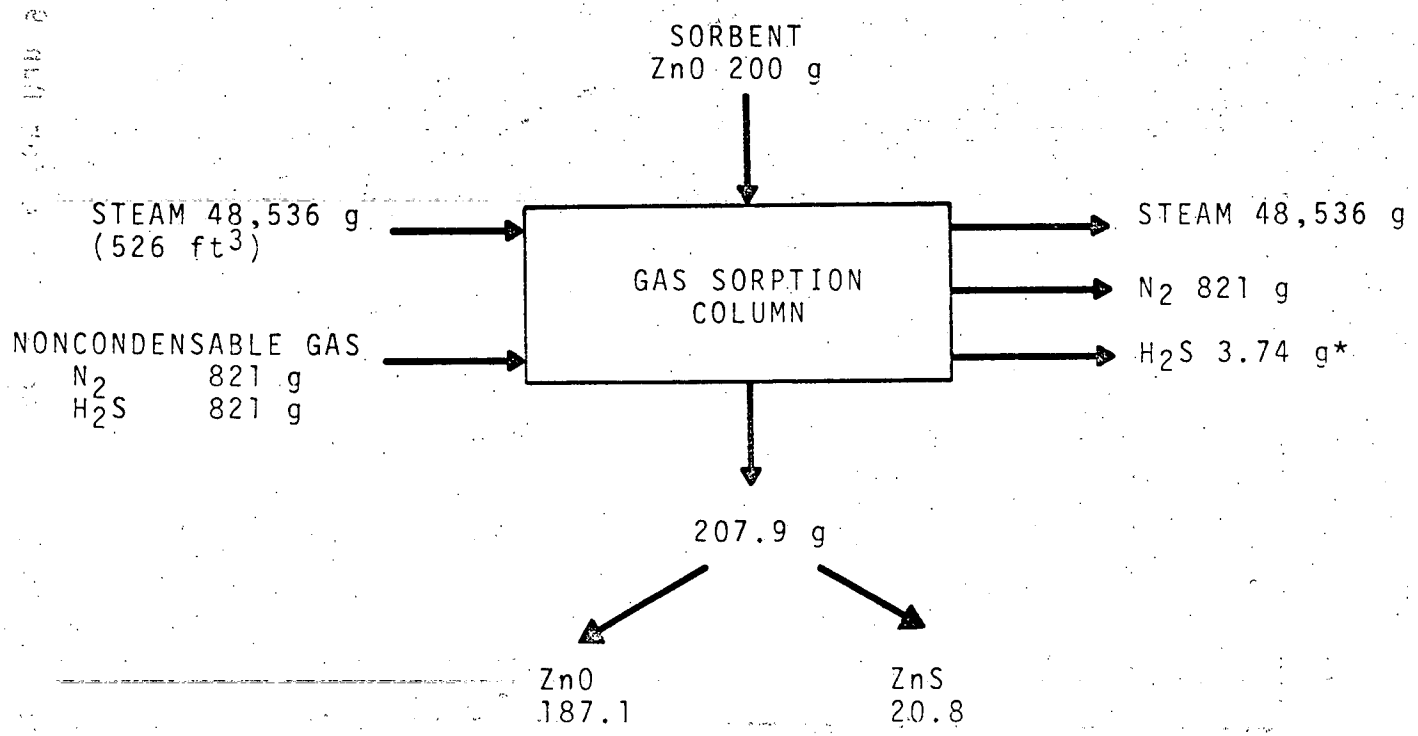


FIGURE 11. The Breakthrough Curve for Run 7



*THIS NUMBER IS CALCULATED BY DIFFERENCE

FIGURE 12. Material Balance for Run 9

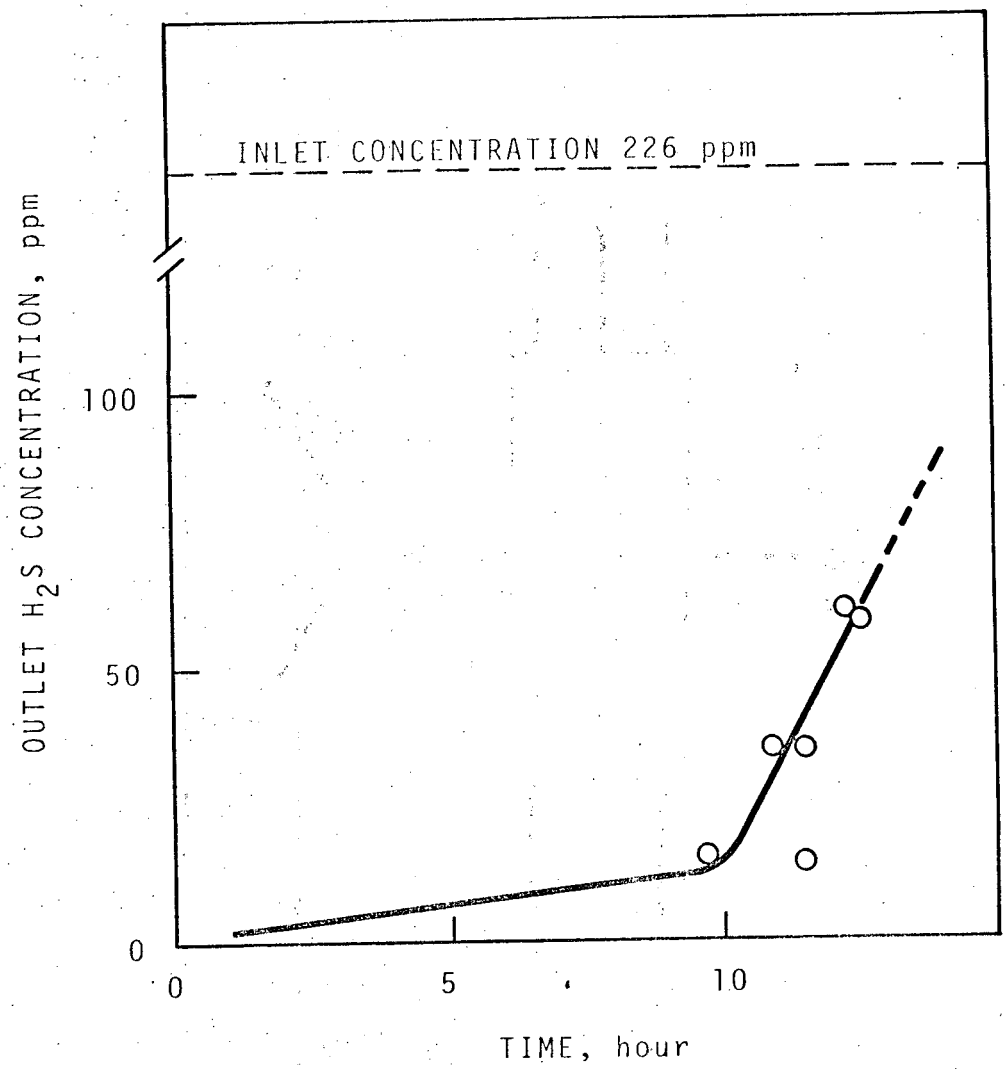


FIGURE 13. Breakthrough Curve for Run 9

The breakthrough point occurred 10.5 hours after the initiation of the experiment, which is significantly longer than in Run 7. The reason for a longer breakthrough time compared with Run 7 was mainly the use of a slower space velocity. The decrease of steam flow rate by half increases the breakthrough time almost four times. It was decided, after Run 9, that for later experiments a steam flow rate around 1.6/sec would be used.

Spherical particles of zinc oxide (Sorbent-3021) were used in Run 12. Due to the sorbent density only 174 grams of sorbent were charged into the gas sorption column. The H_2S concentration in the inlet steam was 230 ppm, and a space velocity of 1.65/sec was used for this experiment. Although the breakthrough occurred about 6 hours after the experiment had begun, in order to determine the maximum capacity of the sorbent the experiment was purposely continued until the outlet concentration reached 70 percent that of the inlet. The total run time was about 25 hours. The weight increase due to the sorption of hydrogen sulfide after 25 hours was 12%. The operating conditions and the breakthrough curve are shown in Table 6 and Figure 14 respectively. In this run two shut-offs and re-starts

TABLE 6. Operating Conditions for Run 12

Run Number:	12
Date:	1/28/76
Sorbent:	Sorbent-3021
Amount of sorbent charged:	174 grams
Bed height:	45 cm
Total run time:	25.1 hrs
Shut-off & re-start at:	11.2 hr & 19.3 hr
Steam pressure:	102 psig
Temperature:	155°C
H_2S concentration at inlet:	230 ppm
Sorbent weight increase at the end of experiment:	12%
Gas measure in wet testmeter:	425 ℓ

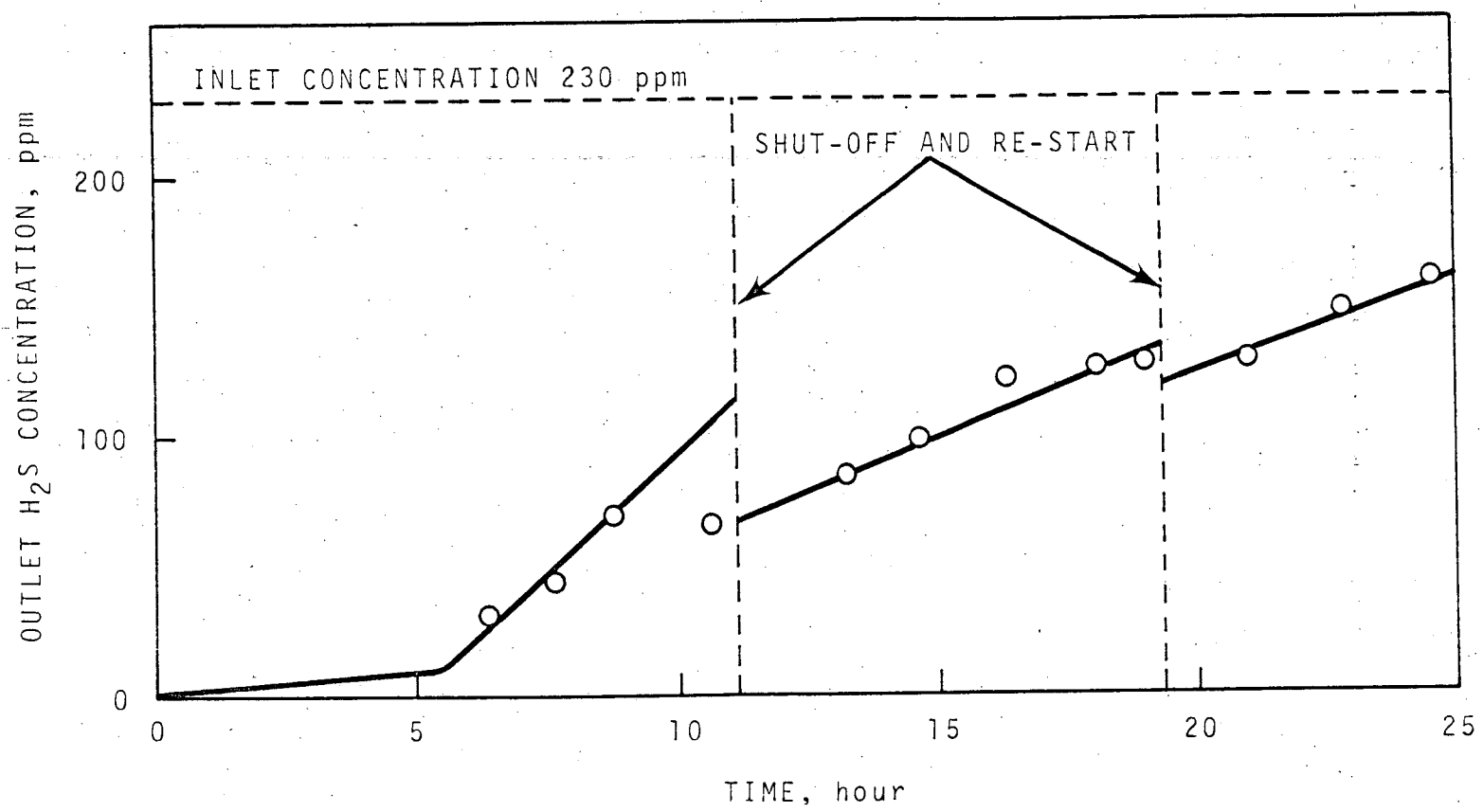


FIGURE 14. Breakthrough Curves for Run 12

were necessary due to the laboratory working schedule. In each successive period of run the slope of the breakthrough curve decreased meaning that the rate of gas sorption gradually fell off. The H_2S concentration at the beginning of each re-start was substantially lower than the concentration at the end of the previous run indicating that some of the physically adsorbed H_2S was released from the surface of the sorbent due to the existence of some residual heat in the sorption column even though the system had been shut off.

From these three runs (Run 7, 9 and 12) we found that sorbents with the same chemical composition perform differently in removing H_2S from an H_2S-steam system. Depending upon raw materials, methods of preparation, and surface characteristics sorbents could have different types of breakthrough curves. The effect of change in space velocity on the breakthrough time as in Run 7 and 9 means that kinetics of the reaction between H_2S and ZnO are important. In Figure 14, although breakthrough occurred six hours after the start of the run, sorbent kept on reacting with hydrogen sulfide until the weight increase of sorbent reached 12 percent (after 25 hours). At the breakthrough point only a small portion of active sorbent was reacted and the remaining large quantity of sorbent was intact.

Sorbent-4201 (molybdic oxide on γ alumina) which showed good activity in the H_2S-air system as in the sorbent evaluation test, was used in Run 16. Unfortunately this sorbent lost its activity drastically and the breakthrough occurred within five minutes of the start of the experiment. The low quantity of MoO impregnated on the γ-alumina substrate and the large quantity of water vapor present may have caused the fast breakthrough. Activated carbon (Sorbent-0601) was a good sorbent in the H_2S air system; however, it lost activity completely when used in the H_2S-steam system. Presence of steam in the inlet stream definitely killed the capability of adsorbing H_2S because the conventional method of regenerating spent activated carbon is by blowing superheated steam through the bed. Redwood chips impregnated with iron oxide, used in the classical iron oxide box for removing H_2S from producer gas, were also tried in our laboratory. The experiment only lasted for a few minutes and the impregnated iron oxide was leached out. The laboratory prepared sorbent designated as Formula IV, a mixture of ZnO, Fe_2O_3 and Al_2O_3, worked well in the H_2S-air system and

was also tested in the H_2S-steam system. H_2S was detected immediately after the start of the experiment. Later it was found that sorbent in the form of 1/8" extrusion disintegrated into powder upon contact with steam. Efforts to use binding agents, such as glass frit, failed. The above examples are some of the sorbents which passed the sorbent evaluation test using H_2S-air gas and failed in the H_2S-steam system.

Having searched for inorganic H_2S removal sorbents we concluded that thus far zinc oxide is the only metal oxide sorbent commercially available which removes H_2S from simulated geothermal steam. However, as will be discussed later, the regeneration of zinc oxide is technically infeasible.

Organic sorbents stable under the geothermal conditions were then sought. Two kinds of sorbents, one prepared in our laboratory and the other obtained from a resin manufacturer were investigated.

The first organic sorbent tried in our laboratory was activated carbon impregnated with diethanolamine. Diethanolamine is commonly used in wet gas purification processes. It was thought that if diethanolamine was supported on activated carbon, the resulting sorbent might have good H_2S removing capability. However, the results from laboratory testing were discouraging; very little H_2S was removed. A small amount of yellowish liquid had been collected in the condensate catch pot indicating that the impregnated diethanolamine had been leached out from the activated carbon. The low quantity of available amine in the column could be the reason for the quick breakthrough.

The sorbent obtained from a resin manufacturer and designated as Sorbent-0091 was the other organic sorbent tested in our laboratory. Sorbent-0091 is a polymeric sorbent which reacts with H_2S and can be regenerated by merely purging the spent sorbent with superheated steam. The chemical composition of the sorbent has not been revealed by the supplier due to proprietary considerations. The sorbent was tested in the H_2S-air system and worked satisfactorily. As noted by the supplier, the sorbent had to be preconditioned by loading the sorbent with H_2S and regenerating the sulfided sorbent with superheated steam for several times before the sorbent developed its full capacity. In our laboratory the sorbent was loaded and regenerated more than 10 times and the capacity of each successive run increased gradually.

In Run 61, 69 grams of preconditioned sorbent were charged into the sorption column. The length of the bed was estimated as 7.8 in., and space velocity was calculated as 4.45/sec, rather higher than those runs using metal oxides. The bed temperature was 182°C and pressure was 100 psig. The operating conditions are summarized in Table 7 and the breakthrough curve is shown in Figure 15. The breakthrough occurred about 40 minutes after the start of the experiment and the H_2S concentration of the outlet stream increased rapidly. The experiment lasted two hours and the H_2S concentration of the exit steam reached 100 ppm.

The regeneration of the sulfided sorbent was done immediately by passing superheated steam (100 psig, 340°C) through the spent sorbent-packed column. When

TABLE 7. Operating Conditions for Run 61

Run number:	61
Date:	5/19/76
Sorbent:	Sorbent-0091
Amount of Sorbent charged:	69 grams (after 14 sorption-desorption cycles)
Bed height:	7.8 in.
Total run time:	
Sorption:	130 minutes
Regeneration:	40 minutes
Steam Pressure:	100 psig
Temperature:	182°C
H_2S concentration in inlet stream:	262 ppm
Sorbent weight increase at the end of experiment:	Not available
Gas measured in wet testmeter:	33 ℓ
Space velocity:	4.45/sec

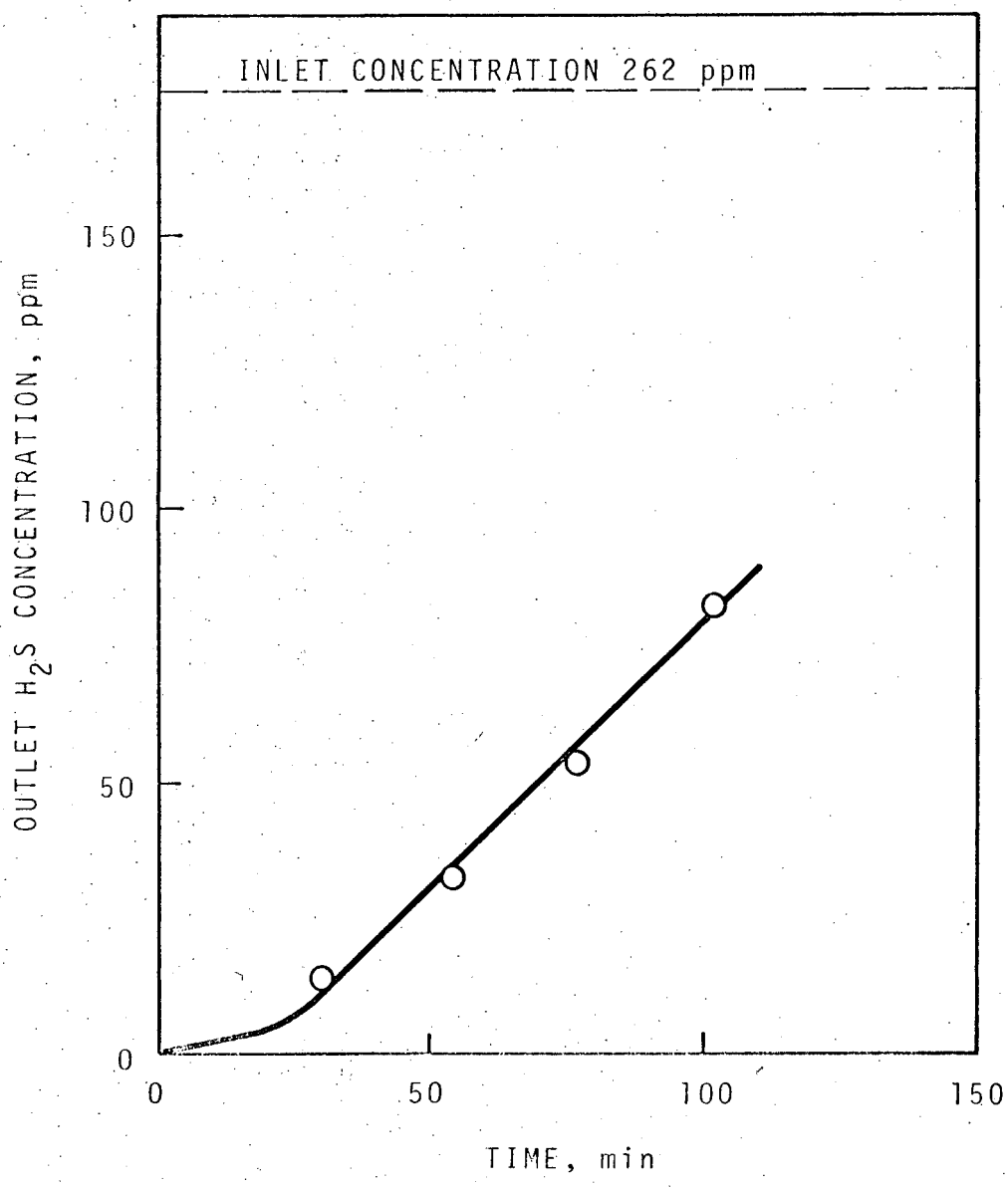


FIGURE 15. Breakthrough Curve for Run 61 Using Sorbent-0091

the temperature of resin bed reached 320°C the desorption of H_2S began, and the rate of H_2S desorption reached its maximum within a few minutes. The gas chromatographic analysis showed that the column effluent contained H_2S, steam and another unknown component. The unknown component was later identified as sulfur dioxide. The formation of sulfur dioxide was unexpected since the dissolved oxygen in the boiler feed water was less than 15 ppm. Further confirmation of the unknown component is necessary. Also, some milky liquid was collected in the condensate catch pot during the regeneration. This milky liquid was collected separately and extracted with CS_2. When CS_2 was evaporated from the extract, a white precipitate was found. This white powder was analyzed and was identified as sulfur. The steam rate during the regeneration was about 102 gram/min, and the regeneration was completed within 40 minutes. The regenerated sorbent was used in the next gas sorption experiment, and the activity of sorbent with respect to H_2S had not significantly decreased.

Overall, Sorbent-0091 is a good regenerable sorbent; however, the following conditions influence its efficiency. The particle size of the sorbent is small (about 40 mesh), thus the pressure drop in the sorption column is large. In a bed height of 8 in., the pressure drop is about 10 psi, whereas with zinc oxide (1/8" spherical particle) the pressure drop of the bed is about 3 or 4 psi. The large pressure drop in the bed causes a significant loss in the amount of power which can be generated. To reduce the pressure drop either larger particles or another kind of gas contactor, such as a fluid bed, must be used. Secondly, the amount of steam needed for regeneration is large. The required steam almost equaled the amount of steam processed up to the point where breakthrough occurred. In other words, the energy consumed for regeneration exceeds energy obtained from the processed steam because in regeneration superheated steam is used. Further research on regeneration and recovery of H_2S (or sulfur) is required in order to effectively use Sorbent-0091 to remove H_2S from geothermal steam.

VI. REGENERATION OF SPENT ZnO SORBENT

Regeneration of spent sorbent is an important operation in any H_2S removal process based on solid sorbents. Unless the sorbent is very cheap, and disposal of the spent sorbent is no problem, a once-through sorbent will not be practical (see VIII). Regeneration, therefore, is necessary for almost any practical process.

In our laboratory, ZnO has been verified as an effective sorbent for removal of H_2S from geothermal steam. Thermodynamic studies show that regeneration of spent ZnO sorbent is difficult, and to identify sources of difficulties two sets of experiments were carried out. To have a uniform spent sorbent sample for regeneration tests, fresh ZnO pellets were first saturated with H_2S in a flask and the sulfided sample was put into a vacuum oven at a temperature of 90°C, to remove moisture produced during the sulfurization. The dried sample was used for the following experiments.

i. Selection of Regenerating Gas

The sulfided zinc oxide sample was charged into a 1/2-inch stainless steel tubular reactor, and the reactor was heated to 500°C while being purged with nitrogen. When the desired temperature was reached, the regenerating gas containing nitrogen and oxygen in various ratios, was introduced. After regeneration the resulting sorbents were subjected to the gas up-take experiment described previously. The effectiveness of regeneration was measured by the capability of gas up-take (or resorption) of the regenerated sorbent. Regenerating conditions and results of regeneration are shown in Table 8.

The sorption capacity of regenerated sorbent decreases significantly from the fresh sorbent which has a sorption capacity of 14×10^{-4} g-mole/g of sorbent. The concentration of oxygen in the regenerating gas significantly affects the resorption properties; resorption capacity increases as the concentration of oxygen in regenerating gas decreases from 100 percent to 50 percent. However, oxygen concentration below

TABLE 8. Regeneration of Sulfied ZnO Sorbent Using Various Gas Composition

Run	Composition of regenerating gas[1] $\%O_2$	$\%N_2$	Sulfur loss %	Sorption capacity[2] g-mole H_2S/g sorbent
R-1	100	0	77	1.33×10^{-4}
R-2	50	50	60	3.65×10^{-4}
R-3	20	80	59	2.22×10^{-4}
R-4	10	90[3]	61	2.09×10^{-4}
	20	80		

(1) 10 grams of spent sorbent were charged into regenerator, gas flow rate was 10 ml/sec, and regeneration took four hours.

(2) The gas sorption capacity of a fresh sorbent is about 14×10^{-4} g-mole H_2S/g-sorbent.

(3) First two hours 10% O_2, 90% N_2; second two hours 20% O_2, 80% N_2,

50 percent shows little effect on the sorption capacity. To verify the idea (see Chapter III-4) that a more active sorbent can be obtained by using various oxygen concentrations during a regeneration cycle, in R-4 two levels of oxygen concentration are tried. The result of H_2S resorption is not very much different from R-3 where oxygen concentration is kept at a constant throughout the regeneration. Thus, the aforesaid idea shows no merit except saving of some oxygen. Though the optimal regenerating gas, as shown in Table 8, is 50 percent oxygen and 50 percent nitrogen, considerating the cost increase in using such kind of gas, it was decided that for the following experiments air would be used as the regenerating gas.

ii. Selection of Regenerating Temperature

In these experiments about 200 grams of H_2S-saturated samples, were charged to a reactor made of 1-inch stainless steel pipe (45 inches long). The regenerator was heated by a tubular furnace. Temperatures of 780, 500 and 300°C were used

for regenerations. Resorption capacities were determined under the simulated geothermal conditions. A summary of regenerating conditions and capacities of resorption are shown in Table 9. The capacity of resorption decreases as the regenerating temperature increases. To study the surface properties of regenerated sorbent, surface areas of regenerated sorbents were measured by the BET method based on the adsorption of nitrogen.[10] It was found that the surface area of sorbent decreases drastically from 24 m^2/g for a fresh sorbent to less than 1 m^2/g for the sorbent regenerated at 780°C. The maximum SO_2 concentrations in the outlet stream during regenerations are also shown in Table 9. The SO_2 concentration in high temperature regeneration is higher than that in low temperature regeneration. At 300° regeneration, no SO_2 was detected meaning that either no reaction took place or most of the sulfide was converted to sulfate.

TABLE 9. Regeneration of Sulfided ZnO Sorbent under Various Regenerating Temperatures

Run	Temperature °C	Regenerating gas	SO_2 in Outlet Gas %	Resorption Capacity g-mole H_2S / g Sorbent	Surface Area m^3/gram
R-5	780°C	air	23	6.75×10^{-5}	<1
R-6	500°C	air	16	1.44×10^{-4}	12
R-7	300°C	air	0	1.54×10^{-4}	13

The following conclusions can be drawn from the above experiments:

a. The low resorption capacity resulting from pure oxygen regeneration is belived to have been caused by the sharp temperature rise in the sorbent during the regeneration. The localized sharp temperature rise can cause sintering of the sorbent, and thus decrease the available surface of sorbent able to react with H_2S.

b. High temperature regeneration is favorable for SO_2 formation, but it also increases the chance for sorbent sintering and reduction of surface area. On the other hand, low temperature regeneration which causes little change in sorbent surface properties is favorable for sulfate formation. These phenomena confirm the prediction of the thermodynamic study.

c. The regeneration of spent zinc oxide sorbent is extremely difficult if it is possible.

VII. SELECTION OF GAS-SOLID CONTACTOR

As discussed in Chapter III-3, sorbents to be used in the H_2S removal process must have a reasonably high sorption capacity. A 55 MWe geothermal power plant uses 1×10^6 lb/hr of steam.[11] Based on 225 ppm H_2S concentration, 2.7 tons/day of H_2S must be removed. If we assume that three columns (sorption, regeneration, and a spare column) are required, the sorption column needs to be regenerated once a day and if the capacity of the sorbent (weight increase in sorbent due to the sorption of H_2S/weight of sorbent) is assumed to be 1, 5, 10, and 15 percent, the amount of sorbent initially required is 381, 76.2, 38.1 and 25.4 tons respectively. If the period of regeneration cycle is reduced to every three hours, the above sorbent inventories are reduced to 47.6, 9.5, 4.8 and 3.2 tons respectively. Results of such calculations are summarized in Table 10. The table shows that the amount of sorbent required is inversely proportional to the sorbent loading capacity and directly proportional to the time required for one sorption-regeneration cycle. In other words, the most economical way to operate a sorption process is to use a sorbent with high loading capacity and regenerate the spent sorbent as often as possible (if the operating cost of regeneration is negligibly small). The process with continuous regeneration will require the least amount of sorbent in the removal system.

TABLE 10. Amount of Initial Sorbent Required for a 55-MWe Geothermal Power Plant

	Time required for one sorption-regeneration cycle, hr.			
% Loading	24	12	6	3
1	381*	190.5	95.2	47.6
5	76.2	38.1	19.1	9.5
10	38.1	19.1	9.5	4.8
15	25	12.7	6.4	3.2

* Tons

Fluidized beds are the most common type of continuously regenerating solid-gas contactor now used. In a fluidized bed, the fluid (or geothermal steam in our case) is introduced from the bottom of the contactor and passes through a gas distributor which holds solid particles on top of it. Due to the upward flow of the fluid, particles are suspended and form a fluidlike state. Solid particles and fluid contact intimately, and mass and heat transfer between fluid and solid take place. The fluid passes through a disengage zone where most of the solid particles separate from the fluid. Fine particles still carried by the fluid are separated by a cyclone separator or a bag filter. The solid in the contactor can be continuously withdrawn from the contactor and sent to a regenerator. The regeneration of sorbent can also be done in a fluidized bed. A general fluidized bed sorption and regeneration scheme is shown in Figure 16. The sorbent used in the fluidized bed must be physically durable; otherwise, fine particles generated from the collision or abrasion of particles will be carried out of the contactor by the fluid. As the amount of particles present in the steam fed to the steam turbines is critical, the formation of fine particles and elutriation of fines are not tolerable in any H_2S removal processes for geothermal steam power generation. The use of a filter bag to remove fines creates a significant pressure drop which reduces the amount of available power.

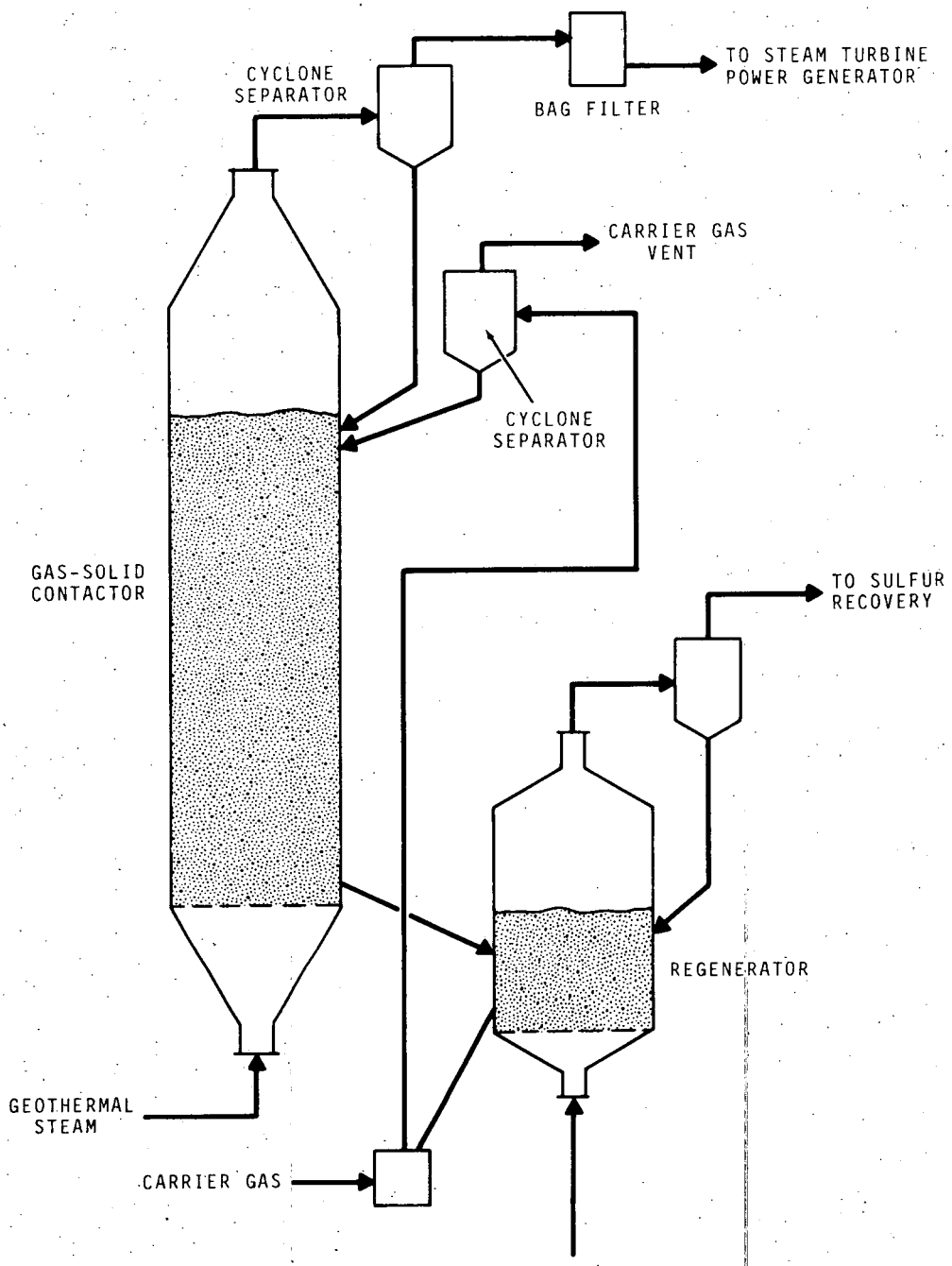


FIGURE 16. A General Flowchart of a Fluidized Bed Sorption Regeneration Scheme

A multifluidized bed system, as shown in Figure 17, can also be used. Sorbent particles and fluid flow countercurrently. At the last fluidized bed particles are transferred to a regenerator and the revived sorbent is charged back to the first bed at the top of column.

Moving bed gas-solid contactors in which solid and gas move concurrently, countercurrently or crosswise can also be used. A moving bed cross flow gas-solid contactor with a fluidized bed regenerator, as depicted in Figure 18, is typical. This contactor is essentially the same as the moving bed granular filter developed by Combustion Power Company, Inc. It is formed by two co-axial perforated cylinders inside a large container. Solid particles move downward in the annular space between two cylinders, and gas (or steam) flows perpendicular to the solid flow (either inward or outward). H_2S in the inlet gas is removed, while the gas flows crosswise through the descending solid bed. The cleaned gas flows through the outlet directly to the steam turbine for power generation. The spent sorbent is collected at the bottom of the contactor and entrained by a carrier gas to the regenerator located on the top of the gas-solid contactor. The regenerator is a fluidized bed, and the spent sorbent is regenerated by gaseous reactants introduced from the bottom of the fluidized bed. Any fine particles in the circulating solids are separated in the regenerator. The revived sorbent goes back to the contactor.

Advantages of using this kind of moving bed contactor compared to other contactors are: 1) the sorbent is continuously regenerated, 2) the pressure drop is lower than that in a fixed bed, 3) the abrasion of solid particles and the formation of fines, is less than that in a fluidized bed contactor, and 4) the separation of fine particles does not sacrifice the level of power generation. Shortcomings of this contactor are: 1) solid circulation between the contactor and the regenerator requires a sophisticated control system, and 2) the depth of bed (in the direction of gas flow) is limited. In case the gas cannot be sufficiently cleaned to the desirable H_2S concentration an additional contactor may be required.

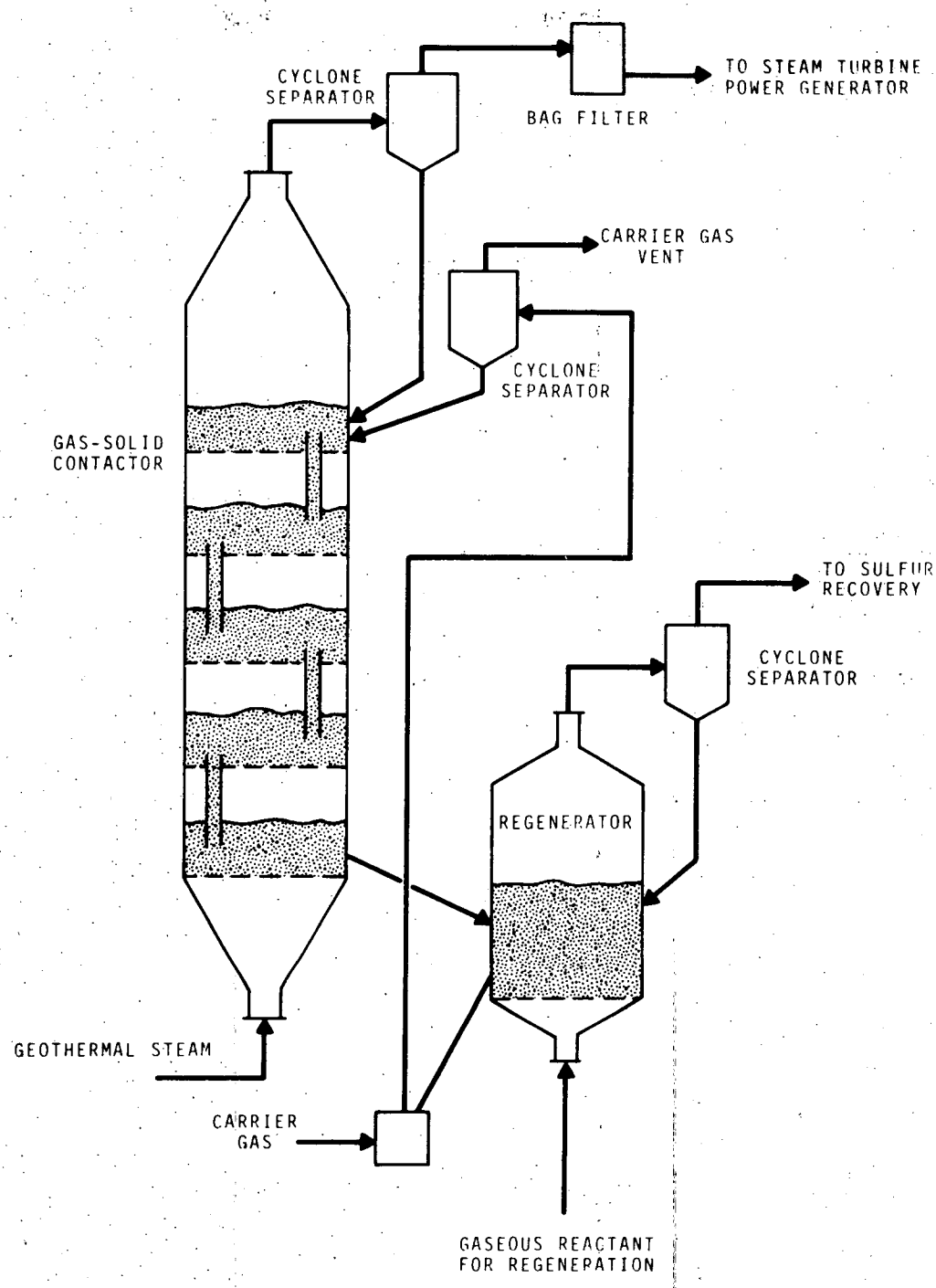


FIGURE 17. Multiple Fluidized Bed H_2S Scrubber Using Solid Sorbent

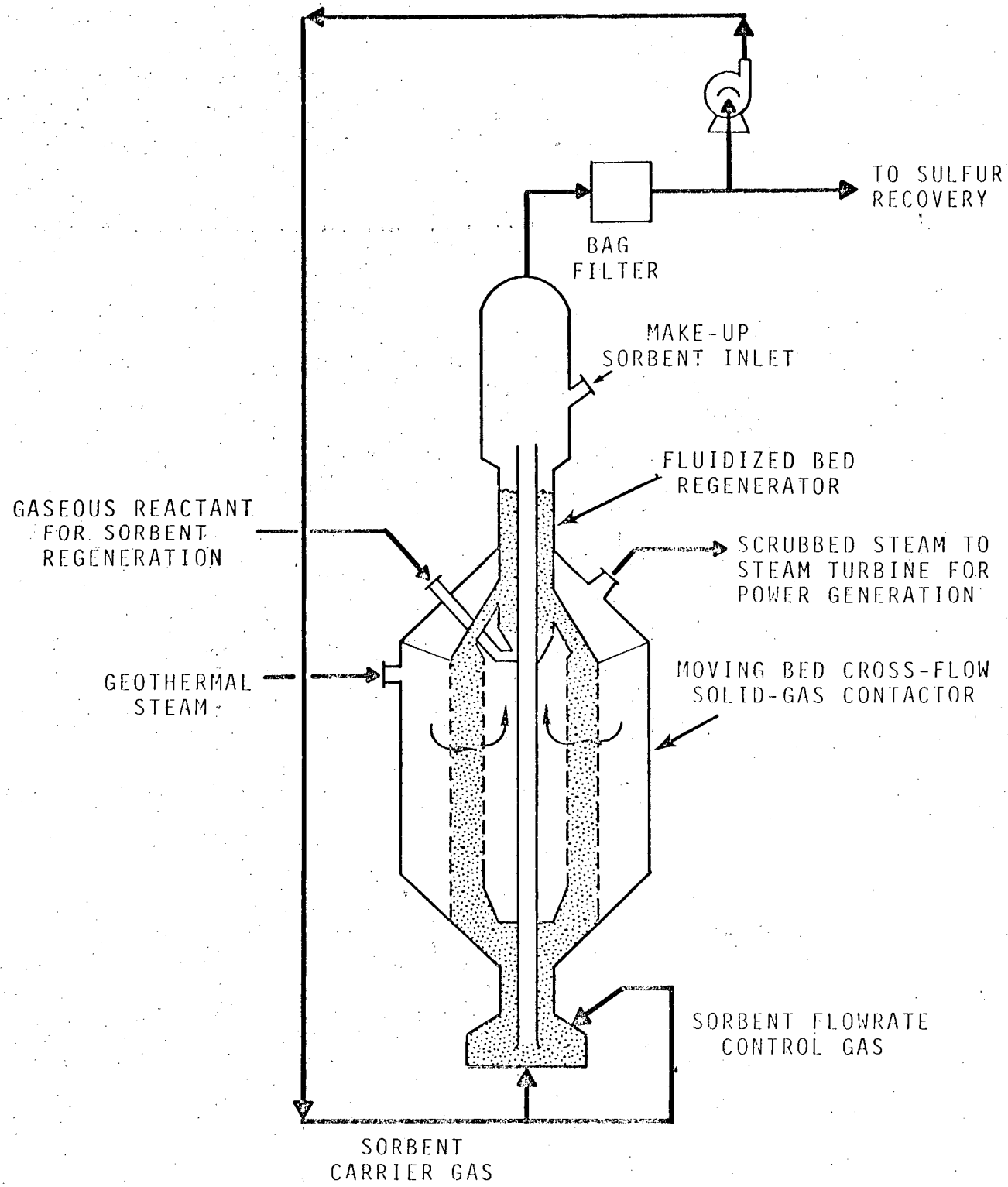


FIGURE 18. Moving Bed Cross-flow Solid-gas Contactor with Fluidized Bed Regenerator

VIII. THROWAWAY OR EXTERNALLY REPROCESSED SORBENTS

It was repeatedly observed that sulfidization of zinc oxide pellets mainly occurred at the surface of pellets, with the major portion of zinc oxide remaining intact. To more effectively utilize zinc oxide (or to increase sorbent loading capacity) sorbents prepared by coating a thin layer of active zinc oxide on the surfaces of cheap inert substrates such as paper, wood shavings or chips was considered. Such sorbents were prepared by impregnating filter paper with zinc acetate solution followed by calcining at 400°C under a nitrogen atmosphere. However, this material was found not active to H_2S in the screening tests.

The process concept of external regeneration of zinc based sorbents was briefly examined. In such a scheme, multiple contactors would be employed in a sequence which would maximize the conversion of zinc oxide to zinc sulfide. The partially sulfided sorbent would be removed from the system at the end of the sorption cycle and might be returned to a smelter for further processing.

To study the feasibility of this approach a rough cost analysis was made. The analysis was based on a 55-MWe power plant using a typical geothermal steam containing 225 ppm H_2S. If a sorbent H_2S capacity of 10% was assumed, 4.3 ton/day of fresh zinc oxide would be required. The spent zinc oxide can be considered as a zinc concentrate and sold to zinc smelters. Based on the assumed composition of spent zinc oxide sorbent and the current toll charge schedules for the purchase of zinc concentrates (Cominco Ltd., Trail, B. C., Canada),[12] the value of the spent sorbent is approximately $530/ton. Contact with present suppliers of zinc oxide sorbents revealed that the current price of zinc oxide sorbent is in a range of $1 to $3/lb. When translated to power costs the sorbent cost with consideration of spent sorbent credit would be 0.53 to 1.6¢/kW hr. This cost range does not include transportation and plant operating costs. It is evident that this approach is not economically attractive even without these additional costs.

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APPENDIX I-A

CHANGE OF FREE ENERGY OF REACTION OF CANDIDATE SORBENT WITH HYDROGEN SULFIDE AT 176°C

Sorbent	Sorbent Product	ΔG
ZnO	ZnS	-17.5
Fe	FeS	-14.17
Fe	FeS_2	-13.9
FeO	FeS	-11.5
FeO	FeS_2	-81.1
Fe_2O_3	FeS,FeS_2	-22.4
SnO	SnS	-5.89
Ag	Ag_2S	-1.19
Ag_2O	Ag_2S	-54.02
Al	Al_2S_3	-87.26
Al_2O_3	Al_2S_3	+119.16
Ba	BaS	-32.96
BaO	BaS	-15.41
Bi	Bi_2S_3	-8.87
Bi_2O_3	Bi_2S_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_2O_3	Co_2S_3	--
Cu	CuS	-63.37
CuO	CuS	-28.13
Cu_2O	Cu_2S	-32.48
Cu (with CS_2)	Cu_2S	-109.60

APPENDIX I-A (cont'd)

Sorbent	Sorbent Product	ΔG
K	K_2S	-73.53
K_2O	K_2S	-64.77
Li	Li_2S	--
Mg	MgS	-66.67
MgO	MgS	-3.18
Mo	MoS_2	-33.50
MoO_2	MoS_2	-34.61
MoO_3	Mo_2S_3	-24.78
Na	Na_2S	-65.42
Na_2O	Na_2S	-33.18
Nb	Nb_2S_3	--
Ni	NiS	-1.42
Ni	Ni_3S_2	-8.02
NiO	NiS	-6.14
Sb	Sb_2S_3	+4.47
Sb_2O_3	Sb_2S_3	-30.49
Si	SiS	+19.50
Si	SiS_2	-30.00
SiO_2	SiS_2	+56.15
Ta	Ta_2S_4	--

-- Thermodynamic data insufficient to permit calculation.

APPENDIX I-B

CHANGE OF FREE ENERGY OF OXIDATION OF METAL SULFIDES AT VARIOUS TEMPERATURES

Reactant	Product	(-ΔG°) at 176°C	at 800°C	at 1000°C
ZnS	ZnO, SO_2	97.8	86.96	83.48
ZnS	ZnO, SO_3	111.2	86.14	78.12
ZnS	$ZnSO_4$	148.64	97.38	80.98
ZnS	ZnO, S	25.63	13.02	8.98
ZnS, SO_2	ZnO, S	-17.95	-44.67	-53.30
ZnS, SO_3	ZnO, S	-18.89	-58.6	-71.30
ZnS, CO_2	ZnO, S,CO	32.71	32.36	32.25
ZnS, H_2O	ZnO, H_2SO_4, H_2	13.78	-51.21	-72.01
ZnS, CO_2	$ZnCO_3$, S, CO	-34.48	-60.29	-68.56
FeS_2	$FeSO_4$, SO_2	204	141.31	121.25
FeS	$FeSO_4$	146.7	75.34	52.52
FeS	FeO, S	31.98	19.43	15.42
Bi_2S_3	$Bi_2(SO_4)_3$	415.66	209.84	143.98
Bi_2S_3	Bi_2O_3, SO_2	288.43	262.56	254.28
Bi_2S_3	Bi_2O_3, SO_3	150.53	97.49	80.51
CaS	$CaSO_4$	188.59	134.83	117.63
CaS	CaO, SO_3	112.79	87.3	79.15
CaS	CaO, SO_2	99.45	88.13	84.51
CdS	CdO, SO_2	89.25	77.99	74.38
CdS	CdO, SO_3	102.59	77.17	69.04
CdS	$CdSO_4$	150.03	98.65	82.21
CoS	$CoSO_4$	155.53	111.21	97.03
CoS	CoO, SO_2	95.37	77.79	72.18
CuS	CuO, SO_3	101.01	74.59	66.14
CuS	$CuSO_4$	133.51	79.25	61.89

APPENDIX I-B (cont'd)

Reactant	Product	(-ΔG°) at 176°C	at 800°C	at 1000°C
Cu_2S	Cu_2SO_4	103.34	24.03	-1.36
Cu_2S	CuO, SO_3	118.57	75.22	61.34
K_2S	K_2SO_4	217.57	182.57	171.36
K_2S	K_2SO_3	133.97	88.04	73.34
K_2S	K_2O_2, SO_3	85.01	46.72	34.47
MgS	$MgSO_4$	188.4	140.84	125.61
MgS	MgO, SO_3	141.68	122.7	116.63
MoS_2	MoO_2, SO_3	223.84	168.64	150.98
MoS_2	MoO_3, SO_3	271.42	212.39	193.56
Na_2S	Na_2SO_3	154.11	129.98	122.26
Na_2S	Na_2SO_4	213.79	174.87	162.42
Na_2S	Na_2O, SO_3	95.97	83.87	79.99
SnS	SnO, SO_2	109.91	94.78	89.94
SnS	SnO, SO_3	123.25	93.96	84.58
SnS	SnO, S	37.71	20.85	15.45
SnS, SO_2	SnO, S	3.22	-32.24	-43.59
SnS, SO_3	SnO, S	17.35	-35.09	-51.88
SnS, CO_2	SnO, S, CO	-20.63	-24.53	-25.77
SnS, H_2O	SnO, H_2SO_4, H_2	-94.86	-164.11	-186.26
Ag_2S	Ag_2O, SO_2	61.78	49.39	45.43
Ag_2S	Ag_2O, SO_3	75.13	48.58	40.08
Ag_2S	Ag_2SO_4	124.82	71.68	54.68
Al_2S_3	Al_2O_3, SO_2	466.58	433.38	422.76
Al_2S_3	Al_2O_3, SO_3	328.67	268.31	248.99
Al_2S_3	$Al_2(SO_4)_3$	577.98	420.59	368.63
BaS	BaO, SO_2	97.15	95.47	94.93
BaS	BaO, SO_3	112.9	100.42	96.43
BaS	$BaSO_4$	214.45	172.94	159.66
BaS	$BaSO_3$	143.67	97.72	83.02
NiS	$NiSO_4$	159.92	110.29	94.41

APPENDIX I-B (cont'd)

Reactant	Product	$(-\Delta G°)$ at 176°C	at 800°C	at 1000°C
NiS	NiO, SO_3	123.01	105.79	100.28
Sb_2S_3	$Sb_2(SO_4)_3$	400.08	216.32	157.51
Sb_2S_3	Sb_2O_4, SO_2	523.54	420.53	387.57

APPENDIX II

SORBENTS OBTAINED FROM MANUFACTURERS

Code Name	Description	Size
Sorbent-0601	Activated carbon	4 x 8 mesh
-3001	Zinc oxide	3/16 in. extrusions, for sulfur removal
-3002	Zinc oxide	1/8 in. to 3/16 in. spheres for sulfur removal
-2601	Promoted iron oxide; Fe_2O_3 60%, K_2CO_3 26%, Cr_2O_3 2.5% Dehydrogenation catalyst	
-2901	Low temperature CO conversion catalyst	1/4 in. x 1/8 in. tablets
-4201	Molybdic oxide on gamma alumina (Nominal composition 3-4% MoO_3)	3/16 in. x 1/8 in. tablets
-2902	Copper, zinc, chrome catalyst Cr 5.9%, Zn 52%, Cu 13%	3/8 in. x 3/8 in. tablets
-2903	Copper manganese catalyst	3/16 in. x 3/16 in. tablets
-2701	Cobalt oxide on gamma alumina (Nominal composition 3% Co)	3/16 in. x 1/8 in. tablets
-2702	Cobalt molybdate on gamma alumina	1/8 in. extrusion for hydrodesulfurization and olefin hydrogenation
-2602	High temperature CO conversion catalyst (Nominal composition Fe 54.5%, Cr 6%)	3/8 in. x 3/16 in. tablets
-2904	Low temperature CO conversion catalyst	1/4 in. x 1/8 in. tablets
-2603	High temperature CO conversion catalyst	3/8 in. x 3/8 in. tablets
-3011	Zinc oxide, for removal of sulfur from gas stream	3/16 in.
-1311	Alumina catalyst	3/16 in.

APPENDIX II (cont'd)

Code Name	Description	Size
Sorbent-3012	Zinc chromite, for methanol synthesis	1/4 in.
-2611	Iron catalyst, for dehydrogenation	1/8 in.
-4210	Molybdena alumina catalyst for hydrogenation, dehydrogenation and hydroforming	1/8 in.
-2710	Cobalt molybdate catalyst for desulfurization and denitrogenation	1/8 in.
-3021	Zinc oxide	
-3022		
-3023		
-2621	Iron Oxide	
-2631	Iron Oxide	
-1441	Silica gel catalyst, grade 57 57 - 08 - 5 x - 1950	
-1442	Silica alumina pellets grade 980 - 08.5 x 1950	3/16 in. x 3/16 in.
-3051	Activated zinc oxide	4 x 4 - 6mm
-1461	Green sand	
-1171	Strong-acid cation exchange resin, sodium form. DS 25575	
-0081	Composition unknown	
-0082	Composition unknown	3/8 in. x 3/16 in.
-0083	Composition unknown	4/8 mesh

APPENDIX II (cont'd)

Code Name	Description	Size
Sorbent-3081	ZnO catalyst	
-0084	4/8 LVM attapulgite	
-0085	8/16 LVM bauxite	
-2681	Iron oxide impregnated on redwood chips	
-2682	N-536 Iron oxide	
-2683	Pure red iron oxide	
-2684	Pure red iron oxide	
-2685	Pure red iron oxide	
-2686	Iron sulfate	
-2687	Iron oxide	
-2481	Chromite-spinel	
-2687	Iron oxide powder	
-0086	Composition unknown	
-0681	Melamine	
-0091	Composition unknown	
-0682	Lignosite	

APPENDIX III

DETERMINATION OF TOTAL VOLUME OF GAS SORPTION EVALUATION APPARATUS AND THE AMOUNT OF H_2S REACTED WITH SORBENT

1. TOTAL VOLUME OF GAS SORPTION EVALUATION APPARATUS

Let the volume of gas sorption apparatus excluding the gas sample reservoir equal V_1, and the gas sample reservoir be V_2. The pressure of the gas sample reservoir after being partially evacuated is P_2, and the pressure of the total system after the reservoir is connected is P_2'. The moles of gas originally in the apparatus excluding the gas reservoir equal N_1, and those of the gas in the reservoir are N_2. Then

$$N_1 = \frac{P_1 V_1}{RT} \tag{1}$$

where

P_1 is atmospheric pressure (1 atm.)
T is the temperature of system (298°K), and
R is the gas constant; and

$$N_2 = \frac{P_2 V_2}{RT} \tag{2}$$

When the gas reservoir is connected to the system, the total moles of gas in the system are:

$$N_1 + N_2 = \frac{P_2' \ (V_1 + V_2)}{RT} \tag{3}$$

From equations (1), (2), and (3)

$$\frac{P_1 V_1}{RT} + \frac{P_2 V_2}{RT} = \frac{P_2' \ (V_1 + V_2)}{RT}$$

$$V_1 = \frac{V_2 \ (P_2' - P_2)}{P_1 - P_2'} \tag{4}$$

If Rm and Rm' are the manometer reading (Cm) of pressure P_2 and P_2' respectively, then equation (4) can be written as:

$$V_1 = \frac{V_2\,(76 - Rm' - 76 + Rm)}{76 - 76 + Rm'} = \frac{V_2\,(Rm - Rm')}{Rm'}$$

or

$$V_1 = \frac{V_2\,(Rm - Rm')}{Rm'} \tag{5}$$

The total system volume is:

$$V_T = V_1 + V_2 = V_2\left[\frac{Rm - Rm'}{Rm'} + 1\right] = V_2\left[\frac{Rm}{Rm'}\right]$$

$$V_T = V_2\left[\frac{Rm}{Rm'}\right] \tag{6}$$

2. AMOUNT OF H_2S REACTED WITH SORBENT

Assumptions:

a. The gas sorption test is run under an isothermal condition and the system temperature equals the room temperature (25°C).

b. The gas in the sorption system is saturated with water vapor at room temperature once the experiment is started. The saturated water vapor pressure P_W is 0.03 atm at 25°C. The excess water vapor condensed from the system during the sorption test exists as liquid water; the volume of liquid water is negligible compared to the volume of total system.

The number of moles of H_2S charged into system is described by

$$N^o_{H_2S} = N_2 = \frac{P_1 V_2}{RT} \tag{7}$$

where

$N^o_{H_2S}$ is moles of H_2S at time zero. The moles of air (or inert gas) in the system equal

$$N_{air} = \frac{P_1 V_1}{RT} \tag{8}$$

At time t, the manometer reading is R_m^t.

The total moles of gas in the system at time t are

$$N_T^t = \frac{[(76 - R_m^t)/76]\ (V_1 + V_2)}{RT}$$

$$= \frac{[1 - Rm^t/76]\ V_2 \left[\frac{Rm}{Rm^t}\right]}{RT} \tag{9}$$

Water vapor in the system is:

$$N_W = N_T^t \cdot \frac{P_W}{P^t} \tag{10}$$

where

P^t is the system pressure at time t.

From equation (9) and (10)

$$N_W = \frac{[1 - Rm^t/76]\ V_2 \left[\frac{Rm}{Rm^t}\right]}{RT} \cdot \frac{P_W}{[76 - Rm^t]/76}$$

$$= \frac{V_2 \left[\frac{Rm}{Rm^t}\right] P_W}{RT} \tag{11}$$

Amount of H_2S in the system at time t is

$$N_{H_2S}^t = N_T^t - N_{air} - N_W$$

$$= \frac{[1 - Rm^t/76]\ V_2 \left[\frac{Rm}{Rm^t}\right]}{RT} - \frac{P_1 V_1}{RT} - \frac{V_2 \left[\frac{Rm}{Rm^t}\right] P_W}{RT}$$

$$= \frac{1}{RT} \left\{ V_2 \frac{Rm}{Rm^t} - \frac{Rm}{Rm^t} \cdot \frac{Rm^t}{76} V_2 - P_1 V_1 - V_2 \left[\frac{Rm}{Rm^t}\right] P_W \right\}$$

$$= \frac{1}{RT} [(1 - P_W)\ V_2 \frac{Rm}{Rm^t} - P_1 V_1] - \frac{V_2 Rm Rm^t}{76 RT Rm^t} \tag{12}$$

And amount of H_2S adsorbed is:

$$A_{H_2S} = N^{o}_{H_2S} - N^{t}_{H_2S}$$

$$= \frac{P_1 V_2}{RT} - \frac{1}{RT}\left[(1 - P_W)\, V_2 \frac{Rm}{R\overset{t}{m}} - P_1 V_1\right] + \frac{V_2}{76}\frac{Rm}{RT}\frac{R\overset{t}{m}}{R\overset{t}{m}}$$

$$= \frac{P_1 V_T}{RT} - \frac{1}{RT}\left[(1 - P_W)\, V_T\right] + \frac{V_2}{76}\frac{Rm}{RT}\frac{R\overset{t}{m}}{R\overset{t}{m}}$$

if P_1 = 1 atm, then

$$A_{H_2S} = \frac{P_W V_T}{RT} + \frac{V_T\,(R\overset{t}{m}/76)}{RT}$$

$$A_{H_2S} = \frac{V_T}{RT}\left(P_W + \frac{R\overset{t}{m}}{76}\right) \qquad (13)$$

APPENDIX IV

FORMULAS FOR SORBENTS PREPARED IN LABORATORY

Formula	Ingredients		Note
I	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Zn(NO_3)_2 \cdot 6H_2O$	158.5 g	
	H_2O	2000 ml	
II-a -b	$Al(NO_3)_3 \cdot 9H_2O$	200 g	In II-a the precipitate was not washed with water. In II-b the precipitate was washed with water.
	$Zn(NO_3)_2 \cdot 6H_2O$	158.5 g	
	$Cu(NO_3)_2 \cdot 3H_2O$	64.4 g	
	H_2O	2000 ml	
III	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Fe_2(SO_4)_3 \cdot XH_2O$	200 g	
	H_2O	2000 ml	
IV	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Zn(NO_3)_3 \cdot 6H_2O$	158.5 g	
	$Fe(SO_4)_3 \cdot XH_2O$	200 g	
	H_2O	2000 ml	
V	$Fe_2(SO_4)_3 \cdot XH_2O$	5 g	Soak pellets in Fe solution. Drain off solution, dry, and calcine at 800°C overnight.
	Water	150 ml	
	Alumina pellets 3/16 in.		
VI	$Zn(NO_3)_2 \cdot 9H_2O$	5 g	Soak pellets in Zn solution. Drain off solution, dry, and calcine at 800°C overnight.
	Water	150 ml	
	Alumina pellets 3/16 in.	10 g	

Formula	Ingredients		Note
VII	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Fe_2(SO_4)_3 \cdot XH_2O$	100 g	
	$Zn(NO_3)_2 \cdot 6H_2O$	158.5 g	
	$Cr(NO_3)_3 \cdot 9H_2O$	100 g	
	Water	1000 ml	
VIII	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Zn(NO_3)_2 \cdot 6H_2O$	158.5 g	
	$Fe_2(SO_4)_3 \cdot XH_2O$	200 g	
	$MnSO_4 \cdot H_2O$	100 g	
	Water	2400 ml	
	Celite	80 g	
IX	$Al(NO_3)_3 \cdot 9H_2O$	200 g	
	$Zn(NO_3)_3 \cdot 6H_2O$	158.5 g	
	$Fe(SO_4)_3 \cdot XH_2O$	200 g	
	Water	2000 ml	
	Celite	80 g	
X	$Al(NO_3)_3 \cdot 9H_2O$	100 g	
	$Zn(NO_3)_2 \cdot 6H_2O$	76.8 g	
	$Fe(NO_3)_3 \cdot 9H_2O$	108 g	
	Water	1000 ml	
XI	$Al(NO_3)_3 \cdot 9H_2O$	100 g	
	$Zn(NO_3)_2 \cdot 6H_2O$	76.8 g	
	$Fe(NO_3)_3 \cdot 9H_2O$	25 g	
	$Fe(SO_4)_3 \cdot XH_2O$	75 g	
	Water	1000 ml	
XII	$Al(NO_3)_3 \cdot 9H_2O$	100 g	
	$Zn(NO_3)_2 \cdot XH_2O$	76.8 g	
	$Fe(NO_3)_3 \cdot 9H_2O$	108 g	
	Celite	15 g	
	Water	2000 ml	

Formula	Ingredients		Note
XIII	ZnO	25 g	
	Iron oxide	75 g	
	Celite	5 g	
	Corn starch	10 g	
	Sodium silicate	5 g	
	Water	1000 ml	
XIV	Activated carbon	10 g	
	ZnO	25 g	
	Iron oxide	75 g	
	Celite	5 g	
	Sodium silicate	5 g	
	Water	1000 ml	
XV	Fe_2N		Fe_2O_3 reduced by H_2 then reacted with NH_3 at 350 - 550°C
XVI	Biguanide	10.5 g	Dissolve biguanide in methanol. Soak activated carbon in solution, then dry the impregnated carbon.
	Activated carbon	135 g	
	Methanol	200 ml	

* Unless otherwise noted, the general procedure for sorbent preparation is: coprecipitation with ammonium hydroxide (28%); extrusion through a meat grinder; drying in a vacuum oven; and calcination in a muffle furnace overnight at 800°C.

APPENDIX V

A SUMMARY OF RESULTS OF SORPTION SCREENING TESTS

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
106	3002	1.437	1.927	2.344		2.938	Amount of sorbent used 1.16 g
107	3002	0.991	1.238	1.370 (80 min)			Repeat of Run 106, except 5.04 g sorbent was used
108	3002	0.904	1.175	1.320			Repeat of Run 107
109	3002	0.988	1.254	1.379	1.444	1.461	Repeat of Run 108
110	3002	1.031	1.268	1.382	1.422	1.439	Repeat of Run 109
111	2902	0.965	1.089	1.327	1.195	1.275	Cu, Zn, and Cr Oxides
112	2902	0.972	1.104	1.244	1.336	1.353	Repeat of Run 111
113	3002-R	0.222	0.273	0.315			Regenerated sorbent of Run 109
114	3002-R	0.210	0.249	0.285			Regenerated sorbent of Run 110
115	2902-R	0.230	0.270	0.309			Regenerated sorbent of Run 111
116	3002	0.365	1.179	1.352	1.420	1.440	Preconditioned at 750°C overnight
117	2902-R	0.231	0.304	0.375			Regenerated sorbent of Run 112
118	3002	0.190	0.318	0.383			Preconditioned at 900°C overnight
119	Formula I	0.355	0.386	0.408 (70 min)			Al, and Zn oxides
121	3002	0.284	0.967	1.267	1.334		Preconditioned at 800°C overnight
122	3012	1.097	1.253				Catalyst for methanol synthesis

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
123	3002	1.182	1.365	1.400	1.400		Repeat of Run 122
124	Formula II-a	0.835	0.929	0.969	0.983		Al, Zn, and Cu oxides
125	Formula II-b	1.082	1.177	1.215	1.233	1.244	Al, Zn, and Cu oxides
126	Formula III	0.583	0.669	0.783	0.885		Al, and Fe oxides
128	3012-R	0.470	0.553	0.587			Regenerated sorbent of Run 122
129	3002-R	0.160	0.191 (20 min)				Regenerated sorbent of Run 121
130	3002-R	0.107					Regenerated sorbent of Run 116
131	30011	0.343	0.418				ZnO from Harshaw
133	3012	0.265	0.293 (25 min)				Preconditioned at 800°C overnight
135	0601	1.182	1.275	1.283 (55 min)			Activated carbon
136	Formula II-a	0.429	0.475				Regenerated sorbent of Run 124
137	Formula II-b	0.358	0.431				Regenerated sorbent of Run 125
138	3012-R	0.284	0.367				Regenerated sorbent of Run 128
139	Formula III-R-1	0.551	0.630	0.853	1.122		Regenerated sorbent of Run 126
140	Formula III-R-2	0.530	0.601	0.755	0.973	1.159	Regenerated sorbent of Run 139
141	Formula III	0.661	0.775	0.920	1.069	1.212	Repeat of Run 126
142	Formula III-R-3	0.493	0.574	0.743	0.943		Regenerated sorbent of Run 140
143	0601	1.283	1.379	1.400	1.400		Repeat of Run 135

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
144	3012	1.006	1.104	1.118	1.118		Repeat of Run 122
145	Formula III-R	0.659	0.701	0.727	0.727		Regenerated sorbent of Run 141
147	3011	0.353	0.420	0.482	0.526		Repeat of Run 131
148	Formula III-R	0.662	0.734	1.017	1.344	1.474	Regenerated sorbent of Run 145
149	3012	0.288	0.395	0.467	0.504		Regenerated sorbent of Run 144
150	0601	1.249	1.366	1.380	1.380		Vacuum dried and regenerated sorbent of Run 143
151	Formula III	0.536	0.608	0.647	0.676		Second batch of Formula III
152	3011	0.207	0.227				Preconditioned at 800°C overnight
153	Formula IV	0.602	0.839	1.006	1.150	1.269	Zn, Al, and Fe oxides mixture
154	1311	0.248	0.251 (20 min)				Al_2O_3 catalyst support
155	Formula III-R	0.633	0.648	0.767	0.942		Regenerated sorbent of Run 148
156	Formula V	0.607	0.637	0.668			Al_2O_3 impregnated with $Fe_2(SO_4)_3$
157	Formula VI	0.389	0.427				Al_2O_3 impregnated with $Zn(NO_3)_2$
158	Formula IV-R	0.716	0.857	1.035	-	1.253	Regenerated sorbent of Run 153
159	Formula III	0.460	0.478	0.597	0.638 (101 min)		Regenerated sorbent of Run 151, a second batch of Formula III
160	Formula IV	0.841	1.072	1.205	1.327 (80 min)	1.417	Fresh sorbent was baked at 100°C overnight
161	Formula IV	0.814	1.036	1.258	1.382	1.436	Same as Run 160
162	Formula IV-R	0.600	0.710	0.829	0.917		Regenerated sorbent of Run 161

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
163	Formula IV-R	0.680	0.824	0.973	1.092		Regenerated sorbent of Run 160
164	Formula IV	0.909	1.127	1.345	1.433	1.452	Same as Run 160
165	Formula IV	0.641	0.861	1.124	1.322	1.409	In a H_2S-N_2 atmosphere
166	Formula IV-R	0.603	0.736	0.869	0.966		Regenerated sorbent of Run 158
167	Formula III	0.466	0.541	0.597	0.631		Regenerated sorbent of Run 159
168	Formula IV	0.635	0.825	1.071	1.237	1.331	Repeat of Run 165
169	Formula IV-R	0.561	0.671	0.810	0.936 (100 min)		Regenerated sorbent of Run 166
170	Formula VII-a	0.508	0.569	0.633 (70 min)	0.665 (100 min)		Al, Zn, Fe, and Cr oxides mixture in powder form
171	Formula VII-b	0.469	0.520				Al, Zn, Fe, and Cr oxides mixture extrusion
172	Formula IV-R	0.728	0.781	0.925	1.117	1.222	Regenerated sorbent of Run 164
173	Formula IV-R	0.547	0.728	0.901	1.028	1.130	Regenerated sorbent of Run 169
174	Formula IV	0.772	0.927	1.145	1.322	1.443	Gas circulation rate doubled
175	Formula IV-R	0.734	0.829	0.928	1.031 (100 min)	1.072	Regenerated sorbent of Run 172
176	Formula IV	0.810	0.950	1.134	1.285	1.403	Repeat of Run 174
177	Formula VIII	0.433	0.508	0.557			Al, Zn, Fe, and Mn oxides mixture
178	Formula VIII	0.427	0.486	0.524			Repeat of Run 177
179	Formula IX	0.513	0.599	0.682	0.741	1.335 (240 min)	Al, Zn and Fe oxides with celite
181	Formula XI	0.468	0.714	1.001	1.158	1.261	Al, Zn, Fe^{++}, and Fe^{+++} oxides mixture

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
182	Formula X	0.800	1.236	1.435			Al, Zn and Fe^{+++} oxides mixture
183	Formula XI-R	0.444	0.722	0.987	1.145	1.263	Regenerated sorbent of Run 181
184	Formula X-R	0.712	1.064	1.408	1.472 (80 min)		Regenerated sorbent of Run 182
185	Formula X-R	0.637	1.034	1.398		0.765 (175 min)	Regenerated sorbent of Run 184
186	Formula XI-R	0.433	0.656	0.907	1.083		Regenerated sorbent of Run 183
187	3002	1.317	1.405				Repeat of Run 106
188	3012	1.347	1.409	1.414 (40 min)			
190	3012-R	0.397	0.447				Regenerated sorbent of Run 188
191	Formula X-R	0.585	1.228	1.460			Regenerated sorbent of Run 185
192	Formula XI	0.392	0.632	0.879	1.043	1.168	Regenerated sorbent of Run 186
193	3002	1.430	1.481	1.494			Repeat of Run 187
194	3002-R	0.191	0.277			0.361	Regenerated sorbent of Run 193
195	Formula XI	0.499	0.833	1.098	1.236	1.338 (135 min)	Repeat of Run 181
196	Formula X-R	0.629	0.884	1.257	1.424		Regenerated sorbent of Run 191
199	Formula XI-R	0.459		0.908	1.068	1.181	Regenerated sorbent of Run 195
202	Formula XI-R	0.457	0.669	0.866	1.034	1.271 (150 min)	Regenerated sorbent of Run 199
217	Formula X	0.730	0.842	0.962	1.180	1.470	5 hr calcination

Run	Sorbent	Gas Up-Take* X 10^{-3} g-mole H_2S/g Sorbent 10 min	30 min	60 min	90 min	120 min	Note
218	Formula X	0.730	0.899	1.430	1.530	1.530	7 hr calcination
219	Formula X	0.759	0.914	1.350	1.750	1.780	12 hr calcination
223	Formula X	0.489	0.765	1.080	1.280	1.435	24 hr calcination
224	Formula X	0.535	0.702	1.020			40 hr calcination
225	Formula X	0.664	0.915	1.410	1.530	1.530	14 hr calcination
226	0091	1.365	1.436 (20 min)	1.442 (48 min)			Rohm & Haas polymeric sorbent
227	0091-R	1.339	1.408 (20 min)	1.419 (35 min)			Steam regenerated sorbent of Run 226
228	0091	1.434	1.495				Repeat of Run 226
229	0091-R	1.405	1.486 (20 min)				Steam regenerated sorbent of large scale exp.
232	Formula XV	1.394	1.538				Fe_2N powder
233	2682	1.323	1.552				Iron oxide, the raw material of Formula XV
234	Biguanide	0.212	0.324 (25 min)	0.556		0.878	Organic compound with high basicity
235	Formula XVI	1.310	1.390				Biguanide impregnated on activated carbon
236	Formula XVI	1.29	1.370				Repeat of Run 235
237		1.44	1.51				Activated carbon used in Formula XVI

* Unless otherwise noted, nominal amount of sorbent used for gas up-take test was 5 g.

APPENDIX VI

SUMMARY OF LABORATORY SCALE GAS SORPTION TESTS USING SIMULATED GEOTHERMAL STEAM

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 1	3002	150 g	Initial test of simulated geothermal steam	10 in.	H_2S, N_2	160 ppm	37 min	The system worked well. The sorbent removed H_2S from the simulated geothermal steam.
Run 2	3002	75 g	Repeat of Run 1	5 in.	H_2S, N_2	87 ppm	29 min	
Run 3	2621	192 g	New sorbent evaluation	16 in.	H_2S, N_2	190 ppm	instantaneous	
Run 4	3051	200 g	Evaluation of new sorbent	13 in.	H_2S, N_2	241 ppm	6 min	The sorbent did not have the capacity of removing H_2S from steam.
Run 5	0087		Evaluation of new sorbent	14.6 in.	H_2S, N_2	170 ppm	instantaneous	
Run 6	Formula IV (see Appendix IV)	122 g	Evaluation of new sorbent	about 12 in.	H_2S, N_2	304 ppm	20 min	This sorbent was good in a dry test, but failed to remove H_2S from simulated geothermal steam.
Run 7	3002	200 g	Repeat Run 1 Increase amount of sorbent charged	15 in.	H_2S, N_2	239 ppm	80 min	By increasing the amount of sorbent charged, breakthrough occurred later. Steam rate may be too high.
Run 8	2621	160 g	Repeat Run 3	13.3 in.	H_2S, N_2	154 ppm	instantaneous	This sorbent is no good in geothermal steam conditions.
Run 9	3002	200 g	Reduce steam rate to half of Run 8 and repeat Run 1	15 in.	H_2S, N_2	226 ppm	12.5 hr	By lowering the steam rate (or space velocity) breakthrough occurred later.
Run 10	2621	168 g	Repeat Run 8 using lower steam rate	13.5 in.	H_2S, N_2	273 ppm	instantaneous	Sorbent did not react with H_2S even at the lower steam rate.
Run 11	3021	187 g	Evaluation of new sorbent	14.5 in.	H_2S, N_2	-	-	Ran out of H_2S at the middle of this run.
Run 12	3021	174 g	Repeat Run 11	17.7 in.	H_2S, N_2	230 ppm	4.5 hr	The experiment was stopped and restarted at 11.6 hr and 19.3 hr. The final H_2S concentration in the outlet gas was 161 ppm. The space velocity was 1.65/sec. About 23% of available ZnO was converted to ZnS.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 13	0086	100 g Alumina 50 g	Sorbent evaluation	8.5 in.	H_2S, N_2	240 ppm	instantaneous	Particle size of sorbent is small; alumina (3/16 in. extrusion) was added.
Run 14	3012	200 g	New sorbent evaluation	11.2 in.	H_2S, N_2	200 ppm	instantaneous	This sorbent is a methanol synthesis catalyst. It reacted with H_2S in a dry test but failed to remove H_2S from simulated geothermal steam.
Run 15	3012	240 g	Repeat Run 14 using smaller particles	13.2 in.	H_2S, N_2	268.8 ppm	instantaneous	The sorbent was not active in a steam system.
Run 16	4201	160 g	New sorbent evaluation	14 in.	H_2S, N_2	282 ppm	less than 5 min	This sorbent reacts with H_2S in a dry system; however, the capacity of the sorbent is low. With simulated geothermal steam only a very small percent of sorbent reacted with H_2S (indicated by color change of the sorbent).
Run 17	2901	183 g	New sorbent evaluation	13 in.	H_2S, N_2	234 ppm	instantaneous	This catalyst is a combination of copper and zinc oxide. In the presence of a large amount of geothermal steam this sorbent failed to react with H_2S.
Run 18	2602	176 g	New sorbent evaluation	Not determined	H_2S, N_2	228 ppm	instantaneous	This sorbent consists of iron oxide, which reacts with H_2S in a dry system. This sorbent was inactive.
Run 19	0601	107 g	New sorbent evaluation	17.5 in.	H_2S, N_2	about 200 ppm	instantaneous	Activated carbon is very active in the dry system but not in the steam system.
Run 20	0083	200 g	New sorbent evaluation	18 in.	H_2S, N_2	200 ppm	instantaneous	
Run 21	2601	200 g	New sorbent evaluation	12.4 in.	H_2S, N_2	200 ppm	-	Gas sampling line was plugged. Some chemicals in the sorbent (K_2CO_3?) leached out.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 22	2601	200 g	Repeat Run 20	12.4 in.	H_2S, N_2	111 ppm	instantaneous	
Run 23	ZnO bound with glass frit, a laboratory prepared sorbent	200 g	To check the reactivity of ZnO + glass frit sorbent	11.3 in.	H_2S, N_2	about 200 ppm	instantaneous	ZnO powder was pelletized with glass frit and fired at 750°C. The sorbent so prepared has low activity toward H_2S. Low surface area and formation of Zn-silicate might be the problem.
Run 24	3022	176 g	New sorbent evaluation	16.8 in.	H_2S, N_2	about 200 ppm	5 min	Sorbent did not have good activity.
Run 25	2621	200 g	New sorbent evaluation	Not determined	H_2S, N_2	about 200 ppm	instantaneous	
Run 26	1461	200 g	New sorbent evaluation	11 in.	H_2S, N_2	about 200 ppm	Less than 5 min	
Run 27	2702	100 g	New sorbent evaluation	15.8 in.	H_2S, N_2	about 200 ppm	Less than 3 min	
Run 28	0081	100 g	New sorbent evaluation	11 in.	H_2S, N_2	200 ppm	instantaneous	
Run 29	2681		New sorbent evaluation	Not determined	H_2S, N_2	200 ppm	Less than 7 min	After 15 min of run, 20 ml of H_2O was added and the experiment was restarted. There was no significant change in H_2S removal capacity by adding water to the system. Redwood chips with iron oxide are used typically in removing H_2S from synthesis gas.
Run 30	2601	175 g	It was found in Run 22 that K_2CO_3 was leached out from sorbent pellets. In this run K_2CO_3 was purposely removed from the sorbent to see the activity of iron oxide.	12.2 in.			Less than 20 min	This run was better than Run 22, but the breakthrough still occurred too early.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 31	Formula IV with frit	76.4 g	New sorbent evaluation	Not determined	H_2S, N_2	about 200 ppm	Less than 7 min	
Run 32	4210	100 g	New sorbent evaluation	11 in.	H_2S, N_2	about 200 ppm	instantaneous	
Run 34	3021	100 g	To perform a series of sorption-regenerations.	6.9 in.	H_2S, N_2	199 ppm	55 min	A fresh sorbent was used for a series of sorption regeneration cycles.
Run 35	3021-R	100 g	To study the effect of regenerating conditions	6.9 in.	H_2S, N_2	about 200 ppm	Less than 10 min	The sorbent was first saturated with H_2S and then regenerated with air at 780°C. The H_2S sorption capacity decreased drastically.
Run 36	3021-R	92 g	To study the effect of regenerating conditions	6.5 in.	H_2S, N_2	302 ppm	instantaneous	The sorbent was regenerated at 500°C. The H_2S conc. of inlet gas was unusually high. The experiment was terminated right after the breakthrough was detected.
Run 37	3021	100 g	To study the effect of regenerating conditions	6.9 in.	H_2S, N_2	221 ppm	30 min	The sorbent was regenerated at 760°C. Steam used for this experiment was slightly superheated (176°C, 100 psig). This is considered a bad run.
Run 38	3081	100 g	New sorbent evaluation	8.8 in.	H_2S, N_2	157 ppm	41 min	
Run 39	3021-R	100 g	To study the effect of regenerating conditions. Repeat of Run 37.	6.9 in.	H_2S, N_2	150 ppm	-	Temperature controller of G.C was broken. Experiment was terminated.
Run 40	3021	100 g	Repeat of Run 34, except a superheated steam was used	6.9 in.	H_2S, N_2	200 ppm	105 min	This run lasted longer than Run 34.
Run 42	3021-R	100 g	To study the effect of regenerating conditions	6.9 in.	H_2S, N_2	180 ppm	32 min	Sorbent was regenerated at 300°C with air.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 43	2701	100 g	New sorbent evaluation					A bad run.
Run 44	2701	100 g	New sorbent evaluation					This sorbent did not work in steam system.
Run 45	3021-R	100 g	To study the effect of regenerating conditions	6.9 in.	H_2S, N_2	205 ppm	6 min	The sorbent was regenerated at 500°C with 10% O_2 and 90% N_2.
Run 46	0091	100 g	New sorbent evaluation	11.3 in.	H_2S, N_2		High H_2S conc. was detected at the very beginning of the test.	Preconditioning of the sorbent was required. This was done by passing superheated steam through the bed.
Run 47	0091	100 g	Repeat Run 46	11.3 in.	H_2S, N_2	178 ppm	47 min	After preconditioning the sorbent worked better.
Run 48	0091	72 g	To check the activity of regenerated sorbent.	9.8 in.	H_2S, N_2	144 ppm	32 min	After 2.5 hr, the regeneration of sorbent was started; this was done by passing superheated steam (145 psig, 390°C) through the sorbent. Most of absorbed H_2S came off within 20 min of regeneration. White milky material was observed in the steam condensate.
Run 49	0091	72 g	To check the activity of regenerated sorbent.	9.8 in.	H_2S, N_2	227 ppm	Within 3 min	The sorbent was regenerated right after Run 48; however, much H_2S was detected before this run. The sorbent, therefore, was reconditioned again just before Run 49. Breakthrough came early. Reason is unknown. After this experiment sorbent was regenerated again at 150 psig and 300°C. H_2S came out within 28 min of regeneration.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 53	0091	100 g	To check the activity of regenerated sorbent.	11.3 in.	H_2S, N_2	209 ppm	Within 15 min	Breakthrough took place quite early. The H_2S-loaded sorbent was regenerated at 330°C, 100 psig. Most H_2S came off within 40 min of regeneration.
Run 58	0091	85 g	To study the activity of regenerated sorbent.	9.5 in.	H_2S, N_2	115 ppm	3.5 hr	This run lasted longer than usual. Sampling line was plugged by foreign material. The H_2S conc. in outlet of column might not be accurate. Regeneration was done immediately after the run using steam at 365°C, 100 psig. It took about 100 min to finish the regeneration. A second peak was noticed on gas chromatogram. The second peak could be SO_2.
Run 59	0091	85 g	To study the activity of regenerated sorbent.	9.5 in.	H_2S, N_2	238 ppm	Less than 30 min	Steam of 365°C, 100 psig was used for regeneration. A second peak, later identified as SO_2, was also detected as in the previous run. Regeneration took about 40 min and steam rate was estimated as 74 ml/min. Too much steam was used for regeneration.
Run 60	0091	85 g	Same as previous Run	9.5 in.	H_2S, N_2	232 ppm	1.9 hr	Water rate was 99 ml/min during the sorption run. Resin beads had been blown out of reactor after the run in an attempt to wash the resin with water. The resin was collected, washed with water and dried in an oven purged with N_2.
Run 61	0091	61 g	To check the activity of the water-washed sorbent.	7.8 in.	H_2S, N_2	224 ppm	About 40 min	The water-washed sorbent showed no loss of activity. Regeneration by washing with water could be the way of effective regeneration.
Run 62	0091-R	65 g	To study the activity of regenerated	7.5 in.	H_2S, N_2	211 ppm	About 27 min	Regeneration of spent sorbent was done by steam at 340°C and 100 psig; it took about 40 min.

APPENDIX VI. (contd)

	Sorbent	Amount	Purpose	Bed Height	Noncondensable Gases	H_2S conc.	Breakthrough	Note
Run 63	0091-R	65 g	To study the activity of regenerated sorbent.	7.5 in.	H_2S, N_2	219 ppm	About 30 min	Water rate was 88 ml/min during the sorption run. Steam (340°C, 100 psig) was used for regeneration; the process took about 40 min. The water rate was 94 ml/min during regeneration. The amount of steam used for regeneration is larger than steam scrubbed.
Run 64	0091-R	65 g	To check the activity of regenerated sorbent.	7.5 in.	H_2S, N_2	136 ppm	1.3 hr	The H_2S conc. in inlet stream was lower than usual, which might explain the longer run. Water rate during the sorption cycle was 100.7 ml/min.

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