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CONTROL OF HYDROGEN SULFIDE EMISSION
FROM GEOTHERMAL POWER PLANTS

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SUMMARY

A process for controlling H₂S emissions at geothermal power plants has been evaluated in laboratory scale equipment and by process engineering analysis. The process is based on scrubbing geothermal steam with a metal salt solution to remove selectively and precipitate the contained H₂S. The metal sulfide is roasted or oxygen/acid leached to regenerate the metal salt, and sulfur is rejected from the system as elemental sulfur or as sulfate.

Primary attention was focused on cupric ion (Cu²⁺) as the H₂S precipitant. Laboratory scrubbing experiments confirmed the extreme low solubility and rapid formation of copper sulfide precipitate at the temperature of geothermal steam (about 350°F) and at the relatively low pH (1-2) resulting from the primary reaction $\text{H}_2\text{S} + \text{CuSO}_4 \rightarrow \text{CuS} + \text{H}_2\text{SO}_4$. Consistent with this behavior, measured H₂S removal rates for packed-column and tray-tower scrubbers were determined entirely by mass transfer of H₂S between steam and liquid phases.

Up to 95% removal of H₂S from simulated geothermal steams was obtained in a 2" diameter scrubbing column packed with 3 feet of 5/8" Flexirings by use of a recirculating slurry of copper sulfate/copper sulfide. Measured k_{ga1} 's exceeded, by a factor of 5, values calculated on the assumption that gas-phase mass transfer was controlling. These experimental values and the relatively low flooding velocities observed suggest that the slurry is surface active, leading to a system with high interfacial area per unit volume. Counterflow sieve trays proved effective for mass transfer, but retained aggregated solids and presented operability problems. Shower trays passed solids, but showed lower efficiency, as expected. A single, high-area-sieve tray with downcomer proved to be very effective both in removing H₂S and in providing stable operation without solids retention and fouling. Tray efficiency was

found to be a function of pH below about pH 1, probably due to the influence of high acidity on froth characteristics.

The solids formed in the continuous laboratory scrubbing tests had a bimodal size distribution, with peaks at about 1 and 20 microns. They showed a pronounced tendency to flocculate and settle rapidly under scrubbing conditions, forming aggregates of the order of 1 mm in size. Settling rates of the order of 1 inch per minute and filtration rates of 3 GPM/ft² were obtained in off-line tests. The solids withdrawn from the recirculating slurry were nonstoichiometric, ranging in composition from Cu_{1.2}S to Cu_{1.7}S. While the condensate obtained from the scrubber contained some sulfur occasionally, most of the oxidized sulfide was converted to sulfate, increasing system acidity beyond that derived directly from H₂S precipitation.

Scoping regeneration tests by oxygen pressure leaching and roasting showed satisfactory high conversions, 96% and 82% respectively, under less favorable conditions than those appropriate for a commercial operation. Approximately 50% conversion, on average, of sulfide to sulfate was obtained in the leaching tests, the balance going to elemental sulfur.

Preliminary corrosion tests on austenitic stainless steels showed that they can be passivated under anticipated service conditions and that they are promising as materials of construction. In particular, there was no evidence of pitting, stress corrosion or weld-zone attack on passivated samples in simulated scrubbing solutions. Unpassivated coupons were corroded, however, and, while some evidence of crevice corrosion was observed in the laboratory scrubber, the main column and piping components (type 316SS) proved resistant to attack by scrubbing solutions at 360°F with pH ~1 and 2 g/l Cu.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
SUMMARY.	1
I. INTRODUCTION	1
1. The Hydrogen Sulfide Removal Problem in Perspective. .	1
2. Properties of H ₂ S Significant for Emission Control . .	3
3. Outline of EIC Approach.	4
4. Scope of Work.	6
II. GENERAL PROCESS DESCRIPTION.	8
1. Major Process Steps.	8
III. DETAILED PROCESS DESCRIPTION	14
1. Chemistry, Thermodynamics and Kinetics	14
2. Process Control.	32
IV. EXPERIMENTAL METHODS	36
1. Scrubber System Design and Hardware.	36
2. Scrubber System Operating Procedures	39
3. Chemical Analysis.	42
V. EXPERIMENTAL RESULTS	47
1. Corrosion Tests.	47
2. Autoclave Scrubbing Experiments.	52
3. Packed and Trayed Column Runs.	56
4. Characterization of the Precipitates	84
5. Experimental Results - Liquid/Solid Separation	90
6. Leach Regeneration Tests	94
7. Roast Regeneration Test.	98
VI. PLANT DESIGN AND COST ESTIMATE	103
1. Process Conditions and Field Data.	103
2. Analysis of Field Data	104
3. Design Basis for Prototype H ₂ S Removal System.	106
4. Process Design	107
5. Cost Estimates	120
REFERENCES	126

TABLE OF CONTENTS

	<u>Page</u>
APPENDIX A: THE USE OF PACKED COLUMNS FOR THE REMOVAL OF HYDROGEN SULFIDE FROM STEAM	A-1
APPENDIX B: THE USE OF TRAYED COLUMNS FOR THE REMOVAL OF HYDROGEN SULFIDE FROM STEAM	B-1
APPENDIX C: ABSORPTION OF CONSTITUENTS OTHER THAN H_2S IN THE COPPER SULFATE SCRUBBING PROCESS	C-1
APPENDIX D: COMPOSITIONS AND STRUCTURES OF SULPHIDES OF COPPER	D-1

I. INTRODUCTION

1. The Hydrogen Sulfide Removal Problem in Perspective

In absolute terms, the total daily discharge of H_2S by a geothermal power plant is appreciable. For example, Axtmann (1) calculates sulfur discharge rates (as of 1973) of 21 tons per day (TPD) at The Geysers, California and 55 TPD at Cerro Prieto, Mexico. However, the H_2S is dispersed and ultimately becomes oxidized, so that toxic levels of this gas are not encountered in the air in the vicinity of geothermal power plants. The legal emissions limits, where they are specified, vary from 0.03 ppm (near the odor threshold) in California to the Federal OSHA standard of 10 ppm average (20 ppm max) for an 8-hour exposure. Compounding the effects of H_2S emissions into the atmosphere is its well-known corrosive behavior, which leads to problems with electrical and other gear. For example, H_2S appears to be primarily responsible for greater than average corrosion of turbines. For these reasons, it is highly desirable, and will perhaps become legally obligatory, to control H_2S emissions in the development of geothermal power.

In any power generation mode operating on geothermal steam, whether dry steam as at Larderello and The Geysers or steam flashed from hot brine as at Wairakei and Cerro Prieto, the H_2S content becomes distributed among three streams. Two of these streams (see Figure 1), namely, the ejected noncondensable gases and the cooling tower evaporate, enter the atmosphere. At The Geysers, the third steam - the cooling tower blowdown - is reinjected into nonproducing wells. Because of the distribution of H_2S among effluent streams, efficient scrubbing of the H_2S discharged at the gas-ejector vents would remove only about one-third of the total H_2S . More than one-half of the total H_2S could still be emitted into the atmosphere from the mixture of condensate and cooling water as it coursed over the cooling tower.

Fig. 1: Simplified steam and condensate diagram for a geothermal power plant (after Finney, Ref. 2). Fractions shown indicate the approximate distribution of H_2S initially present in the steam.

Scrubbing of H₂S from the condensing steam after passage through the turbine generators appears to be impractical. For one thing, the intimate contact required between disengaging noncondensable gas and a reagent-loaded cooling water would require a careful elaborate redesign of the barometric condenser, probable entailing an unacceptable degradation of the vacuum that could be maintained in the condenser. Moreover, the large flow of cooling water required for condensation (over 20 times the mass flow of the steam) makes consumption of reagents for H₂S removal costly. Serious corrosion problems in the entire cooling loop would also be encountered.

In sum, for effective control of H₂S emissions, there are compelling reasons for scrubbing the geothermal steam in advance of the turbines. This is the approach that has been taken in our experimental work and that has formed the basis of our process engineering analyses.

2. Properties of H₂S Significant for Emission Control

The two most obvious properties of H₂S that could be useful for its removal from geothermal steam are its relative ease of oxidation and its propensity to form sparingly soluble solids with many simple metal ions. Certain binary inorganic sulfides, those of copper and molybdenum, for example, are so sparingly soluble that they cannot be dissolved by acid treatment alone, but require the action of an oxidizing agent in order to convert the sulfide sulfur to another form (usually, elemental sulfur or sulfate ion). H₂S is also a weak acid and, consequently, H₂S can be efficiently scrubbed from a gas stream by a strongly alkaline solution. Soluble bisulfide ion is formed in the process:

Although scrubbing with alkali is perhaps the simplest conceivable means of scrubbing H₂S from the steam, the attendant absorption of CO₂, generally present in large excess over H₂S, makes this approach unacceptable.

A brief catalog of relevant properties of noncondensable gases commonly found in geothermal steam is given in Table 1. Nitrogen, not listed, is essentially inert.

Table 1
Selected Chemical Properties of Noncondensable
Gases Found in Geothermal Steam

<u>Property</u>	<u>Gas</u>
Weak acid in aqueous solution	CO ₂ , H ₂ S, H ₃ BO ₃ (HBO ₂ at higher temps.)
Weak base in aqueous solution	NH ₃
Susceptible to oxidation	H ₂ S, H ₂ , (toward strong oxidants: CH ₄ , C ₂ H ₆ , NH ₃)
Formation of insoluble compounds	H ₂ S, CO ₂ (not at low pH).

3. Outline of EIC Approach

The process under development by EIC Corporation is based on scrubbing H₂S from geothermal steam with a solution of a metal salt, the cation of which yields a very sparingly soluble sulfide precipitate. Initial considerations indicated CuSO₄ to be the most suitable salt for steam compositions having H₂S present in considerable excess over NH₃. Where adequate NH₃ can be absorbed from the steam to offset the pH drop (increase in acidity) attending the precipitation reaction, i.e.,

a metal salt producing a somewhat more soluble sulfide can be employed.

A simplified flow chart of the overall process is shown in Figure 2. In operation, the scrubbing liquor is a recirculating copper sulfate/sulfide slurry containing H₂SO₄ and (NH₄)₂SO₄. Carbon dioxide is essentially not absorbed at the prevailing high solution temperature and

Fig. 2: Simplified flow chart of base-case H₂S emission control process.

and low pH. The steady-state concentrations of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ in the recirculating slurry will be determined by the rates of absorption of NH_3 and H_2S , by the purge rate and by the pH of the recycle CuSO_4 solution. Reagent generation, leading to removal of accumulated acid, sulfur and ammonia from the system, is carried out by treatment of the purge stream from the scrubber by either of two modes: sulfation roasting or oxygen pressure leaching of the separated precipitate, together with removal or disposal of $(\text{NH}_4)_2\text{SO}_4$ from the purge liquor. As detailed below, conditions can be adjusted during oxidation of the precipitate, by either route, to compensate for variations in the $\text{H}_2\text{S}/\text{NH}_3$ ratio in the steam.

4. Scope of Work

Early in the program, the intricacies of the process chemistry became sufficiently apparent that concurrence was sought and reached with the program monitors to limit the experimental portion of the study to the scrubbing of H_2S . Effects of other noncondensibles, especially CO_2 and NH_3 , while comprehended in our process engineering and analyses, were not specifically studied in the laboratory. The major components of the program, as carried out, were as follows:

- Chemistry and thermodynamics of the overall H_2S emission control process, including scrubbing, reagent regeneration and sulfur rejection steps.
- Corrosion tests, beginning with screening of corrosion resistant metals and alloys under anticipated scrubber conditions in order to identify suitable materials of construction for the laboratory scrubber system, followed by further materials evaluation preparatory to design of a field unit.
- Preliminary H_2S absorption tests in a small pressure reactor. Only the two most promising metal salt solutions were evaluated in this way, namely CuSO_4 and ZnSO_4 .
- Scrubbing of H_2S from simulated geothermal steam in a laboratory scrubber utilizing a 2-inch diameter absorption column. Selected packed and trayed column internals were evaluated in terms of H_2S removal efficiency, steam-phase mass transfer coefficient and steam throughput.
- Characterization of the precipitate, including alteration subsequent to initial formation, employing chemical analysis, particle size distribution, and mineralogical analysis.

- Preliminary regeneration tests, including oxygen pressure leaching in H_2SO_4 , on precipitates produced in the laboratory scrubber and a single experiment with roast-regeneration.
- Preliminary evaluation of liquid/solid separation characteristics of the precipitate, including sedimentation and filter-leaf tests.
- Process engineering, to produce a preliminary design and cost analysis for a pilot H_2S removal plant to be sited at a geothermal power plant utilizing flashed steam.

II. GENERAL PROCESS DESCRIPTION

1. Major Process Steps

(a) Process Configuration

The copper sulfate process for the removal of hydrogen sulfide from geothermal steam consists of three essential operations (Figure 3):

- A scrubbing step in which the steam is contacted with copper sulfate solution to precipitate hydrogen sulfide as copper sulfide. Ammonia in the steam will also be removed at this stage and neutralize a portion of the sulfuric acid generated by the precipitation reaction.
- Liquid/solid separation to concentrate the copper-sulfide for regeneration and separate a purge stream for disposal of soluble impurities.
- Regeneration of the copper sulfide to form copper sulfate for recycle, with oxidation of the sulfide to sulfates for neutralization and disposal.

All the above process steps utilize established technology; accordingly, conventional equipment and design methods are suitable for specifying the process. The process development effort was directed toward determining the details of process chemistry (reaction stoichiometry and kinetics), mass transfer in the scrubbing operation (k_{ga} 's, tray efficiencies), properties of the precipitate produced (size distribution, flocculating tendencies), liquid/solid separation rates, and regeneration chemistry and kinetics.

(b) Scrubbing

A detailed review of design procedures for packed and tray columns has been carried out and is summarized in Appendix A and B. The evaluations predict that the required scrubber will be of reasonable size and configuration. Specifically, for 90% removal of hydrogen sulfide from typical geothermal steams, towers of 15 ft diameter, with 2 to 5 trays or 10 ft of packing, will handle the steam required to generate 50 megawatts of power. The

Fig. 3a: Simplified block diagram of the integrated H₂S removal process, with CuSO₄ regeneration by roasting.

Fig. 3b: Simplified block diagram of the integrated H₂S removal process, with CuSO₄ regeneration by leaching.

key to mass transfer performance for either style of contact is the hydraulics obtained. It is anticipated, and can be verified, that gas-phase resistance will control mass transfer rates in this system, and correlations exist for the prediction of absolute rates. Internals design can be adjusted to obtain the required contact areas and times for the desired mass transfer rates. It should be noted that operability considerations, such as resistance to fouling and high turndown ratio, may fix the design of the commercial scrubber.

If it can be verified that high mass transfer rates are achievable, simpler, nonstaged contacters may be advantageously used. Devices such as Venturi scrubbers or simple spray columns have advantages of economy of construction and simplicity of design which, in turn, offer potential operability advantages by eliminating the need for internals styles which might prove prone to plugging.

While the experimental studies on H_2S removal from simulated geothermal steams have focused on determining rates and efficiencies for H_2S removal only, it is known that other volatile components, particularly CO_2 , NH_3 and H_3BO_3 , are generally present in geothermal steams. In the case of NH_3 , the extent of co-absorption has a very significant process impact, since it will determine the free acidity in the purge stream exiting the scrubber (if all other variables are controlled). The extent of removal of volatile compounds other than H_2S can be predicted as a function of H_2S removal if the liquid/vapor equilibria are known. The analytical approach, involving considerations of the rate processes involved, is developed in Appendix C.

(c) Liquid/Solid Separation

In general, three liquid/solid separation steps will be required in an integrated process: separation of copper sulfide from the column purge stream, separation of residues from copper sulfate solution after the regeneration step, and separation of soluble waste from insoluble sulfate precipitated after neutralization of the purge stream. Washing may or may not be needed at each liquid/solid separation step, depending upon overall process objectives.

The equipment and techniques required for the first liquid/solid separation operation on the column purge are determined both by the characteristics of the solids precipitated in the column and by the purge flow rate. A large flow containing fine solids would favor the use of centrifuges or thickener/clarifiers; a rapidly filterable material contained in a concentrated stream would favor the use of a continuous vacuum filter. Washing will be required if the solids separated are to be dried for shipment off-site for toll roasting or smelting.

The requirements for the liquid/solid separation step following regeneration will depend on the regeneration technique used. If air or oxygen pressure leach is employed, the residues will contain unreacted copper sulfides and elemental sulfur and may require the use of flocculants or filter aids to obtain acceptable clarity and separation rates. Washing of the cake may also be necessary to minimize copper sulfate losses and to reduce the acidity of the wet solids prior to disposal. For regeneration by sulfate roasting, polishing filtrations may be required to remove entrained fines from the recycle stream. However, copper-containing solids that react with H_2S need not be so removed.

The liquid/solid separation step following purge stream neutralization will employ equipment that is well known in similar applications. Calcium carbonate (limestone) is the most likely neutralizing agent for pH adjustment, and procedures exist for designing neutralizer/crystallizer reactors to produce easily filterable gypsum. In the event that sodium or ammonium hydroxide is used as neutralizing agent, this step may be eliminated.

(d) Regeneration

Fluid-bed roasting is used in the copper industry to convert leach-refractory copper-iron sulfide minerals to soluble copper sulfate/copper oxide mixtures suitable for leaching and to retain iron as insoluble oxides. The temperature and SO_2 pressure are carefully controlled to favor sulfate formation, especially by increasing the rate of oxidation of SO_2 to SO_3 , and to prevent the formation of insoluble copper ferrite

compounds. In the absence of the inert materials (gangue) normally present in concentrate and because of the small ultimate size of the sulfide solids produced in the copper sulfate scrubbing process, roast-regeneration will probably require addition of an inert phase in order to establish fluidization in the bed and prevent sticking and defluidization due to formation of low-melting hydrated sulfates. Design procedures for fluid-bed roasters are well established, but pilot plant testing on representative material will be required to determine the operating characteristics of the bed, residence time required, and sulfate-to-oxide splits.

Oxygen pressure leaching is used effectively to recover copper from the simpler, more readily leachable secondary sulfide minerals, such as chalcocite, Cu_2S , and covellite, CuS . For normal chalcocite concentrates, with particle sizes of the order of 200 mesh, reaction rates are relatively rapid, high conversions being obtained in 2 to 4 hours in commercial equipment. The sulfide is oxidized to elemental sulfur and to sulfate, the actual split being a function of pH, temperature, and residence time. High conversions to elemental sulfur are possible under carefully controlled conditions. Design requirements for oxygen pressure leaching include a determination of the kinetics of the oxidation of the sulfides produced in the scrubber as a function of operating conditions, uncoupled from the mass-transfer considerations involved in dispersing oxygen into the leach liquors.

III. DETAILED PROCESS DESCRIPTION

1. Chemistry, Thermodynamics and Kinetics

(a) H₂S, CO₂, and NH₃ Absorption

Utilization of a sulfide precipitation route to H₂S absorption results in the scrubbing solution becoming distinctly acidic, i.e., much more acidic than could result from the acid ionization of dissolved H₂S and CO₂. Equation (3) shows this important feature of the process chemistry. Consequences of acid generation in H₂S scrubbing are that absorption of CO₂ (and H₃BO₃, if present) will be limited to the equilibrium (Henry's Law) concentration of the neutral form of these gases in the recirculating slurry and that absorption of NH₃ will be favored by the neutralization reaction

Thus, when NH₃ is present in the steam, a buildup of (NH₄)₂SO₄ can be anticipated, as illustrated by a numerical example below.

For ready reference, equilibrium constants for H₂S, CO₂, H₂O and NH₃ are collected in Table 2. Note that, owing to the increased ionization of H₂O, the pH of a neutral solution at 150°C is: $-1/2 \log K_w = 5.82$. Note also that the acid ionizations of H₂S and CO₂ are so weak that only the first ionization need be considered in all but strongly alkaline solutions. Thus, no further consideration need be given here to S²⁻, CO₃²⁻, (or HCO₃²⁻).

It is useful to be aware that, for acid ionization, the ratio of ionized to un-ionized forms of a given weak acid is unity when $\text{pH} = -\log K_a$. The corresponding relation for NH₃ ionization is $\text{pH} = +\log K_b$. For each pH unit removed from this equivalence pH, the ratio of ionized to un-ionized forms changes by one order of magnitude. For example, referring to Table 2, $[\text{H}_2\text{S}] = [\text{HS}^-]$ at 150°C and pH 6.72. At pH 4.72,

Table 2

**Equilibrium Constants for Water and Selected Gaseous
Constituents of Geothermal Steam**

<u>Reaction</u>		<u>K</u>	<u>Log K</u> <u>50°C</u>	<u>Log K</u> <u>150°C</u>
$\text{H}_2\text{S}(\text{g})$	$\rightleftharpoons \text{H}_2\text{S}(\text{aq})$	$[\text{H}_2\text{S}]/P_{\text{H}_2\text{S}}$	-1.20	-1.52
$\text{H}_2\text{S}(\text{aq})$	$\rightleftharpoons \text{HS}^-(\text{aq}) + \text{H}^+(\text{aq})$	$[\text{H}^+][\text{HS}^-]/[\text{H}_2\text{S}]$	-6.77	-6.72
$\text{HS}^-(\text{aq})$	$\rightleftharpoons \text{S}^{--}(\text{aq}) + \text{H}^+(\text{aq})$	$[\text{H}^+][\text{S}^{--}]/[\text{HS}^-]$	-13.13	-10.62
$\text{NH}_3(\text{g})$	$\rightleftharpoons \text{NH}_3(\text{aq})$	$[\text{NH}_3]/P_{\text{NH}_3}$	1.31	0.10
$\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq})$	$\rightleftharpoons \text{NH}_4^+(\text{aq})$	$[\text{NH}_4^+]/[\text{H}^+][\text{NH}_3]$	8.51	6.53
$\text{CO}_2(\text{g})$	$\rightleftharpoons \text{CO}_2(\text{aq})$	$[\text{CO}_2]/P_{\text{CO}_2}$	-1.70	-2.07
$\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	$\rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$	$[\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2]$	-6.31	-6.73
$\text{HCO}_3^-(\text{aq})$	$\rightleftharpoons \text{CO}_3^{--}(\text{aq}) + \text{H}^+(\text{aq})$	$[\text{H}^+][\text{CO}_3^{--}]/[\text{HCO}_3^-]$	-10.17	-10.29
$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$	$[\text{H}^+][\text{OH}^-]$	-13.27	-11.64

Note: Units are [molal activities], P in atmospheres.

$[H_2S] = 100 [HS^-]$, and $H_2S(aq)$ is essentially un-ionized. Accordingly, the imposition of still lower pH's should have no perceptible influence on the degree of ionization of $H_2S(aq)$ or on its "solubility" (i.e., its concentration of equilibrium with $H_2S(g)$). In this respect, it may also be remarked that the equilibrium ratio (Henry's Law constant) of $NH_3(aq)$ concentration to $NH_3(g)$ partial pressure is much greater than for H_2S and CO_2 , with obvious consequences for solute buildup.

The significance of these thermodynamic data may be further illustrated by the following example. A solution in which the pH is maintained at 1.7 ($[H^+] = 0.02$ molal activity) is equilibrated with saturated geothermal steam at $150^\circ C$ ($P_{H_2O} = 4.70$ atm). The steam contains the following amounts of the gases in question: $CO_2 = 0.133$, $H_2S = 0.0117$, $NH_3 = 0.0205$, all percent by volume. These volume percentages correspond to those of average Geysers steam. After equilibration, the solution would contain:

$$[H_2S] = 1.65 \times 10^{-5} \text{ molal}$$

$$[CO_2] = 5.3 \times 10^{-5} \text{ molal}$$

$$[NH_3] = 1.2 \times 10^{-3} \text{ molal}$$

At the maintained pH of 1.7, the weakly acidic solutes H_2S and CO_2 are un-ionized, so that the concentrations given are the total concentrations of these species. For ammonia, however, $[NH_4^+]/[NH_3]$ is calculated to be 6.8×10^4 . Thus, the total ammonia activity, $[NH_3] + [NH_4^+]$, would be 81.6 molal. This is clearly an impossibility, but illustrates that under process conditions, the $(NH_4)_2SO_4$ concentration could build up to high values in the scrubber solution - limited, in principle, by the solubility of the solid ammonium compound.

Avoidance of scrubbing CO_2 , which seems to be present in typical geothermal steams in large excess over H_2S and NH_3 , is a significant advantage of the sulfide precipitation route of H_2S emission control. Moreover, any scrubbing of H_3BO_3 and NH_3 that is achieved is environmentally beneficial. There is a further potential economic benefit associated with co-scrubbing of NH_3 , in that alkali requirements for acid

neutralization are diminished. This is tied in with the chemistry of the CuSO_4 regeneration route selected, as discussed subsequently.

(b) Metal Sulfide Solubilities

Many metal sulfides are classed as insoluble. Among those that can be formed by direct precipitation from aqueous solution, the number of sulfides that are sufficiently insoluble for scrubbing H_2S from geothermal steam is much more limited. This is because of the relatively high temperature and low pH of the scrubber solution in contact with typical geothermal steam. Table 3 lists some standard free energy changes, ΔG° , per mole of H_2S , for the general precipitation reaction

where z is the valence of the metal ion. The tabulated ΔG° values indicate that the simple metal cations divide into three groups, as follows:

Fe, Ni, Co	positive ΔG° (largest equilibrium $P_{\text{H}_2\text{S}}$)
Zn, Cd, Pb	small, negative ΔG°
Cu, Ag, Hg	large, negative ΔG° (smallest equilibrium $P_{\text{H}_2\text{S}}$)

In order to visualize what the thermodynamics mean in a physical situation, consider a dry geothermal steam at 175°C ($P_{\text{H}_2\text{O}} = 8.81 \text{ atm}$) containing 220 ppm (by wt) H_2S . If a scrubber is designed to remove 90% of the H_2S , leading to 22 ppm (wt) $\times 18.016/34.06 \times 8.81 = 1.0 \times 10^{-4} \text{ atm}$ H_2S partial pressure in the scrubbed steam, we can calculate the minimum metal ion concentration, for various scrubber solution pH's, that must be maintained in order to insure that the equilibrium H_2S partial pressure is below the design value of 10^{-4} atm . The results are shown graphically in Figure 4.

The sulfides of silver and mercury, although more sparingly soluble than CuS , are not included in the figure; the corresponding salts are obviously not good candidates for practical H_2S scrubbing. At the other end of the solubility range, Fe^{2+} , Ni^{2+} , and Co^{2+} would not serve the intended purpose in the presence of the anticipated distinctly acid pH.

Table 3
Standard Free Energies
of Metal Cations and Sulfides

	<u>ΔG° (kcal/mol)</u>		
	<u>150°C</u>	<u>175°C</u>	<u>200°C</u>
H ⁺	-0.76	-1.10	-1.47
H ₂ S(g)	-25.91	-27.17	-28.54
Fe ⁺⁺	-11.10	-11.14	-11.36
FeS	-30.04	-30.63	-31.22
Co ⁺⁺	-12.7	-12.7	-12.7
CoS _{0.89}	-26.47	-26.93	-27.3
Ni ⁺⁺	-10.2	-10.1	-10.0
NiS	-27.93	-28.39	-28.85
Cu ⁺	11.96	11.20	10.43
Cu ₂ S	-31.92	-32.92	-33.92
Cu ⁺⁺	23.85	23.74	23.46
CuS	-18.65	-19.17	-19.68
Zn ⁺⁺	-27.33	-27.40	-27.66
ZnS	-54.35	-54.82	-55.28
Ag ⁺	16.93	16.06	15.07
Ag ₂ S	-22.62	-23.63	-24.82
Cd ⁺⁺	-12.53	-12.83	-13.31
CdS	-43.04	-43.59	-44.14
Hg ⁺⁺	42.61	42.15	41.53
HgS	-22.47	-23.08	-23.68
Pb ⁺⁺	-2.62	-3.19	-3.93
PbS	-33.56	-34.23	-34.9
<hr/>			
Per mole H ₂ S:			
Eq. (7), p. 24	-17.2	-17.1	-16.9
Eq. (8), p. 24	-22.1	-21.5	-20.6

Fig. 4: Minimum metal ion activities (molal) to achieve $P_{H_2S} = 10^{-4}$ atm at 175°C and various scrubber solution pH values.

Of the remainder, only Cu^{2+} and Zn^{2+} are reasonable candidates, the well-known toxicity of Pb^{2+} and Cd^{2+} making their use impractical. Because Cu^{2+} exhibits an orders of magnitude advantage over Zn^{2+} in terms of equilibrium H_2S partial pressure and allowable acid buildup, use of the former was contemplated in the base-case process. Pertinent properties of the Cu-S- H_2O system are treated next.

(c) Pertinent Features of the Cu-S- H_2O System

Equilibria in the system Cu-S- H_2O are more readily understood by first considering the component system sulfur-water. The S- H_2O diagram of Figure 5 shows the major pertinent equilibria in this system and their dependence on solution redox potential (E_h) and pH at 423°K (150°C, 302°F). The dashed diagonal lines represent the equilibrium potentials of oxygen reduction ($\text{O}_2 + 4\text{H}^+ + 4e = 2\text{H}_2\text{O}$, upper dashed line) and hydrogen ionization ($2\text{H}^+ + 2e = \text{H}_2$), respectively. By convention, the latter equilibrium fixes the zero of the E_h scale for pH = 0 and $P_{\text{H}_2} = 1$ atm (unit activities of H^+ and H_2) at all temperatures. For reference purposes, cupric ion (which is much less oxidizing than O_2) has an equilibrium potential at 150°C with respect to metallic copper of $E_h = +0.085\text{V}$ ($\text{Cu}^{2+} + 2e = \text{Cu}$). By contrast, a powerful reducing agent such as metallic iron has a negative potential, e.g., $E_h(\text{Fe}^{++}/\text{Fe}) = -0.434\text{V}$ at 150°C.

One of the first points to note is that elemental sulfur lies entirely within the stability domain for water (dashed lines). The area of sulfur stability shrinks as the activities of sulfur-containing ions are decreased. (Compare, in Figure 5, 10^{-1}M and 10^{-4}M HSO_4^- and SO_4^{2-} .) In the scrubbing of H_2S from geothermal steam, the recirculating scrubber solution will almost certainly have total sulfate activity ($[\text{HSO}_4^-] + [\text{SO}_4^{2-}]$) in excess of 0.1M. Comparison of S- H_2O diagrams at other temperatures would show that the upper pH limit of stability of the sulfur zone moves to lower pH as the temperature is increased. Consequently, at geothermal steam temperatures, elemental sulfur could be indefinitely stable only at acidic pH's.

It is well known, but can stand repeating, that sulfur is a low-melting substance (m.pt. 107-115°C, depending upon the crystalline form)

Fig. 5: Equilibrium diagram for sulfur at 423°K and 1 atm pressure. Activities of sulfur-containing ions, 10^{-1} and 10^{-4} M.

and that the liquid has an appreciable vapor pressure, e.g., 1 mm Hg at 184°C (363°F).

At a solution pH below about 5 at geothermal steam temperature, H_2S can be oxidized to S° or to HSO_4^- or SO_4^{2-} . Conversely, direct reduction of sulfate to sulfide (i.e., without the intermediacy of the sluggishly reacting S°) is favored by higher pH.

The equilibrium diagram for the Cu-S- H_2O system is complicated by the existence of two common oxidation states of copper ion and by the formation of solid oxides and sulfides of each. (See Figure 6, in which the S- H_2O equilibria of the previous figure are shown as light dashed lines.) Below about pH 3 at geothermal steam temperatures, the copper oxides need not be considered. There are zones of stability for the condensed phases S° , CuS, Cu_2S and even Cu° . Note that the stability zone of S° lies within that of CuS (hence, the two can coexist) and that the stability zone of CuS is enveloped by that of Cu_2S . At a pH below about 7, CuS can be more or less stable than Cu_2S , depending upon the system E_h .

In sulfate solutions, the stability of the cuprous ion (Cu^+) increases with temperature, but even at 423°C, the existence of Cu^+ can be neglected if the activities of the copper-containing ions exceed about 10^{-3}M (Figure 6). Except in extremely acidic solutions, at geothermal steam temperatures in the presence of Cu^{2+} , S° is unstable with respect to CuS (and Cu_2S) and HSO_4^- , and CuS is itself unstable with respect to "enrichment" to Cu_2S . This behavior is further considered below.

(d) Precipitation of Copper Sulfide

The simplest direct combination of cupric ion and H_2S produces CuS according to the overall equation

which is equivalent to Eq. (3) above. The rate of this reaction is not anticipated to be sensitive to pH, for distinctly acid solutions, because aqueous sulfide is present almost entirely as H_2S , with very low HS^- and

Fig. 6: Equilibrium diagram for copper oxides and sulfides in water at 423°K and 1 atm pressure. Activities of copper-containing ions, 10^{-3} and 10^{-6} M; sulfur-containing ions, 10^{-1} M.

entirely negligible S^{2-} (see above). It is possible that a kinetic hindrance could begin to be felt at high acidities if the reaction mechanism involves an ionic species of H_2S as a reaction intermediate. Thus, considering the cupric ion to exist as the aquo complex, e.g., $Cu(H_2O)_4^{2+}$, it is conceivable that reaction initiation involves replacement of a bound H_2O by the chemically similar H_2S . Ionization of the bound H_2S would then be required for nucleation of a CuS precipitate. Soluble complexes of Cu^{2+} with HS^- are known (3), but they are formed only at high H_2S pressures, a condition not compatible with maintaining an excess of Cu^{2+} in the solution. We have no direct evidence for acid inhibition of the precipitation of CuS .

Combined redox/precipitation reactions are possible whereby H_2S is oxidized by Cu^{2+} to sulfur or sulfate. Cuprous sulfide is formed as a product:

In spite of the relatively favorable thermodynamics (Table 3) for reactions (7) and (8), it is highly probable that CuS is the initial reaction product. A mechanism exists for converting CuS to Cu_2S , in that S^0 or $\underline{CuS}$ can react further at a rate that increases with increasing $[Cu^{2+}]$, temperature and pH (4,5):

The actual copper sulfide reaction sequence may be more complicated than is indicated by the foregoing equations. Thus, a series of binary compounds and solid solutions is known, of which CuS and Cu_2S are the end-members. A listing and description of the best characterized of the end-member and intermediate compositions are given in Appendix D. In general,

the nonstoichiometric sulfides ($0 < x < 1$ in Cu_{1+x}S) and Cu_2S are more reactive than CuS . For some compositions, this can be attributed to a basic structure of large, closely packed sulfide ions with interstices that are incompletely occupied by copper ions. Such structures can exhibit anomalously high metal ion diffusion rates, and some have been observed to undergo structural transformations with change of stoichiometry, during oxidative leaching (6).

Copper sulfide precipitate formed by introduction of H_2S gas into a CuSO_4 solution tends to be colloidal, poorly recoverable by froth flotation and difficult to filter and dewater (7). The fine particle size of the precipitate, the composition of which corresponds to covellite (CuS), is responsible for its adverse process behavior. By avoiding local excess of H_2S during precipitation and by recycling the solids, a significant increase in mean particle size was achieved, e.g., $0.05\text{--}0.25\text{ }\mu\text{m} \rightarrow 3\text{--}75\text{ }\mu\text{m}$ (8). In the specific instance cited, the larger particles were found to be aggregates of 3–5 μm primary particles. Separation properties were correspondingly greatly improved; in particular, rapid flotation was achieved without use of collecting or frothing reagents. The design basis for a geothermal steam scrubber includes conditions favorable for formation of well-behaved precipitates, namely excess of cupric ion and recirculation of the copper sulfate/copper sulfide slurry.

(e) Acid Balance and Copper Sulfate Regeneration

It will be noted that the ratio of H_2SO_4 produced to H_2S consumed by reaction with CuSO_4 is 1:1 for formation of CuS , 1:1 for formation of Cu_2S and S^0 , and 1.8:1 for formation of Cu_2S and SO_4^{2-} (Eqs. 6–8 above). Accordingly, the removal of 90% of the hydrogen sulfide from 10^6 lb/hr of steam containing 220 ppm H_2S would result in the generation of 6.84 tons/day of H_2SO_4 within the scrubbing tower, if the product composition is CuS (kinetically favored). If the product composition is $\text{Cu}_2\text{S} + \text{SO}_4^{2-}$ (lowest equilibrium H_2S partial pressure), the corresponding rate of acid production is 12.3 tons/day.

If the steam also contains about 100 to 200 ppm NH_3 , as is the case at The Geysers, there will be partial acid balance within the tower, and

the pH of the scrub solution can be controlled by adjusting the size of the slurry purge stream and the acid content of the recycled copper sulfate solution. For steams containing low $\text{NH}_3/\text{H}_2\text{S}$ ratios, supplemental pH control in the scrubber (e.g., by NH_3 injection) may be required. In any event, the regeneration step must be controlled to achieve the proper overall system acid balance and sulfur removal. There are at least two good options available, using known technology, for achieving acid balance in conjunction with CuSO_4 regeneration, viz., the sulfation roasting and oxygen pressure leaching of precipitated copper sulfides (Figure 7).

Sulfation Roast. As discussed in an earlier section, selective sulfating roast is employed in the industry to convert a nonferrous metal or metals into a soluble form and thereby to effect a separation from iron, which is converted to an insoluble iron oxide under the same roasting conditions. The chemistry and thermodynamics of sulfation roasting are illustrated by the stability diagram of Figure 8 (from Toguri (9)).

Figure 8 is based on the equilibria

where M is the nonferrous metal. Each straight line in the figure is the boundary between the stability fields for the oxide and the sulfate (to the right of the line). For example, the full line passing through $P_{\text{O}_2} = 0.001$ atm and $P_{\text{SO}_2} = 0.1$ atm is the phase boundary at 680°C between CuSO_4 and $\text{CuO} \cdot \text{CuSO}_4$ (to the left of the line). This phase boundary nearly coincides with the equilibrium iso- P_{SO_3} line at the same temperature.

The curved lines in Figure 5 are drawn for $P_{\Sigma\text{O}} = 0.1$ and 0.2 atm, where $P_{\Sigma\text{O}}$ is the total pressure of oxygen and oxygen-containing gaseous species, i.e., $P_{\text{O}_2} + P_{\text{SO}_2} + P_{\text{SO}_3}$. Toguri (9) points out that in most industrial practice, when air is used for roasting, $P_{\Sigma\text{O}}$ is about 0.1 atm. For gas compositions in this range, the diagram shows that between 630° and 730°C , CuSO_4 is the stable copper phase. At the higher temperatures, in the presence of iron, difficulty soluble ferrites can form, e.g., CuFe_2O_4 . For purposes of geothermal steam scrubbing, ferrite formation

Fig. 7: Simplified flow charts of alternate regeneration processes.

Fig. 8: Stability diagram of various non-ferrous sulphates.

is a matter to be cognizant of, but would become a concern only in the unlikely event that appreciable iron were introduced into the copper sulfide precipitate.

It is apparent that sulfation roasting will generally be carried out at conditions removed from equilibrium. Since the overall reaction involves three gaseous species and two or more solid species, the roasting process is diffusion controlled. Fluidized-bed roasting can assure close process control and a high degree of conversion of the copper sulfide.

The combined H₂S scrubbing and regeneration systems have the flexibility of accommodating a range of products, from full sulfation (CuSO₄) to partial sulfation (CuO·CuSO₄) to dead roasting (CuO). All of the possible products are either directly soluble in the acid scrubbing solution or will be converted to copper sulfide by reaction with H₂S; e.g.,

is strongly favored thermodynamically. Even reasonable percentages of unreacted sulfide would not be detrimental.

The amount of neutralization of the scrubbing solution that can be achieved by controlling the conditions during roasting is determined by the percentage of copper present as CuO, whether neutralization occurs indirectly via Eq. (12) or directly as

Of course, the acid neutralizing capacity appears as SO₂ and SO₃ in the off-gases of the roaster, and this aspect of the overall chemistry must be comprehended in the process design.

Pressure Leach. A feature of the chemistry of oxygen pressure leaching of sulfides is that sufficient anions and hydrogen ions must be provided to ensure that the desired leach product is soluble. Both requirements can be met by maintaining an excess of H₂SO₄. The half-reaction of oxygen reduction consumes acid:

If the sulfide is reacted to elemental sulfur in the simultaneous oxidation half-reaction, i.e.,

there is a net consumption of acid during leaching, e.g.,

If, on the other hand, the sulfide is oxidized to sulfate, i.e.,

there is no net acid consumption in the leaching step, for precipitate of composition CuS:

Thus, when elemental sulfur is the principal product of oxygen pressure leaching, the net scrubbing/regeneration reaction is, in the simplest situation,

giving internal acid balance and allowing sulfur to be rejected from the system as elemental sulfur.

When sulfate is the principal form of the leach product, there is a net acid production:

This acid must ultimately be neutralized and, in so doing, excess sulfur will be rejected from the system as a sulfate (NH_4HSO_4 , if neutralization

is by NH_3 , whether present in the geothermal steam or added to the system; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, if limestone is used for neutralization). Note also that oxidation to sulfate requires four times the quantity of oxygen or air as for oxidation to S^0 .

In the pressure leach-regeneration step, one needs to be concerned not only with product mix and reagent consumption, but also with the reaction rate and severity of process conditions necessary to attain an acceptable yield and rate. As mentioned above in connection with roast-regeneration, a reasonable fraction of unreacted copper sulfide can be returned to the scrubber slurry system; however, unreacted copper sulfide would first need to be separated from any elemental sulfur produced during leaching.

A summary of factors determining product mix, rates and yields is in order. In general, formation of elemental sulfur is favored by lower pH and lower temperature (10) and by less aggressive oxidants. (See E_h -pH diagram for $\text{S-H}_2\text{O}$, Figure 5). Since the pressure leach reaction is heterogeneous, its rate and extent will be determined by accessibility and availability factors. Specifically, fine particle size and suspension (i.e., vigorous stirring) of the solid sulfide are important, as is the availability of $\text{O}_2(\text{aq})$ to the reaction interface (11). It is important that the pressure reactor internals and operation provide maximum transfer rate of oxygen from the gas phase to the dissolved state in order that the reaction rate not be limited by the supply of $\text{O}_2(\text{aq})$; otherwise, dissolved oxygen depletion can occur even at high O_2 overpressures.

There are also chemical and mineralogical influences on pressure leach rates. It has been known for a long time that chalcocite is normally oxidized in two stages, the first leading to covellite (12)

Natural CuS reacts rather slowly. For example, under favorable reaction conditions, viz., an oxygen absorption coefficient of $40 \text{ g/l}^{-1}\text{hr}^{-1}\text{atm}^{-1}$ in 675 ml of liquid, 180°C , pH 0.75 and 100 psi O_2 , 37% of the copper was

leached in 90 minutes from a suspension containing 10.5 g of minus 100 mesh covellite (13). Under comparable conditions and time, chalcocite was completely dissolved. This may be taken as indication that the finely divided covellite produced as an intermediate in the leaching of chalcocite is appreciably more reactive than natural covellite of coarser particle size.

Confirmation that finely divided covellite produced as a reaction intermediate is appreciably more reactive than natural covellite was obtained recently (14). In 2M H_2SO_4 and 100 psi O_2 , reaction was complete in about two hours after reaching the final temperature of 93°C; within analytical error, all of the sulfide was oxidized to elemental sulfur under the given mild leach conditions.

Others have noted a dependence of oxidative leach kinetics on the stoichiometry of the copper sulfide. For example, the steady-state leach rate of $Cu_{1.76}S$ was more than double that of $Cu_{1.95}S$ at 100°C and 10 atm O_2 (15). In addition, the composition of some nonstoichiometric copper sulfides has been observed to change during oxidative leaching (16), i.e., the chemical reaction was accompanied by solid-state diffusion and corresponding structural changes in the solid.

It is apparent, therefore, that unless one is dealing with the stoichiometric end-members, CuS or Cu_2S , it is impossible to predict rates and product mix in pressure oxygen leaching. In this respect, the conditions of the regeneration process are more sensitive to the precise nature of the precipitate than is the case with the roasting option.

2. Process Control

By varying process conditions in scrubbing and by selecting the regeneration mode and operating conditions in regeneration, it is possible to achieve sulfur balance within the integrated process to fix the desired form of sulfur for disposal. The overall process material balance is fixed by the hydrogen sulfide to ammonia ratio of the steam, the degree of removal, or contact efficiency, and the regeneration kinetics. It will probably be desirable to keep the concentration of cupric ion relatively high (i.e., about 2 g/l) in the scrubbing step, to ensure effective scrubbing (low hydrogen sulfide partial pressure) and to passivate stainless steel,

the preferred material of construction, in the presence of reasonably high hydrogen ion concentrations. For high ammonia to hydrogen sulfide ratios, the system is essentially self-buffering; little excess acid is produced, and the scrubber can be run with the minimum volume of purge stream consistent with maintaining a reasonable slurry density. The desired high concentrations can be obtained by recycling a concentrated copper sulfate solution (possibly containing suspended copper oxide, as discussed above). The buffering action of NH_3 will be effective to an extent limited by the accumulation of ammonium sulfate in the scrubber-liquor, in that a high concentration of NH_4^+ will yield a sufficiently high ammonia pressure to limit ammonia absorption (Eq. (4)).

For low ammonia to hydrogen sulfide ratios, the option exists to add ammonia to the incoming steam to neutralize acid or to recycle copper oxide as well as copper sulfate to the scrubber. The alternative to these techniques is to dilute the purge stream by adding additional water or by recycling scrub solutions at lower copper sulfate concentration, to prevent buildup of unacceptably high levels of sulfuric acid.

In either case, a selective ion electrode could be used in a cooled slip-stream of scrubber solution to control the flow rate of make-up copper sulfate solution, thereby maintaining the desired cupric ion concentration in the recirculating slurry. A pH electrode could then be used to monitor the addition of ammonia or water to achieve the desired acidity control. Other possible process analyzer/controllers involve a direct photometric measurement of $[\text{Cu}^{2+}]$ in the near I.R. and automatic titration of free H_2SO_4 (i.e., $[\text{H}^+] + [\text{HSO}_4^-]$).

It is envisioned that a large geothermal power source would consist of a system based on a multiplicity of 50-200 megawatt sites. The steam requirements for generating power in these blocks is of a size convenient for placing a scrubber at each generating station. However, the mass flow of hydrogen sulfide, as copper sulfide, removed at each station would be so small as to preclude the economic operation of conventional regeneration plants at each site. Therefore, the purge stream from each scrubber

would be manifolded, and all slurries pumped to a central regeneration plant. Regenerated copper sulfate solution would be redistributed to all scrubbing stations using a parallel piping network.

While the composition of the purge stream from each scrubber will be different, in general, depending on the specific composition of the steam treated, the composition of the recycle scrub solution to each unit will be the same, since it is derived from a single source. It is envisioned, therefore, that there will be a requirement for trim control of acidity by dilution or by ammonia addition or acid addition at each site. In addition, the requirement exists for providing surge capacity for blending and storage at each site.

The regeneration mode most appropriate for a given installation depends not only on the desired form of sulfur removal, as previously noted, but, also on size of the operation. Very large installations, or steams containing high hydrogen sulfide contents, which generate relatively large amounts of copper sulfides, would favor a fluid-bed roaster. Small installations or lean steams would favor the use of oxygen pressure leaching, since leach reactors can be scaled down and operated more economically than roasters at small throughputs.

The choice of method of disposal for sulfide oxidized to sulfate depends on the relative cost of disposal of soluble and insoluble compounds. Reinjection of soluble ammonium sulfate represents a potentially attractive alternative, especially if suitable reinjection wells are available. However, ammonia as an acid neutralizer costs of the order of 10 times the equivalent quantity of calcium oxide derived from limestone, so that, unless the disposal costs of inert solids (gypsum) are unusually high, it is likely that sulfates will be fixed as insoluble salts.

A major concern of the site operator is the degree at which the scrubbing of raw steam for hydrogen sulfide removal will affect its quality in terms of power generation. Typically, geothermal steam is of a low quality, being available at 100 to 150 psig. Some pressure drop is inevitable in passing through a scrubbing apparatus, and drops of the

order of 2 to 3 psi, including entrance and exit and piping losses, are to be expected. Furthermore, the activity of water in the scrubbing solutions is typically of the order of 0.97, due to the presence of the dissolved salts. Since it is to be expected that the species H_2O will come to equilibrium in the steam and liquid phases, both temperature and partial pressure must be matched. Thus, some H_2O in the incoming steam must condense to raise the temperature of the scrubber solution and steam until equilibrium is achieved. Therefore, steam exiting the scrubber will be reduced slightly in mass flow rate and pressure, but will be slightly superheated. If dry steam is supplied to the scrubber, the net effect is to reduce the work available from the steam by the order of 1/2%.

IV. EXPERIMENTAL METHODS

1. Scrubber System Design and Hardware

The system used in the laboratory studies of H_2S removal by scrubbing with $CuSO_4$ is shown schematically in Figure 9. Its major components include a packaged boiler for generating the required amount of steam, cylinders of H_2S/N_2 and N_2 gases and a rotameter for metering H_2S into the system, a 2-inch ID scrubber column with liquid sump and vapor disengaging sections, scrubbing solution (slurry) circulating pump(s), a holding tank and pressurized metering system for injecting make-up $CuSO_4$ to the system, and a condenser and condensate disposal system for cleaned steam. Commencing with the check valve upstream of the gas injection point, all lines and wetted parts are of 316 or 304 stainless steel.

Steam was generated in a 6.2 HP Fulton vertical, tubeless boiler rated for 250 psi service, with a capacity of 214 lb/hr at 212°F. No condensate was returned to the boiler, which was supplied from city water. The city water was preheated and deaerated by sparging a portion of the boiler steam output into a 55-gal deaeration tank, to maintain the boiler feed water temperature above about 90°C. The boiler steam, usually at 175-185 psig, passed through a pressure regulating valve. The steam pressure regulator and a manual flow control valve downstream of the column were set to deliver the required flow rate at the desired pressure in the column. Condensate in the steam was trapped out in advance of impurity gas injection, and the steam flow passed through an orifice. This flow rate indicator was made up by clamping a 1/32" disk, with a 3/16" diameter through-hole, into a pipe union, with pressure taps brazed to the steam line immediately adjacent to the union in the standard configuration. The orifice pressure drop was measured with an Orange Research differential pressure gauge, with a range of 0-5 psig.

Hydrogen sulfide was introduced to the system as a mixture, with N_2 , of certified composition (nominally, 6% by volume H_2S). A cylinder

regulator was used to maintain a constant pressure upstream of a 1/4" needle valve used for flow control. The gas mixture flow rate was obtained from a Brooks Model 1110 rotameter. A N₂ source was teed into the H₂S/N₂ line in advance of the H₂S regulator, to permit flushing at the end of a run. The gases were injected through 1/4" OD line into the 1" OD steam line at an elbow, and the mixture was superheated prior to introduction into the column. Superheating was obtained by means of Variac-controlled electrical heating tapes wrapped around the steam line.

The active portion of the scrubber column consisted of a 4-foot length of 2" IPS Schedule 40, T316 SS pipe. Transition hubs on the column top and bottom, fitted with Grayloc connectors, expanded the column assembly to 3" internal diameter. A 10" long chamber on the top of the column served as a disengaging section and was tapped and fitted with nozzles for temperature and pressure instruments, steam outlet, and recirculated scrub solution (slurry) inlet piping. The scrubbing liquid inlet nozzle extended into the chamber and was directed downward along the column centerline. A 30" long x 3" ID chamber below the column served as a steam injection and slurry accumulation section. This sump was tapped and fitted with nozzles for temperature and pressure instruments, a level gage glass, steam inlet, recirculated solution (slurry) outlet and return, make-up CuSO₄ solution inlet, and sample withdrawal piping.

The accumulation section and column proper were heated by Variac-controlled electrical heating tapes and insulated with fiberglass batt. Both top and bottom 3" ID sections, fabricated of T316 SS, were fitted with Grayloc connectors to permit rapid disassembly for inspection of the column components, etc. The 2" ID column proper had no fittings or piping.

The scrubbing solution, a slurry of precipitated sulfides in copper sulfate solution, was recirculated to the top of the scrubber by a Hills McCanna Model UM 2F dual-head metering pump. The pump had a maximum capacity of 0.5 GPM per head, with rate controlled by adjustment of the piston stroke. The pump body and check valve seats were of Alloy 20; piston and check balls were alumina ceramic, and piston packing was Teflon-impregnated asbestos. The solution (slurry) piping was 1/2" OD tube,

heated by Variac-controlled electrical tapes placed at appropriate locations. In the majority of runs, one of the two pump heads was used to redirect solution (slurry) to the column sump in an effort to keep solids suspended. However, the solids settled so rapidly that this effort was largely ineffectual and was discontinued in the final series of runs. All joints in the piping system were Swagelok or Tylok compression fittings.

Make-up CuSO_4 solution was introduced to the system by pressurizing a make-up tank, consisting of a 3-ft section of 3" IPS type 316 SS pipe, with nitrogen to 300 psig. The nitrogen supply to and solution discharge from the tank were conducted through flexible hose and looped stainless steel capillary tubing, respectively. The tank was hung on a scale, so that the weight loss with time could be used to derive the integrated make-up rate of CuSO_4 solution. The rate of addition of CuSO_4 was controlled by a needle valve on the inlet line at the column sump.

Scrubbed steam was condensed in a 20-ft section of 3/8" OD SS coiled tube over which condensing (tap) water was passed. The condensate, nitrogen, and unscrubbed H_2S were bubbled into a 2-gal plastic container, holding a "heel" of concentrated caustic, which neutralized and removed unscrubbed H_2S . The overflow from this H_2S absorber, together with cooling water, passed to a floor sump and was pumped out to drain.

2. Scrubber System Operating Procedures

Prior to initiating a run, the column - and scrub solution (slurry) piping, if necessary - were disassembled, inspected, and thoroughly flushed, first with water and then with steam. Necessary repairs or modifications were made at this stage. Particular attention was paid to the circulating pump(s), since considerable difficulty was experienced in maintaining adequate seal on the pistons; this appeared to have resulted from fine sulfide solids leaking under the packing and building up on the ceramic pistons.

Once the desired column internals were in place and system mechanical integrity had been established (by water pressure testing, if necessary), the boiler was fired and steam was admitted to the clean system.

Cooling water to the condenser was turned on at this time. During the heat-up period, condensate was allowed to collect in the scrubber sump to a level within the gage glass. The scrub solution circulating pump was then started, and Variacs controlling the electrical heating tapes were turned on. A flow of nitrogen at approximately the desired $\text{H}_2\text{S}/\text{N}_2$ flow rate was established in the H_2S feed system.

During heat-up of the scrubber system, CuSO_4 solution was charged to the make-up tank, the tank was pressurized with nitrogen, and the initial weight recorded. A supply of caustic solution was prepared for absorbing unscrubbed H_2S in the condensate and other required analytical materials, e.g., ammoniacal CdSO_4 solutions, and supplies needed for the test were assembled. Ventilation and exhaust fans were turned on and final safety checks were made.

It normally required 1-2 hours for the system to reach thermal steady state. During this period, the excess condensate formed by the steam heating of the system components was blown down from time to time, to maintain a visible level in the sump gage glass. In due course, the rate of accumulation of condensate in the sump decreased, and final adjustments were made in Variac settings so that the liquid level held constant, indicating that heat losses were just being offset by the electrical heating tapes. Higher Variac settings were needed at higher steam flow rates (indicating that the incoming steam was slightly wet), as well as when running at higher pressures. When the level had stabilized, the flow rate of steam through the system was determined by collecting and weighing condensate for known short periods of time. Final adjustments were made with the steam flow control valve, and the orifice pressure drop and condenser inlet pressures were noted.

Flow of make-up CuSO_4 solution was then initiated, and the relatively concentrated (typically 40 g/l Cu^{++}) solution mixed into the system by the action of the recirculating pump(s). Samples of the solution in the sump were withdrawn periodically and analyzed to determine when the contents were at the concentration desired for the run. When the target concentration had been achieved, the flow of make-up solution was stopped.

and the system run with steam and N_2 for an additional period of time, typically 1/2 hr, to ensure that the system was at steady state. In some early runs, when several non-stainless steel internal fittings were (inadvertently) in use, a decrease in copper content was noted, reflecting the corrosion which was occurring.

Upon determining that the system was, in fact, at steady state, the flow of H_2S/N_2 was initiated, and flow of make-up $CuSO_4$ solution was resumed. Adjustments were made from time to time in the flow rates of steam and recirculated scrub solution (slurry) to obtain the desired scrubber column hydraulics. The flow of make-up $CuSO_4$ solution was periodically adjusted to maintain the copper content in the system at the desired level. The solution (slurry) copper content and pH were determined at frequent intervals by analysis of samples withdrawn from the recirculation line.

At selected intervals, full sets were obtained of operations data. At these times, the condensate was diverted into the ammoniacal $CdSO_4$ solution for analysis of unscrubbed H_2S and simultaneous precise determination of the steam flow rate. Samples were also taken of the scrubbing solution (slurry) to determine copper content and pH. All system temperatures, pressures, and other instrument readings were recorded.

At the end of a test, the flow of H_2S and make-up $CuSO_4$ were stopped and the final weight of the make-up tank noted. The gas feed lines, H_2S regulator and rotameter were purged with nitrogen, and the heating tapes were turned off. After the system had been purged of H_2S , the flow of nitrogen was stopped, the circulating pump(s) turned off, and steam flow discontinued while maintaining the column under autogenous pressure.

The column was allowed to cool and depressurize, usually overnight, and the contents of the sump and circulating lines were then drained and the contents collected for analysis. A few liters of water was usually then added and circulated through the system to ensure that all solids had been removed; this flush solution was added to the sample originally drained, and the total volume was then recorded. The column and components would then be opened for inspection, as required.

3. Chemical Analysis

Table 5 lists the substances analyzed in the three major process materials of the laboratory scrubber operation. It proved to be impractical to measure H_2S directly in the steam. Accordingly, H_2S was determined in the mixture of condensate and noncondensibles as it emerged from the condenser. The pH of the condensate was measured as indication of possible entrainment of slurry liquid in the scrubbed steam. A sensitive test for copper in the condensate was employed as a indication of possible carryover of solids from the scrubber. The occasional presence of sulfur in the condensate, in the form of a very dilute colloidal suspension, was merely noted.

Rapid Cu^{2+} and pH analyses of solution from the scrubber were performed for purposes of process control during operation. Solution analyses for material balance were performed for Cu^{2+} , H_2SO_4 and total sulfate. Materials closure is obtained when $[Cu^{2+}] + [H_2SO_4]_{\text{titratable}} = [SO_4^{2-}]_{\text{total}}$, all expressed as mol/l (M).

Slurry solids - essentially, the $Cu_{1+x}S$ precipitate - were separated, washed and vacuum-dried. For copper and sulfide analysis, weighed samples were decomposed in $HNO_3/NaClO_3$ until any elemental sulfur produced in this reaction had been dissolved (i.e., converted to sulfate). Following removal of excess oxidant by evaporation to virtual dryness and re-dissolution in water, the final solution was analyzed for Cu^{2+} and SO_4^{2-} .

Supplemental analyses of precipitates were performed with a scanning electron microscope (SEM). Elemental analysis capabilities (energy dispersive x-ray, or EDAX) of the instrument employed permitted detection of impurities, such as corrosion products, and gave an indication of differences in the copper to sulfur ratio.

H_2SO_4 Analyses. Solution pH's were measured at room temperature, measurements under reaction conditions (high T and P) not being feasible with available pH probes. For determination of acid concentration (rather than thermodynamic activity, a_{H^+} , of hydrogen ion: $a_{H^+} = 10^{-pH}$), the test solution was titrated with standard NaOH solution. Since Cu^{2+}

Table 5

Substances Analyzed in the Major Process Materials
of the Laboratory Scrubber Operation

<u>Steam/Condensate</u>	<u>Slurry Liquid</u>	<u>Slurry Solids</u>
H ₂ S	Cu ²⁺	Cu ²⁺
pH	pH	Total S ^c
S° (noted)	H ₂ SO ₄ ^a	Misc. impurities (identified)
Cu ²⁺	Total SO ₄ ^b	

^aTitratable H₂SO₄ = [H⁺] + [HSO₄⁻], expressed as H₂SO₄ molarity.

^bTotal sulfate = [HSO₄⁻] + [SO₄²⁻].

^cTotal sulfur = sulfide sulfur + elemental sulfur.

began to be precipitated (as hydroxide) at about pH 5, a pH end point of 4.5 was used in place of a visual indicator end point.

Copper Analyses. Copper was analyzed colorimetrically by either of two colorimetric methods: a rapid, direct determination and a conventional Neocuproine procedure. The rapid method utilized the red and near-infrared absorption band of the uncomplexed aquo-cupric ion, with peak at 825 nm. In the absence of interfering colored ions, as was typical of scrubber solutions, concentrations up to about 10 g/l Cu^{2+} could be determined directly in a 1-cm path length absorption cell. At concentrations above about 1 g/l, the analytical accuracy, $\leq 1\%$, was comparable to that of the widely used atomic absorption method. At 0.1 g/l Cu^{2+} , measurement reliability was about 5%.

For lower copper concentrations, as in analysis of condensate, copper was determined as the cuprous Neocuproine complex. The determination required chemical reduction of Cu^{2+} ; hydroxylamine was employed as reducing agent. Generally, no extraction was required, as interfering ions were absent. Solutions were diluted to the range 1-14 ppm, and optical density was measured at 457 nm. An accuracy of about 1% was achieved.

Sulfate Analyses. Three analytical procedures for sulfate were evaluated, exclusive of the classical gravimetric determination as BaSO_4 , which was deemed to be too time-consuming for the needs of this project. These included (a) titration with $\text{Ba}(\text{ClO}_4)_2$ with use of Thorin as visual indicator, (b) photometric determination, with use of Ba chloranilate and (c) potentiometric titration with $\text{Pb}(\text{ClO}_4)_2$ with use of a lead specific-ion electrode as end point indicator. The last named procedure, which suffered less from interferences, particularly by the NO_3^- and Cl^- introduced in dissolving the precipitates, was employed in the majority of sulfate analyses. Interference by copper was eliminated by ion exchange with the hydrogen-ion form of the cation exchanger Rexyn 101.

H_2S Analyses. Substantial effort was devoted to finding an analyzer for the direct determination of H_2S in steam. A number of instrumental methods was considered, including (a) gas chromatography

with flame photometric detection, (b) U.V. absorption at 228 nm (du Pont Model 400 Photometric Analyzer), (c) electrochemical detection by use of a gas diffusion membrane (Energetics Science H₂S Analyzer) and (d) photoionization detector employing ionizing U.V. light from a hydrogen lamp (HNU Systems Photoionization Detector).

The high background of steam in the gas to be analyzed made the chromatographic separation and detection of H₂S highly uncertain. Our particular analytical problem had not been encountered by the dozen or so instrument manufacturers contacted, and none could give assurance that their gas chromatograph could perform the necessary analyses, particularly at the desired ppm level of sensitivity (for scrubbed steam).

U.V. photometric detection appeared to have the requisite selectivity for H₂S, but the U.V. instrument was expensive and the absorption cells were cumbersome for a laboratory scrubber. For example, an optical absorption cell of 1-meter path length was required for the scrubbed steam line. Condensation had to be prevented on the quartz optical windows, which also had to be sealed against steam temperature and pressure. A further drawback was the error that could be introduced by entrained droplets in the steam.

Steam temperature and pressure were much beyond the capability of an electrochemical analyzer to cope with, leaving the photoionization detector as the instrument of choice. Unfortunately, the manufacturer did not comprehend the character of steam as background gas at above the normal boiling point of water and was not able to build sufficient heating capacity into the sample line filter and detection chamber to prevent condensation of the steam upon expansion through the analyzer. After several unsuccessful attempts by the manufacturer to correct the problem, we abandoned the notion of a direct instrumental approach for H₂S analysis in steam and adopted a chemical method.

Quantitative H₂S-in-steam analyses were carried out by absorbing the gas in ammoniacal cadmium solution, which caused precipitation of yellow CdS. The absorbing solution composition was 10 g/l Cd²⁺ (as

3CdSO₄·8H₂O) and 100 ml/l conc. NH₄OH. The quantity of Cd²⁺ removed from solution was generally determined by EDTA titration of the starting solution and the final solution, the latter including collected condensate. Standard 0.01M Na₂EDTA solution was employed in the titration, with use of Eriochrome Black T visual indicator.

V. EXPERIMENTAL RESULTS

1. Corrosion Tests

Information on the suitability of materials of construction has been obtained from three sources: corrosion literature, coupon testing, and inspection of the column assembly at the conclusion of H₂S scrubbing tests. Literature sources and operating practices in the copper industry show that the austenitic stainless steels are acceptable materials of construction for cool (not higher than 60°C), strongly acid copper sulfate solutions, but no data are available on materials of construction under geothermal scrubber operating conditions. It is known that sulfide stress corrosion is a problem at these higher temperatures (>150°C) in petroleum well-case materials, for example, but there is nothing in these systems which would act in a manner analogous to the cupric ion to maintain system redox potentials high enough to maintain stainless steels in the passive state.

Coupon testing was carried out in the early stages of the program to select suitable construction materials for the laboratory column. These tests showed that austenitic stainless steels were acceptable, certainly for short term service, although some results were anomalous. For example, some type 316 stainless steel specimens corroded at rates less than 5 mils per year in synthetic scrubber slurry, while others showed greater than 10 mils per year. Some type 304 stainless steel coupons showed better resistance than type 316, an unexpected result. In general, however, alloys which are known to provide better service under reducing conditions, for example, Hastelloy B and ferritic stainless steels, failed; whereas, those that are known to be better in oxidizing environments, for example, titanium or Alloy 20, were acceptable. Results of these screening tests are summarized in Table 6.

While these tests were suitable for guidance in constructing the laboratory scrubber which would be subjected to relatively short-term

Table 6

Summary of Corrosion Screening Tests in Copper Sulfate/Copper Sulfide Slurry[†]

Slurry Sample	Temp. (°C)	Time (hrs)	Cumulative Residence Time of the Solid Sul- fide (hrs)	Corrosion Tested Specimens [*]			
				Severely Corroded (>100 mils/yr)	Moderately Corroded (100>C.R.>15)	Lightly Corroded 15>C.R.>5	Corrosion Resistant (<5 mils/yr)
5718	175	24	24		Durimet 20 Chlorimet 2		Zirconium Titanium-Palladium
5721	175	24	24	Durcomet 100 RA 330 & 333		Chlorimet 3	Titanium
5724	175	24	48	Inconel 600 Monel		316 S.S.	304 S.S. 310 S.S.
5729	175	24	72	Hastelloy B	303 S.S.	Hastelloy C 316 S.S.	Titanium 316 S.S. #
5801	200	67	139			316 S.S. Hastelloy C	304,310,316 S.S. Titanium Tantalum
5818	175	24	163	410,416,420, 431, 440C S.S.			Carpenter 20 316L,321,347, 430 S.S.
5918	175	17	180	Copper Brass Bronze			316 S.S.

[†] Initial slurry composition in g/l: CuSO₄, 2.5; CuS, 79; (NH₄)₂SO₄, 100; H₂SO₄, 3.7.

^{*} C.R. = Corrosion Rate (mils per year); S.S. = Stainless Steel

Specimens from two different suppliers.

operation, they were not carried out on certified materials and, therefore, the exact composition of the alloys tested is not known. In addition, no stressed or welded pieces were tested, nor were any potentially troublesome trace elements, especially chloride ion, present in the solutions. Therefore, a second series of coupon tests was undertaken; results are summarized in Table 7. Certified types 304 and 316 test specimens were used, and stressed and welded coupons were tested in the presence of chloride ion under simulated process conditions.

The corrosion rates obtained were extremely variable. It was noted, however, that those specimens which were severely corroded had surfaces which had become unevenly coated with a tenacious, black scale. The surfaces of the essentially unattached coupons, while covered by loosely adhering sulfide material, were only lightly stained. No specific evidence was found of stress corrosion, pronounced weld-zone attack, or pitting. Corroded samples showed general loss of metal, and uncorroded samples showed at most only light grain-boundary etching.

These tests are not entirely representative of the situation in a real system, since test periods were necessarily short and possible contaminants in addition to chloride were absent. Moreover, as before, the synthetic cupric sulfide initially charged to the autoclave was altered ("enriched") during the course of the corrosion tests, resulting in the formation of some cuprous sulfide and thereby decreasing the concentration of cupric ion in solution and increasing solution acidity. These changes in test solution composition undoubtedly reduced its passivating capability. In an open system (for example, the laboratory scrubber), as opposed to autoclave tests, solids are continuously removed after a limited residence time, and cupric ion is continuously made up to the system in order to maintain the appropriate level of precipitant as acid is purged. From this standpoint, continuous operation is less severe.

At the conclusion of H_2S scrubbing tests, the laboratory apparatus was disassembled and inspected carefully for evidence of corrosion. No evidence of severe corrosion was found on any column parts or piping, or on a corrosion test specimen generally placed within the column, but

Table 7

Coupon Corrosion Tests on
Austenitic Stainless Steels

<u>Material</u>	<u>Test No.</u>	<u>Sample</u>	<u>% C</u>	<u>Composition</u>			<u>Corrosion Rate, MPY</u>	<u>Comments</u>
				<u>% Ni</u>	<u>% Cr</u>	<u>% Mo</u>		
304-4	1	Plain	0.062	8.23	18.35	0.06	4.5	No visible attack, no surface coating.
304L-2	1	Plain	0.025	10.06	18.45	0.11	1.1	No visible attack, no surface coating.
304L-7	2	Welded	0.014	10.3	18.0	-	2800	General loss of metal in wetted area, erosion of leading edge. Surface coated with tenacious, black scale. Weld-affected areas generally less attacked.
316-2	1	Plain	0.018	11.67	16.84	2.14	2200	General loss of metal in wetted area. Surface partially coated with tenacious, black scale.
316-11	2	Stressed	0.067	13.31	16.48	2.17	0.9	No visible attack, no surface coating.
316-18	2	Welded	0.050	13.11	17.63	2.76	1200	General loss of metal in wetted area. Surface coated with tenacious, black scale. Weld-affected areas generally less attacked.
316L-18	2	Welded	0.020	13.6	17.71	2.67	900	General loss of metal in wetted area. Surface coated with tenacious, black scale. Weld-affected areas generally less attacked.
316L-4	1	Plain	0.009	13.07	17.42	2.15	10.4	No visible attack, no surface coating.

- Notes: (1) Test duration 24 hrs, penetration rate calculated from weight loss.
 (2) Test conditions: 175°C, 115 psig with mixing by turbine agitator at 300 RPM, with coupons as baffles. Metal exposure 125 ml solution/in².
 (3) Initial solution compositions: 5 g/l CuSO₄, 100 g/l (NH₄)₂SO₄, 6 g/l H₂SO₄ (pH 2), 5 ppm Cl⁻, 95 g/l CuS.
 (4) Final solution compositions ~1 g/l CuSO₄, pH 1.7.

most surfaces eventually acquired some light etching. No tenacious black scale could be found on any column parts. Some parts, such as the bottom hub on the column sump, appeared to be completely unaffected, showing no etching whatsoever.

Some evidence was found of local metal loss and galling at those areas where the sealing rings bore on the Grayloc fittings. This may have resulted from crevice corrosion or the formation of galvanic couples, since the sealing rings were coated and of a different composition (347SS) from the hubs. Some corrosion was also noted in a few compression fittings on the 1/2" tubing used in the piping loop, where ferrules were not properly seated. This allowed solution to seep underneath the fittings, and crevice corrosion was observed behind the ferrules, sometimes with deposition of metallic copper.

The only severe local corrosion which occurred within the column system was on the sieve tray downcomer at a location facing the steam injection port. Approximately 10-20 mils of metal had been removed over an area of approximately 1-2 sq. in., and a small spot of black scale adhered to the center of this area. Because of a constriction in the column in passing from a 3 in. to a 2 in. diameter at this point, clearance around the downcomer was less than 1 in., and steam containing hydrogen sulfide impinged directly on the downcomer at approximately 15 ft per second. Undoubtedly, some copper sulfate solution leaked from the tray down the outside of the downcomer pipe, and sulfide may have been precipitated at a high rate, with consequent depletion of copper and liberation of acid, in a localized area. In addition, the high steam velocities probably served to inhibit the retention of a passive film on the metal.

Some auxiliary components of the system corroded very rapidly in the early stages of testing and subsequently proved not to be of stainless steel. Once these faulty components were replaced, no evidence of rapid component corrosion, such as the presence of elemental copper in the slurry solids or as a coating on adjacent stainless steel surfaces, recurred.

In general, it was found that there was little tendency for slurry solids to adhere to the surfaces of the column or auxiliaries which were completely wetted with scrubbing solution. Some tendency was observed for small masses to accumulate on the walls of the column above the trays. These accumulations did not grow to appreciable size and could be removed easily, usually disappearing during the course of the next run. No evidence of pitting or crevice corrosion in column wall areas formerly masked by these solids has been observed. Alloy 20 and ceramic components of the circulation pump appear to have been completely unaffected by contact with hot slurry. The same is true of Teflon seats and seals of valves located in the piping system.

2. Autoclave Scrubbing Experiments

(a) H₂S Precipitation with CuSO₄

Preliminary precipitation experiments were carried out in a type 316 SS autoclave (a two-liter, Parr Model 4761 Bomb with gage block assembly). The general arrangement involved sparging steam, into which H₂S was bled, through a CuSO₄ solution contained in the autoclave bomb. The sparger was a stainless steel, porous tip inserted into a stainless steel tube. Heat balance was maintained by heating the autoclave electrically.

H₂S was introduced as a nominally 6% H₂S-N₂ mixture that was metered into the steam to yield a concentration of 250 ppm (by weight). The outflow from the reactor was condensed and sparged into a sodium hydroxide solution for scrubbing any unreacted hydrogen sulfide.

Hydrogen sulfide was sparged through the reactor for approximately 30 minutes. The odor of H₂S in the mixture of disengaging nitrogen gas and condensate was practically imperceptible, signifying virtually quantitative (>99%) scrubbing of H₂S under the experimental conditions.

Experimental conditions were as follows:

CuSO ₄ Solution in Reactor:	850 ml of 1.87 g/l Cu ²⁺
Steam Pressure:	130-150 psig
Steam Line Temperature:	170°C (340°F)
Reactor Pressure:	65-70 psig
Condensate Collection Rate:	50-54 cc/min
Steam Flow Rate:	6.6-7.1 lb/hr
H ₂ S Concentration:	200-250 ppm

Hydrogen sulfide was sparged through the reactor for approximately 30 minutes. The concentration changes observed are illustrated by the following analyses:

	<u>Start</u>	<u>End (30 min)</u>
Copper Concentration	2.94 x 10 ⁻² M (1.87 g/l)	0.36 x 10 ⁻² M (0.23 g/l)
pH	2.08 (room temperature)	1.48 (room temperature)
H ₂ SO ₄	1.41 x 10 ⁻² M	3.67 x 10 ⁻² M

Precipitate formed in the reactor was collected and characterized by chemical analysis, scanning electron microscopy, and x-ray diffraction as reported below. Chemical analyses on vacuum-dried samples yielded about 67% Cu (66.5 to 69.5%), indicative of a composition predominantly CuS (theoretical 66.5% Cu) with some Cu₂S.

The autoclave experiments confirmed the anticipated low solubility and rapid formation kinetics of copper sulfide under geothermal steam conditions. The major unexpected result was the pronounced tendency of the precipitate formed under these conditions to aggregate and, consequently, to settle rapidly. This is a very favorable characteristic from a process standpoint.

(b) H₂S Removal by ZnSO₄ Solution

As discussed above, ZnSO₄ is a reasonable candidate precipitant for H₂S at geothermal steam temperatures, provided that the pH of the scrubber solution is not allowed to drop below about 3. Preliminary experiments entailing sparging steam with H₂S through a ZnSO₄ solution contained in a 2-liter pressure reactor confirmed that some ZnS formed, but experimental difficulties precluded quantitative results. A third reactor run was successful and gave the following information:

Steam Composition

Steam line temperature 368°F
Corresponding steam pressure 154 psig
Average steam flow rate 6.2 lb/hr (2.82 kg/hr)
Average H₂S/N₂ flow rate 0.50 l/min (70°F, 1 atm)

H₂S flow rate: $0.40 \times 60 \times 0.066 = 1.58$ l/hr (70°F, 1 atm)
@ 0.701 l/g = 2.26 g/hr

∴ Concentration of H₂S in steam = 800 ppm (by weight)

Reaction Conditions (2-hr Run)

Reactor pressure 144 psig
Reactor temperature 352°F (thermowell)
Nominal initial solution volume, 1 l
Nominal initial Zn²⁺ concentration, 5 g/l

Solution Material Balance

	<u>Initial</u>	<u>Final</u>
Volume, l	0.990	1.045
Zn ²⁺ concentration, g/l	4.82	0.97
pH	4.72	1.71
Titrateable H ₂ SO ₄ , mol/l	-	0.0255
Zn ²⁺ , mol/l	0.0737	0.0148
Total SO ₄ ²⁻ , mol/l	0.0756	0.0656

Zn and S Material Balance

Weight of ZnS ppt collected (washed and dried) = 5.232g*
Weight of contained Zn at 67.1% = 3.51g
Weight of Zn removed from solution (by anal.) = 3.76g

Total H₂S sparged through solution = 4.52g
Weight Zn equivalent to total H₂S = 8.67g
Average H₂S removal efficiency = 52%

* Recovery of ZnS not entirely quantitative - see text.

The indicated average H₂S removal efficiency of 52% over the 2-hr duration of sparging requires interpretation. It will be recalled that H₂S removal by CuSO₄ under similar conditions was virtually quantitative. Efficiency of H₂S removal was undoubtedly high in the ZnSO₄ initially, before the pH was lowered by the reaction $\text{Zn}^{2+} + \text{H}_2\text{S} \rightarrow \text{ZnS} + 2\text{H}^+$. It is reasonable to consider that H₂S absorption and precipitation ceased when the pH achieved a sufficiently low value that the rate of the back reaction (ZnS dissolution) became equal to that of the forward reaction. Stated in another way, the final slurry containing ZnS, 0.015 mol/l Zn²⁺ and 0.026 mol/l H₂SO₄ at about 360°F was in equilibrium with steam containing 800 ppm, or 2.35×10^{-3} atm H₂S. This interpretation is consistent with the ZnS solubility curve of Figure 4.

It should also be remarked that substantial corrosion of the reactor interior was encountered, particularly on the bottom below the sparge tube, where the 316 stainless steel would have been contacted directly by the H₂S-rich steam. Reactor interior parts had acquired a tenacious, black, glossy film - presumably a sulfide reaction product of the stainless steel. Exposed parts above the solution line were coated with a uniform, thin layer of finely divided ZnS, suggesting that entrainment had occurred. The same conclusion is reached by noting the decrease in total sulfate: 0.075 mol → 0.069 mol.

The substantial introduction of soluble corrosion products (Fe, Cr, Ni) rendered the initially colorless solution a deep blue-violet. However, end point interference in the EDTA titration for Zn²⁺ could be masked by cyanide addition. The introduction of extraneous cations through corrosion of the reactor can account for the discrepancy between [H₂SO₄] + [Zn²⁺] and [SO₄²⁻] in the final solution.

To sum up the comparison of Zn²⁺ and Cu²⁺ as precipitants for H₂S under geothermal steam scrubbing conditions: Zinc is cheaper than copper, and its sulfide chemistry is simpler (essentially, only ZnS). But, the solubility of ZnS is some four orders of magnitude greater than that of CuS, so that a higher pH must be maintained, and Zn²⁺, unlike Cu²⁺, does

not offset the reducing tendency of H_2S , which can cause activation of stainless steel.

3. Packed and Trayed Column Runs

(a) Scope of Test Program

Five test series were carried out on the 2" diameter laboratory scrubbing column fitted with a variety of internals, as follows, to determine mass transfer efficiencies for hydrogen sulfide removal.

- Small ceramic saddles
- Larger, open, high-efficiency Flexirings
- Counterflow sieve trays
- Shower trays
- Sieve tray with downcomer

(b) Packed Tower Scrubbing Tests

The first continuous scrubbing tests were carried out with the column packed with four feet of 1/4" wide x 5/8" ceramic saddles. The small size was chosen to maintain a high ratio of column-to-packing diameter, a condition required to ensure proper liquid distribution and good mass transfer. A packing support plate with 50% open area was used. Because of the high packing factor associated with the small size, the expected maximum steam flow rate was of the order of 30 pph (see analysis in Appendix A).

Initial tests were run at 25 pounds per hour (pph) steam, or 80% of anticipated flooding. Hydrogen sulfide removal was virtually quantitative in that no odor of H_2S could be detected in the condensate from the scrubber. However, after approximately 1/2 to 1 hour of operation, the liquid level in the sump decreased, and scrubbing liquid was primed over into the condensate, signifying that the column had flooded.

When column flooding occurred, steam and scrubbing liquid flows were stopped so that the liquid level was restored in the sump, when operations were resumed. Flooding generally occurred again in a short time after H_2S was readmitted. Again, prior to flooding, no odor of H_2S could be detected in the condensate. Flows were again interrupted to permit liquid to drain from the column and then resumed. Although stable

operation (i.e., without flooding) was possible while recirculating a scrubbing solution (slurry) through the column against steam with no H_2S , operation was possible for only short periods when scrubbing H_2S with a column filled with small ceramic saddles.

The packing support plate and packing were removed for inspection following the tests. The packing, especially the bottom 6", and packing support plate were found to be fouled with accumulated precipitate, undoubtedly constricting liquid passage. While the bulk of the solids could be removed by light washing, the residues were sufficiently bulky and tenacious to prevent normal operation of the column, except for short periods, with the packing employed. Accordingly, the small ceramic packing was removed and replaced with three feet of 5/8" stainless steel Flexirings which are much more open (void volume = 92%) and have good hydraulic characteristics (packing factor = 78). The additional foot of open volume above the packing was a provision for greater liquid capacity in the event of column flooding.

Since the ratio of column-to-packing diameter with the Flexirings was lower by a factor of three than is desirable to obtain good hydraulic and mass transfer performance, a series of steam-water tests was run. The test objective was to confirm established hydraulic correlations for clean systems and validate subsequent mass transfer tests: if system hydraulics were proper, it would be likely that mass transfer, which is a function of hydraulics, would also be proper. The steam-water tests on clean packing confirmed the normal hydraulic behavior of the packing and column configuration, in that flooding occurred at the expected velocities, as shown in Figure 10. The mass transfer results from this test series, along with $k_g a_1$'s calculated using existing correlations (18,19) at the test operating conditions, are summarized in Table 8.

Hydrogen sulfide removal was again near quantitative, outlet concentrations being so close to the limit of detection as to cause problems in analysis. The J_d factor was calculated from a correlation based on test data for spheres, with 5/8" used as the characteristic diameter for the rings. The estimates of interfacial area are based on data from

L = LIQUID RATE, LBS./SEC., SQ. FT.
 G = GAS RATE, LBS./SEC., SQ. FT.
 ρ_L = LIQUID DENSITY, LBS./CU. FT.
 ρ_G = GAS DENSITY, LBS./CU. FT.
 F = PACKING FACTOR
 μ = VISCOSITY OF LIQUID, CENTIPOISE
 g_c = GRAVITATIONAL CONSTANT = 32.2

Run 506-3 60 pph Steam, 300 pph Water, 140 psig

Run 506-4 80 pph Steam, 100 pph Water, 125 psig

Packing Factor = 87-83, Viscosity = 0.16 cp

Fig. 10: Flooding velocities for countercurrent steam and water flows.
Column packing: 3 ft of 5/8" Flexirings.

Table 8

Experimental and Calculated Mass Transfer Coefficients
5/8" Flexirings

<u>Test No. (Run 507)</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>5</u>
Steam Flow Rate, pph	21.3	20.8	11.5	41.0
Scrubbing Liquid Flow Rate, pph	80	40	40	40
System Pressure/Temp., psig/°F	151/366	151/366	155/368	155/368
Copper Concentration, g/l	1.98	3.08	2.21	~2
pH	1.92	1.55	1.51	~1.4
Inlet H ₂ S Concentration, ppm	203	208	376	117
Outlet H ₂ S Concentration, ppm	<0.2	<0.2	<0.2	~1.2
Number of Transfer Units ⁽¹⁾	>6.9	>6.9	>7.5	~4.6
Height of a Transfer Unit, ft.	<0.43	<0.43	<0.40	~0.65
$k_g a_1$, mol/hr ft ³ atm	>10.5	>10.2	>5.9	~13.0
Gas Reynolds Number	1310	1280	710	2530
J_d Factor ⁽²⁾	0.052	0.053	0.067	0.040
k_g , mol/hr ft ² atm	0.198	0.195	0.134	0.284
a_1/a_{1w} ⁽³⁾	0.82	0.79	0.79	0.79
a_1/p ⁽⁴⁾	0.12	0.10	0.10	0.11
Calculated $k_g a_1$, mol/hr ft ³ atm	2.5	2.1	1.4	3.3
Experimental/Calculated $k_g a_1$	>4.2	>4.9	>4.2	~3.9

(1) $N = \ln (Y^o/Y^e)$

(2) $J_d = (k_g \pi / G) (N_{sc})^{2/3}$

(3) Ratio of interfacial area for this system to that for water at the same hydraulic conditions.

(4) Ratio of interfacial area to total packing area.

"clean," nonfoaming systems and are probably low in this case, since some degree of surface activity is to be expected due to the presence of finely divided sulfides. However, while there is some uncertainty built into the calculation of $k_g a_1$ for Flexirings using this approach, it is unlikely that the error (principally in the calculation of a_1/a_p) could be greater than a factor of two or three. Furthermore, since measured values exceed calculated ones by four to five times, it may be concluded with a high degree of confidence that mass transfer rates in this system are limited by gas phase resistance within the range of compositions and hydraulics tested.

As was the case with the lower void volume ceramic packing, however, stable operation could only be maintained for relatively short periods before flooding occurred. Since post-run inspections showed the packing to be essentially clean and free of accumulated solids, and clean steam hydraulics were as expected, it must be concluded that the flooding phenomenon is associated in the first instance with the removal of H_2S within the column -- flooding did not occur when "scrubbing" H_2S -free steam with recycled $CuSO_4/CuS$ slurry.

The flooding may arise if the precipitated sulfides influence interfacial tension in the system such as to lead to formation of a low density froth or foam. With small-sized internals, bubble sizes may be of the order of the packing size and, moving as solid bodies, will prevent free liquid passage. The postulated high surface area would also be consistent with the high values calculated for $k_g a_1$. The froth/foaming hypothesis can be tested in runs on a column of larger diameter equipped with sight glasses, where larger packing sizes can be used.

(c) Trayed Tower Scrubbing Tests

The first test series, with column packing, showed that quantitative H_2S removals are possible with packing if operability problems can be overcome. Accordingly, the packing was replaced with an assembly of counterflow sieve trays, a design known to be effective in resisting fouling due to deposition of solids on tray and hole surfaces. The tray cartridge consisted of five, 16-gage type 304 stainless steel trays at

12-inch intervals. Each tray contained 15 holes, 3/16-inch in diameter, countersunk for deburring. Operating conditions and results for two runs (330 and 414) are summarized in Table 9.

After the system had been brought to temperature, as determined by maintenance of a steady liquid level (condensate) in the column sump, high strength copper sulfate solution (40 g/l Cu^{2+}) was injected to obtain the target concentration of cupric ion, and H_2S at the proper rate was injected into the inlet steam. Occurrence of finely-divided dark precipitate was noted immediately (as with the previously used ceramic packing), along with the odor of H_2S in the vent/condensate steam. Copper sulfate was added intermittently to the system to make up for copper depletion due to precipitation.

Over the course of the run, H_2S removal efficiency was of the order of 40%, with tray efficiencies of the order of 10%, rather lower than had been anticipated.

During the run periods, operations were smooth and conditions changed little. Steam condensate was clear, with no soluble copper detected (<0.1 ppm). After about 3-1/2 hrs of operation, however, a quantity of scrubbing slurry primed over into the condensate, and the runs were terminated. Post-run inspection revealed, in addition to a small but significant (~5 cc) amount of loose, agglomerated precipitate, one or more copper sulfide balls, each about 1 cm in diameter, on the top tray. The balls were nearly spherical, relatively hard, and had an apparent density of about 2 g/cc (pure, fully dense CuS is 4.5 g/cc). Significantly lesser amounts of solids and no balls were found on the lower trays. Staining on the tray support rods indicated that froth heights on the lower trays had been about two inches, but that froth heights on the top tray were at least eight inches. There was evidence of splashing or entrainment even higher up.

It was postulated that, for the hydraulics and tray operating conditions resulting from this tray geometry and flow rates, most of the mass transfer was occurring on the top tray. Agglomeration resulted in the formation of large particles from fines suspended on the froth, which

Table 9

Tray Efficiencies for Counterflow Sieve Trays

Run No.	330(1)	414(1)	415(2)	415(2)
Sample No.	-	-	2	3
Time Into Run, min	180	150	90	120
Steam Flow Rate, pph	47	41	37	37
Scrubbing Liquid Rate, pph	85	49	85	134
System Pressure/Temp., psig/°F	138/360	138/360	140/360	140/360
Column Vapor F Factor	1.0	0.87	0.78	0.78
L/G	1.8	1.2	2.3	3.6
Copper Concentration, g/l	0.6	3.8	1.4	1.23
Inlet H ₂ S Conc., ppm	260	250	280	280
Outlet H ₂ S Conc., ppm	151	153	78.4	14
Number of Transfer Units	0.54	0.49	1.27	3
Tray Efficiency, %	10	9	17	35

(1) Five, 15% area trays.

(2) Seven, 50% area trays.

particles would at some point be prevented from passing through the holes. Since the trays had no downcomers, the agglomerated solids were retained.

The top tray was removed and eight peripheral holes were drilled out to 5/16" diameter, increasing the open area to 26%, with the object of passing larger sized solids. No other trays were altered. The test was repeated, with essentially the same results as for runs 330 and 414. These results are anomalous in the sense that highest mass transfer rates should occur on the bottom tray, where driving forces are normally highest, and solids should accumulate there and not on the feed tray.

The column was cleaned and a steam-water test was run at atmospheric pressure with the column top removed to permit inspection of the tray action just below the feed point. The steam flow rate was set at 20 gph, which simulated the F factor obtained at 60 gph at 150 psig. It was observed that tray action was not good. No stable froth was obtained; rather, a significant "jetting" and entrainment was observed. The major portion of liquid-vapor contact was confined to the inch or so above the tray surface.

Since the design conditions are well within the range where stable operation would be expected, at least for clean systems, the reason for the anomalous behavior is not fully understood. Possibly, it is a consequence of the relatively small number of holes on the 2" diameter trays (a 6" tray would have 10 times as many). In any case, the observed and inferred low froth heights are consistent with the relatively poor H₂S removal efficiency as compared with the packed column runs, where removal was quantitative prior to the occurrence of flooding.

Although still limited in terms of operability, the sieve trays did not foul, an encouraging fact in view of the very poor performance of the ceramic packing. The 15% open-area tray cartridges were then replaced with one consisting of seven counterflow trays on 8" spacing, the trays containing 50% open area as 5/32" holes. It was hoped that these trays would have higher capacity, a more stable operating range, and pass solids more efficiently. Hole velocities, however, would be lower than are usually used. Process conditions and scrubbing efficiencies are also

summarized in Table 9 (Run 415). The operating conditions differ from those of runs 330 and 414, mainly with respect to the liquid-to-gas flow ratios, which were 2.3 to 3.6 in run 415 vs. 1.2 to 1.8 in runs 330 and 414.

It was determined immediately, by the odor of the scrubbed condensate, that H_2S removal was more effective in run 415 than in runs 330 and 414. This observation was confirmed by the increased H_2S removal and tray efficiencies. The significantly improved H_2S scrubbing efficiency was apparently due to improved tray action which, in turn, may have been a function of both lower vapor velocities (reduced "jetting") and higher L/G ratios (hence, higher froth heights).

As was the case for runs 330 and 414, operations were smooth, and conditions changed little during the run. However, the L/G's and velocities reported for run 415 represent a close approach to the limits of stable operation for 50% open-area trays at 8" spacing; attempts to increase either resulted in flooding. This, too, is anomalous, since at the low hole F-factors run, froth heights in a clean system should have been very low, and maximum allowable velocities much higher.

The column was disassembled and inspected at the termination of the run. Again, a significant amount of loose, agglomerated precipitates were found on the trays, but no evidence of hole closure was observed. For these trays, however, most of the solids accumulation was on the lower trays. In addition, three 1+ cm balls and an irregular large fragment of copper sulfide were found on the bottom, and one ball and fragments were found on the second tray. This profile of solids accumulation is consistent with the expected scrubbing rate profile in the column, since higher concentrations should lead to more rapid mass transfer on the lower trays. The extent of staining of the tray support posts and tray undersides suggests that froth heights were significantly higher, by 4-6", for run 415 than for runs 330 and 414, probably as a consequence of the higher L/G ratio. This is consistent with the more effective H_2S removal obtained.

The two key results of testing on counterflow sieve trays are:

- Tray hydraulics in this system are not related to operating variables in the same way as for "clean" systems. The system is apparently surface active.
- The trays proper are resistant to fouling, and acceptable operability will require mainly an improved design for passing solids through or across the tray.

The tests with the 50% area counterflow sieve tray cartridge demonstrated that high hydrogen sulfide removal efficiencies are possible if hydraulic conditions are controlled, but that operability problems may be incurred with this tray style. Consequently, a shower tray cartridge, consisting of 60 segmented discs on 3/4" spacing was installed to test a design which would be more effective in passing solids. Thirty percent of the total column area was removed in the segments, and the spacing chosen to balance axial and radial flow areas. Test results are summarized in Table 10.

Very high degrees of removal were obtained with shower trays, and the tray efficiencies, although low, were of the order expected for this type of device (which does not provide good liquid-gas contact). The allowable vapor velocities, however, were quite low - less than half the desirable range for a commercial installation. Attempts to increase the velocities resulted in flooding the column at the given liquid scrubbing rates. Increases in steam rate, obtained at the expense of decreasing liquid flow rate, resulted in noticeable decreases in H₂S scrubbing efficiency, as judged by the odor of the condensate.

At the conclusion of the test series, the shower-tray cartridge was withdrawn; no evidence of solids accumulation was noted. Thus, the solids accumulation problem which caused operating difficulties with the counterflow sieve trays and packing can evidently be eliminated by use of an open style of internals, although relatively low efficiencies must then be anticipated. It is possible that, as was the case with the packing, the relatively small clearances and surface active nature of the freshly precipitated solids may have contributed to the unusually low

Table 10

Tray Efficiencies for Shower Trays

Run No.	511	511
Sample No.	2	4
Time Into Run, min	20	115
Steam Flow Rate, pph	21.3	40.8
Scrubbing Liquid Rate, pph	80	60
System Pressure/Temp., psig/°F	147/364	147/364
Column Vapor F Factor	0.42	0.82
L/G	3.76	1.47
Copper Concentration, g/l	2.36	2.05
pH	1.79	1.66
Inlet H ₂ S Concentration, ppm	197	227
Outlet H ₂ S Concentration, ppm	17.4	5.5
Number of Transfer Units	2.43	3.73
Tray Efficiency, %	4.0	6.0

allowable velocities. This supposition can be verified by operation in a column of larger diameter or by use of a tray deck having larger intervals between trays.

Tests on the shower tray internals demonstrated that operability problems can be avoided if the solids are provided with an adequate opportunity to pass downward from tray to tray, without being continuously suspended by vapors passing at a velocity sufficient to levitate the solids. Since the tests on the packing had shown high k_{ga1} 's, and since counterflow sieve trays were found acceptable prior to the onset of flooding problems, a single sieve tray equipped with a central downcomer was installed in the column. The downcomer pipe was liquid-sealed in the column sump and projected 1" above the tray deck. The downcomer diameter was 1" and tray active area was 37%. Test results on this tray, runs 513-524, are summarized in Table 11.

Performance of this tray was excellent throughout all tests. No reduction in capacity was noted, no tendency for solids accumulation on the tray deck, in the holes, or in the downcomer was noted, and hydrogen sulfide removal efficiencies were excellent. Relatively high liquid to vapor rates were run in order to obtain good tray action, in view of the relatively low hole velocities obtained for the steam rates run. During initial runs at higher removal rates or during runs of long duration, operating difficulties arose due to solids plugging the circulating pump suction lines. Piping changes were made to alleviate this problem which resulted in obtaining some classification of solids in the column. No effect of this classification on mass transfer efficiency could be detected.

Run 513 was carried out at the vapor velocities previously observed to be at the level of flooding for the shower trays and, when operation at higher steam rates and still higher L/G 's was obtained without flooding, subsequent tests were carried out at higher velocities. The aforementioned piping changes were made following run 514, and it is apparent from the data of Table 11 that no significant change in removal efficiency occurred.

Table 11

Tray Efficiencies for a 37% Open-Area Sieve Tray with Downcomer

Run No.	513	513	513	513	514	514	517	517
Sample No.	1	2	3	4	2	3	1	2
Time into Run, min	40	105	145	265	15	60	25	85
Steam Flow Rate, pph	41.3	40.9	41.3	38.1	59.3	65.7	52.0	55.8
Scrubbing Liquid Rate, pph	285	285	285	285	285	285	285	285
System Pressure/Temp., psig/°F	157/360	175/360	157/360	157/360	146/360	146/360	155/360	157/369
Column Vapor F Factor L/G	0.81 6.9	0.80 7.0	0.81 6.9	0.75 7.5	1.19 4.8	1.32 4.3	1.02 5.5	1.08 5.1
Copper Concentration, g/l	1.73	1.72	2.28	2.50	2.02	1.76	2.83	3.31
pH	1.74	1.5	1.48	1.08	1.81	~1.4	1.67	1.49
Inlet H ₂ S Conc., ppm	217	211	224	243	223	210	266	248
Outlet H ₂ S Conc., ppm	46.2	44.3	47.3	77.3	24.1	65.0	11.4	88.2
Number of Transfer Units	1.55	1.56	1.55	1.15	2.23	1.17	3.15	1.03
Tray Efficiency, %	78.7	79.0	78.9	68.2	89.2	69.1	95.7	64.4

Table 11
(Continued)

Run No.	518	518	518	518	518	519(1)	519(1)	519(1)	519(1)
Sample No.	2	3	4	5	6	1	2	3	4
Time into Run, min	40	100	160	220	275	25	95	145	205
Steam Flow Rate, pph	56.9	57.9	57.0	53.1	58.3	57.9	58.5	57.2	57.6
Scrubbing Liquid Rate, pph	285	285	285	285	285	285	285	285	285
System Pressure/Temp., psig/°F	151/366	152/366	158/368	155/367	156/367	158/368	156/368	155/367	152/366
Column Vapor F Factor	1.12	1.14	1.11	1.04	1.11	1.12	1.14	1.12	1.13
L/G	5.0	4.9	5.0	5.4	4.9	4.9	4.9	5.0	5.0
Copper Concentration, g/l	1.60	1.85	2.72	1.78	1.89	1.96	0.72	2.36	1.99
pH	1.32	1.15	1.02	0.92	1.0	1.8	1.26	1.28	1.27
Inlet H ₂ S Conc., ppm	243	239	242	260	237	239	236	242	240
Outlet H ₂ S Conc., ppm	24.8	59.2	67.6	125	129	14.6	15.3	20.3	22.0
Number of Transfer Units	2.28	1.40	1.28	0.74	0.61	2.80	2.74	2.47	2.39
Tray Efficiency, %	89.8	75.2	72.1	52.0	45.0	93.9	93.5	91.6	90.8

(1) Buffered with (NH₄)₂SO₄.

Table 11
(Continued)

Run No.	520(1)	520(1)	520(1)	520(1)	520(1)	524	524	524	524(2)	524(2)
Sample No.	1	2	3	4	5	1	2	3	4	6
Time into Run, min	35	95	155	215	245	40	100	160	210	370
Steam Flow Rate, pph	58.5	58.6	58.6	57.1	58.0	57.1	57.9	57.0	58.2	54.8
Scrubbing Liquid Rate, pph	285	285	285	285	285	285	285	285	430	430
System Press./Temp, psig/°F	156/366	156/367	156/368	158/368	153/366	158/367	148/365	151/366	154/367	156/368
70 Column Vapor F Factor	1.15	1.14	1.14	1.11	1.14	1.11	1.15	1.12	1.14	1.07
L/G	4.9	4.9	4.9	5.0	4.9	5.0	4.9	5.0	7.4	7.8
Copper Concentration, g/l	2.17	2.27	2.06	2.11	1.83	2.21	2.14	3.37	3.93	3.03
pH	1.0	0.94	0.93	0.94	0.92	1.53	1.19	1.16	1.18	1.01
Inlet H ₂ S Conc., ppm	236	236	236	242	238	242	239	242	530	563
Outlet H ₂ S Conc., ppm	87.6	128	134	123	138	42.8	65.4	62.5	65.7	225
Number of Transfer Units	0.99	0.61	0.57	0.67	0.55	1.73	1.30	1.36	2.09	0.92
Tray Efficiency, %	62.9	46.0	43.0	49.0	42.0	82.3	72.6	74.2	87.6	60.1

(1) H₂SO₄ added to system prior to run to reduce pH.

(2) Run for production of solids.

The results of runs 513, 514, and 517 suggest, however, that efficiencies were decreasing throughout the course of the run. Accordingly, a run of long duration, 518, was scheduled to verify this behavior. The decrease in scrubbing efficiency with time was confirmed as shown in Figure 11. Since, nominally, operating conditions had not varied and the nature of the solids was observed, qualitatively, to be unchanged, it was postulated that the observed change in efficiency was associated with the decreasing pH of the slurry liquid. This decrease in pH resulted from continued formation of acid during hydrogen sulfide removal in the column.

The effect of pH on scrubbing efficiency was further investigated in runs 519 and 520 by buffering the system with ammonium sulfate and by initiating the run at low pH (by extra addition of acid), respectively. The relation between scrubbing efficiency and scrub solution pH during seven runs is shown graphically in Figure 12. Within the general scatter of the data, there is no significant decrease in efficiency from pH 2 to approximately pH 1.2. At pH's <1, however, a significant decrease in efficiency is apparent. No effect of cupric ion concentration on scrubbing efficiency was evident (Figure 13). On the other hand, even at the lowest concentration run, 0.7 g/l Cu^{++} , the calculated equilibrium H_2S pressure above solutions at $\text{pH} \geq 1$ is still essentially zero, so that its mass transfer driving force would not have been decreased, as shown in Table 12. Thus, the lack of correlations between H_2S removal efficiency and copper content in this range is not surprising.

The reason for the decrease in efficiency is not apparent in the absence of direct observation of tray hydraulics and quantitative characterization of the precipitated solids in the appropriate size range but could be associated with the effects of

- reduced k_g 's
- decreased partial pressure driving forces
- decreased interfacial areas, a_i , per unit volume.

While the possibility that decreased pH results in a shift in mechanism which results in a rate controlling step occurring in the liquid phase, no such phenomenon has been reported for similar systems under these

Fig. 11: Variation of H_2S removal efficiency with time during operation of a 2-inch scrubber having a single sieve tray with downcomer.

Fig. 12: Variation of H_2S removal efficiency with scrub solution pH.

Fig. 13: Variation of H_2S removal efficiency with scrub solution copper content.

Table 12
Effect of pH on Mass Transfer Driving Force

<u>Copper Content</u> <u>g/l Cu⁺⁺</u>	<u>pH</u>	<u>Equilibrium⁽¹⁾ H₂S</u> <u>Pressure, atm</u>	<u>H₂S Pressure in⁽²⁾</u> <u>Steam, atm</u>	<u>Partial Pressure</u> <u>Driving Force, atm</u>
0.1	2.0	2.88×10^{-11}	1.059×10^{-5}	1.059×10^{-5}
0.1	1.6	1.82×10^{-10}	1.059×10^{-5}	1.059×10^{-5}
0.1	1.4	4.58×10^{-10}	1.059×10^{-5}	1.059×10^{-5}
0.1	1.2	1.15×10^{-9}	1.059×10^{-5}	1.059×10^{-5}
0.1	1.0	2.88×10^{-9}	1.059×10^{-5}	1.059×10^{-5}
0.1	0.8	7.26×10^{-9}	1.059×10^{-5}	1.058×10^{-5}
0.1	0.6	1.82×10^{-8}	1.059×10^{-5}	1.057×10^{-5}
0.1	0.4	4.58×10^{-8}	1.059×10^{-5}	1.054×10^{-5}

(1) Above the reaction $\text{CuSO}_{4(\text{aq})} + \text{H}_2\text{S}_{(\text{g})} \rightarrow \frac{1}{2} \text{Cu}_2\text{S} + \frac{1}{2} \text{S}_{(\text{l})}^{\circ} + \text{H}_2\text{SO}_{4(\text{aq})}$

(2) After 99% removal from H₂S initially present at 200 ppm in steam at 10 atm total pressure.

conditions. It can be shown (Table 12) that the effect of pH on partial pressure driving force is completely negligible even at high hydrogen sulfide removal efficiencies and low copper contents. Therefore, one is led to conclude that the probable effect of decreasing pH is to alter the surface active nature of the system, perhaps by affecting the rate or extent of flocculation of fines, and that there is a resulting decrease in the interfacial contact area per unit volume.

The results of the characterization of $k_g a_1$'s obtained with packed columns and the observation of relatively low flooding velocity also led to the conclusion that the system is surface active, and it would not be surprising that the activity is pH-dependent. However, it is also possible that the surface activity is a function of the particle size distribution, and since tests were of short duration, less than 6 hrs, and were run under conditions in which pH was continuously changing, it was not possible to determine whether the crystal size distribution had stabilized independent of the pH. Confirmation of this mechanism would require longer test runs in an open system with careful pH control.

It is also apparent that, while conventional internals are likely to be serviceable from an operability viewpoint and also effective for mass transfer in the system, existing correlations for hydraulics and efficiency will have to be revised in view of the surface active nature of the system in order to comprehend the effects of lowered froth density. Froth heights, pressure drop, tray spacings, and efficiencies may be expected to differ from those obtained in normal (nonfrothing) systems at operable liquid and gas velocities.

(d) Material Balance

The material balance for the test runs was established by measuring the copper depletion from beginning to end of the run, along with analytical determination of the solids copper content. This fixed the amount of sulfide sulfur removed from the steam by precipitation. This quantity could then be compared with the known hydrogen sulfide feed rate to give an estimate of H_2S removal efficiency. The removal efficiency was also directly measured at intervals of time by determination of hydrogen sulfide in the condensate.

The copper depletion was estimated by weighing the copper sulfate addition vessel at the beginning and end of the runs and subtracting the residual soluble copper in the sump at run termination. This procedure is subject to some uncertainty, in that spills and sampling removed copper from the system, and has the implicit assumption that no copper is lost to corrosion or by carryover as entrainment. In early runs, corrosion of non-stainless components removed significant copper from the system, but these losses were eliminated during later runs. No soluble copper was found in the condensate at any time (by Neocuproine photometric determinations with limit of detection less than 0.2 ppm), and the condensate pH's were always high, generally greater than 4.5, indicating very little carryover from the system.

The hydrogen sulfide addition rate was determined from the analyzed composition of the H_2S/N_2 gas mixture and the gas rotameter calibration. It was also checked by measuring the hydrogen sulfide rate passing through the system under operating conditions prior to copper sulfate addition. It is estimated that the combination of uncertainties in rotameter reading and analytical procedures restricted the accuracy of hydrogen sulfide rate determination to $\pm 5\%$. Since, in most runs, system steady-state was not reached, scrubbing efficiency changed, and it was necessary to average the H_2S removal over the run time to determine the total mass fed and removed. The material balance calculations are summarized in Table 13. The final pH's are those of the sump solution at the end of the run. Except for runs 519 and 520, in which ammonium sulfate and acid, respectively, were added, the initial solution pH's were approximately 2. The total solution volume includes the sump contents and water flushed through the system at the end of the run, and solution copper contents are the (diluted) concentration in this sample. The active volume of the sump and piping held at operating conditions during the course of the run was approximately 3 liters.

The precipitated solids were analyzed by determining solution compositions after digestion of the sulfides in $HNO_3/NaClO_3$. The reported figure is the average of the direct spectrophotometric and Neocuproine

Table 13

**Material Balances
CuSO₄ Scrubbing Tests**

Run No.	Run Duration Min.	Final pH	Average % H ₂ S Removal Eff.	Total Sol. Vol., l	Sol. Copper Conc., g/l	Total Cu Fed to System g	Wt. Cu Pptd., g	Pptd. Solids Analysis		Wt. S ⁻⁻⁻ in Solids g	Total H ₂ S Fed to System g	Wt. S ⁻⁻⁻ Scrubbed g	S ⁻⁻⁻ Oxidation to S ⁰ /SO ₄ ⁻⁻⁻ g	% of S Scrubbed
								w/o Cu	Cu _n S					
513	265	1.08	76	3.5	2.5	55.6	46.7	70.7	Cu _{1.22} S	19.4	18.9	13.6	-5.8	-43
514	60	1.4	79	5.1	1.76	23.0	14.0	75.3	Cu _{1.54} S	4.6	7.7	5.7	1.1	19
517	85	1.49	81	3.5	3.22	31.6	20.3	76.6	Cu _{1.65} S	6.2	9.4	7.2	1.0	14
518	275	1.0	69	3.1	2.27	64.7	57.8	74.3	Cu _{1.46} S	20.0	30.0	19.5	-0.5	-3
518R	275	1.0	69	3.1	2.27	64.7	57.8	76.7	Cu _{1.66} S	17.6	30.0	19.5	1.9	10
519	205	1.27	93	5.5	2.13	68.2	56.5	75.9	Cu _{1.59} S	17.9	23.0	20.2	2.3	11
520	245	0.92	50	4.0	1.95	48.4	40.6	72.1	Cu _{1.30} S	15.7	26.1	12.4	-3.3	-27
524	370	1.01	80	5.5	2.88	135.5	119.7	72.0	Cu _{1.30} S	46.5	63.3	47.4	0.9	2
Totals							355.9		Cu _{1.39} S	129.1		126.0	-3.1	-2.5

methods. The results of these analyses agreed within 2% (absolute error), with no systematic error detected. These solids analyses were used with the known copper depletion to determine the mass of sulfides scrubbed to precipitated solids. This figure could then be compared with the amount of hydrogen sulfide recovered from that fed, knowing the average removal efficiency and total flow rate.

While in early short-term scrubbing tests and in batch precipitation tests the principal product formed was CuS , in later tests lower sulfides were formed in significant amounts, with as much as two-thirds Cu_2S being found in some runs. No relationship between the extent of Cu_2S formation and operating conditions is apparent. However, the computed stoichiometry is very sensitive to the solids analysis, since the change in copper content from CuS to Cu_2S is relatively small and analytical uncertainties are of the order of 10% of the difference. The impact of analytical error is seen in run 518 (Table 13), where duplicate analyses were carried out on the solids sample. In spite of analytical uncertainties, however, it is clear that a significant amount of Cu_2S is formed, either directly or as a product of CuS alteration, under the process conditions of residence time, temperature, and pH of these tests.

In order to account for the formation of lower sulfides starting with Cu^{2+} , some of the hydrogen sulfide must ultimately have been oxidized to elemental sulfur or sulfate. Therefore, one would expect a systematic "error" in the material balance, with some sulfide unaccounted for. Excluding runs 513 and 520, it is found that 6g of 100g fed are unaccounted for. While this is within the range of inherent error in calculational procedures and analytical techniques, it is felt that this is in fact significant and reflective of sulfide oxidation.

The extent of sulfide oxidation might be determined by analysis of the condensate (and solids) for elemental sulfur and a hydrogen ion balance on the sump solution. It was not possible to establish consistent material balances by these techniques for these experiments because of analytical difficulties and the small masses of sulfide involved. Longer term tests at higher rates should, however, permit reasonable closure of the total balance and determination of the extent of sulfide oxidation.

Some possible reactions of hydrogen sulfide, cupric sulfide, and elemental sulfur under scrubber conditions are summarized in Table 14. Figures 13 and 14 show the relationship between product stoichiometry, acid formation, and cupric ion to hydrogen sulfide ratio required for scrubbing as a function of the extent of oxidation of H_2S to elemental sulfur from these reaction possibilities. A large range of possibilities exists depending upon the kinetics as influenced by operating conditions. The maximum extent of formation of elemental sulfur is one-half of the hydrogen sulfide removed for the formation of pure cuprous sulfide, and the regeneration of 2 moles of hydrogen ion per mole of H_2S scrubbed. Where there is no oxidation to elemental sulfur, the acidity generated ranges from 2 moles per mole for the formation of cupric sulfide to 3.6 moles per mole for the formation of cuprous sulfide, where the extra mole of sulfide per mole of copper is oxidized fully to sulfate. While it did not prove possible to determine quantitatively the extent of oxidation to elemental sulfur during these runs, it is felt that very little sulfur did form, with the majority of the oxidized sulfide converted to sulfate. In some runs, the condensate from the system was slightly milky, suggesting that a small amount of sulfide had been oxidized to elemental sulfur which, in turn, was steam stripped from the system. In other runs, however, the condensate was sparkling clear and, since the sulfide solids produced contained some (at least 20%) cuprous sulfide, the extra sulfide must have been oxidized to sulfate.

The impact on overall process material balance is significant. For a solids product typified by the composition $Cu_{1.5}S$ and no elemental sulfur formation, the copper requirement per mole of sulfur removed is increased by one-third and the extent of acid formation by almost 50%. This will increase the regeneration requirements, since more copper will be in circulation per unit of H_2S removed. And, unless the steam NH_3 content is high, the purge rate will have to be increased to control acidity. Overall, total sulfate (acidity) formation will not necessarily increase (except for the leach/regeneration case with formation of S^0), but the column balance will be affected.

Table 14

Some Possible Reactions in H₂S Scrubbing by Copper Sulfate

Sulfide Precipitation Reaction

Sulfide Concentration/Oxidation Reactions

Sulfur Redox Reactions

Sulfide Oxidation Reactions

Notes: Reaction (4) = Reaction (5) + 4 x Reaction (2)
Reaction (3) = Reaction (7) + 5 x Reaction (1)
Reaction (3) = 1/2 x Reaction (6) + 5/2 x Reaction (2)

RELATION BETWEEN SULFIDE STOICHIOMETRY AND EXTENT OF
SULFUR OXIDATION AND ACID GENERATION

Fig. 13: Relation between sulfide stoichiometry and extent of sulfur oxidation and acid generation

RELATION BETWEEN SULFIDE STOICHIOMETRY AND EXTENT OF
SULFUR OXIDATION AND COPPER REQUIREMENT

Fig. 14: Relation between sulfide stoichiometry and extent of sulfur oxidation and copper requirement.

4. Characterization of the Precipitates

(a) Chemical and Mineralogical Composition

The precipitates produced by scrubbing H_2S from steam with $CuSO_4$ are essentially pure copper sulfide. Occasionally, as revealed by energy dispersive x-ray analyses (EDAX), employed in conjunction with scanning electron microscopy (SEM), minor contaminants were noted. When present, these contaminants were most often chromium, iron, aluminum and silicon (as illustration, see Figure 15). The presence of Cr and Fe could generally be traced to local severe corrosion of specific internal components of the scrubber, which were supposedly type 304 or 316 stainless steel, but of unauthenticated composition - some threaded rods employed as tray supports, for example. Part, at least, of the Al occurrence was derived from the pedestal on which the SEM samples were mounted, but some may have originated in wear of the alumina ceramic plungers (slurry recirculation pump). The small, pervasive silicon occurrence may have been derived from the pump packing.

As noted in previous sections, no readily detectable quantities of elemental sulfur showed up in the precipitates. Figure 17 illustrates the good registry typically obtained when precipitates were separately mapped for Cu and S. The field of view is the same as that of the photomicrograph shown in Figure 16; Cr and Fe were essentially at background levels in this and most instances. Some local variability in the copper-to-sulfur ratio was found by EDAX. In one precipitate examined, Cu:S varied by a factor of 2.5 over the given field of view; normally, however, the variation did not exceed a factor of 1.4 and, sometimes, precipitates appeared to have a microscopically uniform composition.

Considerable variation in average copper percentage was also found from run to run. In general, shorter residence time of precipitate in the reactor tended to give a composition closer to CuS (66.46% Cu) than to Cu_2S (79.85% Cu). For example, quantitative copper analysis of a precipitate produced in the autoclave reactor (maximum residence time, 1/2 hr), by the Neocuproine method outlined above, gave 69.5% Cu.

Fig. 15: Elemental analysis (energy dispersive x-ray) of copper sulfide precipitate.

Fig. 16: SEM photograph of copper sulfide precipitate (Run No. 330). Magnification 500X.

Copper

Sulfur

Fig. 17: Elemental mapping (x-ray photons) of copper sulfide precipitate. Same field of view as for Fig. 16.

A comparison analysis by an outside laboratory using an entirely different procedure* gave 66.5% Cu and 33.1% S, i.e., an atomic ratio of Cu:S = 1.03. The analytical accuracy is thought to be comparable by the two procedures and of the order of $\pm 2\%$ overall. Accordingly, the two results are probably substantially the same, within the analytical accuracy and within the variability in real composition from small sample to small sample.

Average precipitate copper analyses for the major scrubber runs ranged from 70% to 77% (Table 13 above). By comparison, the end members of the Cu-S series are: CuS, 66.46% Cu and Cu₂S, 79.85% Cu by weight. The observed alteration, or enrichment, of CuS to Cu_{1+x}S is consistent with the known chemical and geochemical behavior of CuS in contact with CuSO₄(aq), as discussed above. It is also in agreement with mineralogical observations made on copper sulfide solids present in the preliminary corrosion screening tests. There, the simulated scrubber slurry contained commercial (synthetic) reagent CuS, which acquired an alteration rim of Cu₂S as a result of prolonged contact with the corrosion test solution at test temperature.

Whereas the prime consideration with respect to composition of the solids formed in the scrubber is the percentages of their constituent elements, their mineralogy is also of some interest. This is so because of the clues afforded by knowledge of the minerals formed to the detailed mechanism of precipitation and subsequent alteration. Furthermore, in company with the existence of an extended series of compounds and solid solutions in the Cu-S field, one might anticipate a spectrum of reactivities and sulfur product mixes in regeneration, particularly by pressure leaching. While it is convenient for material balance purposes (previous section, above) to consider the precipitates as being mixtures of covellite (CuS) and chalcocite (Cu₂S), neither phase need be stoichiometric, given the nonequilibrium conditions of formation. Further, additional phases are

*Fusion of the sample in a carbonate-borate flux, extraction of the CuSO₄ produced into aqueous solution, determination of Cu by atomic absorption and determination of sulfur as sulfate by a BaSO₄ method.

possible and are sometimes present in the precipitated solids.

The combination of fine ultimate particle size and nonstoichiometry made difficult the positive identification of mineral phases. Consequently, mineralogical analyses by x-ray diffraction and by optical petrography were not in complete agreement. However, some qualitative observations are worth recording.

Chalcocite-type sulfides ($\text{Cu}_{1.76}\text{S}$ - Cu_2S) are the predominant phases identifiable in four samples by optical methods: runs 304, 330, 504 and 513. X-ray diffraction analyses of the same samples indicated digenite ($\text{Cu}_{1.8}\text{S}$) and djurleite ($\text{Cu}_{1.96}\text{S}$) to be the most prominent of these. By contrast, covellite-like sulfide phases ($\text{Cu}_{1.1}\text{S}$ - $\text{Cu}_{1.4}\text{S}$) appeared to predominate in solids produced in the autoclave reactor (runs R-1 and R-2). Less than about 20 vol.% of a given sample consisted of coarse-grained ($>5\text{ }\mu\text{m}$) material. Most of the coarse-grained sulfides occurred as rinds, which may have formed on the walls of the scrubber; others appear to have formed by crystal growth from the slurry, away from the walls of the scrubber.

The fine-grained fraction of the precipitates showed varying degrees of aggregation, ranging from poorly consolidated clusters to well-compacted large balls (retained by a column sieve tray). One copper sulfide ball (from run 330) was examined in detail and found to possess a compact interior and highly porous exterior. The appearance in the copper sulfide precipitates of both covellite-like and chalcocite-like phases, with the latter predominating, is consistent with a growth mechanism whereby initially formed CuS is gradually replaced and cemented together by fine-grained chalcocite.

(b) Particle Size and Morphology

The typically bimodal distribution of particle size, as revealed by the petrographic and scanning electron microscope (Figure 16), was quantified for a few samples by Coulter Counter analysis. The size distribution shown in Figure 18 was produced by use of a 50 μm orifice. It confirms the presence of particles as large as 20-30 μm as well as, at the other extreme of size, submicron particles. Most of the large

Fig. 18: Particle size analysis of copper sulfide precipitate (Run No. 330, column sump sample).

copper sulfide particles were themselves aggregates of much smaller particles (Figure 19), although more compact and regular structures were occasionally observed (Figure 20).

The aggregates were rather tightly held together. For example, in the 2% NaCl test solution, with added nonionic dispersant, 10 mins of sonification produced a large population of minus 0.5 μ m particles, but a substantial population of particles persisted in the +0.5, -20 μ m size range. Simple drying (under vacuum, without heating) of precipitates resulted in relatively coarse agglomerates, in the range 0.2-0.5 mm.

5. Experimental Results - Liquid/Solid Separation

It was observed in all continuous scrubbing experiments that, while the ultimate particle size of the solids produced was quite small, the solids showed a remarkable tendency to aggregate and to settle rapidly under operating conditions. Large size particles, with a characteristic length of about 1 mm, appeared in slurry samples within ten minutes after initiating H₂S scrubbing, indicating that aggregation occurs even at relatively low volumetric solids densities. (While solids densities were low, less than 1 g/l, the number density of micron-sized particles would have been very high.) The particles observed at operating temperature and pressure within the column level gage often reached sizes over 1-2 mm; larger ones may have settled to the bottom of the sump or have been broken up in circulating through the pump. During runs of longer duration or when hydrogen sulfide was scrubbed at a high rate, operating problems were sometimes encountered with stoppage in the flow of scrub solution, due to blockage of the sump suction line with solids. Solids retained in the packing and on the trays tended to agglomerate and, in the case of counter-flow trays, to form discrete shapes of about 1 cm diameter.

It was observed in most cases that the solids in samples withdrawn from the system and flash-cooled to 100°C settled very rapidly, leaving a clear supernatant solution, as did solids flushed from the system after slow cooling at the end of a run. In some samples, solids which had flocculated hot showed some tendency toward loose consistency upon standing overnight and to settle at a somewhat lower rate than average. This

Fig. 19: High magnification (5000X) view of a typical larger copper sulfide particle.

Fig. 20: SEM photo of scrubber solids at high magnification (5000X) showing presence of occasionally observed more regular structures.

is a qualitative observation only, since settling rates were still high by normal standards and could not be associated with specific changes in column operating conditions.

Slurry samples withdrawn for copper analysis and control were routinely separated at the bench by use of filters with pore size as small as 0.1 μ . These dilute slurries showed no tendency to bind, filtered rapidly, washed well and produced a clear filtrate, although the dry cake showed a tendency to crack. Owing, presumably, to the large microporosity of the aggregates, the solids required more drying time than for average materials, particularly for thick beds. This would be disadvantageous were complete dewatering required. However, it is anticipated that the precipitates would be handled wet or as a slurry in an integrated process.

Qualitative liquid/solid separation rates were obtained in liter cylinder and 0.1 square foot leaf tests on material from run 514. Qualitatively, the solids were observed to settle in a "typical" manner, that is, neither rapidly nor slowly after cooling.

Standard liter-cylinder settling tests were carried out at room temperature. Some difficulty occurred in obtaining uniform suspensions at the initiation of the test because of the tendency toward rapid settling. Larger flocculated particles, characteristically greater than a millimeter in size, settled out completely in less than 2 minutes; the entire sample settled out completely in less than 1 hour. Settling velocity of the fines was observed to be of the order of 1 inch per minute. At the completion of the test, however, there was a significant concentration of very fine particles suspended in the cylinder, and the decantate was turbid. Also, the settled pulp density was quite low, of the order of 20%. It is expected that higher pulp densities will be achievable in ultimate-dilution tests, since most small samples of high solid density material tested could be made to compress significantly with slight raking by stirring rods.

Filtration tests were carried out on a 0.1 square foot test leaf using a low-velocity (Frazier rating 3.5) multifilament, calendered,

polypropylene medium. The medium showed a pressure drop of 10 inches vacuum at a filtration rate of 5 gal/min/sq. foot. Results of the filtration tests are summarized in Table 15.

The data did not show the linearity of pressure drop with flow rate and thickness that is expected for incompressible cakes. In fact, there is no good reason to believe that the cake is necessarily incompressible. On the other hand, the cake thickness was not great, and its determination was, accordingly, subject to error. In any case, the thicknesses were less than desirable for commercial filters, where cake removal could be a problem. Extrapolation of the data, assuming an incompressible cake, leads to a filtration rate of about 0.75 l/min, which translates to an unfactored rate of 120 gals/hr/sq. foot at 18" cake pressure drop, a very high rate. The corresponding solids loading of 12.5 lbs/hr/sq. foot is within the range measured on the low density slurries tested. With a 2 min form time, which may be longer than desirable for the rapidly settling slurry, it would be possible to filter slurries at up to 5% density at acceptable cake thicknesses.

At the conclusion of the filtration tests, the cake was washed and air dried and removed from the medium by flexing. The cake discharged easily on flexing to 1/8" radius, but did show some tendency to crack on drying, which might cause difficulty if high wash efficiencies were required.

Filtrate clarity was excellent in all tests, with sparkling filtrate produced and no carryover of fines or fines penetration to the medium noted. In general, the filtration behavior is consistent with that expected for material observed to flocculate and settle as rapidly as the sulfides produced in the scrubber.

6. Leach Regeneration Tests

Two pressure leach experiments were performed with use of copper sulfides collected during operation of the H₂S scrubber. The purpose of these tests was, basically, to confirm the leachability of real precipitate under mild leaching conditions. The experimental plan included provision of sufficient precipitate to generate 1 liter of approximately 1M CuSO₄

Table 15

Filtration Tests, 0.1 Sq. Ft. Leaf
(Solids from Run 514)

Total Volume of Filtrate, l	1.0	2.0	3.0
Cake Thickness, mm	0.7	1.5	2.3
Filtration Time, sec	30.2	68.0	108.0
Filtration Rate, l/min	1.99	1.59	1.50
Filter Vacuum, "Hg	20.0	20.0	20.0
Apparatus Drop, "Hg	7.4	4.8	4.3
Medium Drop (1), "Hg	10.3	7.4	6.6
Cake Drop, "Hg	2.3	7.8	9.1
Cake Drop/(Rate x Thickness)	1.7	3.3	2.7

(1) Medium is Polymax B, Style 222-003-00

upon complete reaction. The final leach solution would then have a copper concentration in the range appropriate for a CuSO_4 recycle stream in the integrated process.

The equipment used included a 2-liter Parr 316 SS autoclave fitted with a glass liner and provided with a stirrer, thermowell, liquid sampling and gas purge valves, etc. A gas-dispersing stirrer of the hollow shaft variety was not available from the manufacturer, so a double impeller arrangement was used instead. The lower impeller served mainly to keep the solids in suspension; the purpose of the upper impeller, located just below the static liquid/gas interface, was to entrain oxygen gas. Stirring speed was 320 RPM.

In each leach regeneration test, 90g of Cu_nS solids and 1 liter of 1M H_2SO_4 were charged into the autoclave. After purging air from the system with oxygen, the system pressure (O_2 + water vapor) was maintained at near 100 psig by means of the oxygen cylinder regulator. In one experiment, a low-copper sulfide was reacted at temperatures which rose well above 100°C . For the second experiment, the precipitate had a higher copper content and the autoclave temperature did not exceed 110°C . Further experimental details are given in Table 16.

There was very little solid residue resulting from run 1, so that elemental sulfur was not a major oxidation product of sulfide sulfur. The incompletely reacted residue from run 2 (higher percent copper in the precipitate and milder leach conditions) undoubtedly contained some elemental sulfur, consistent with the following material balance considerations.

For copper sulfide of nonstoichiometric composition Cu_{1+x}S , complete reaction to elemental sulfur can be described as:

Note that the concentration changes are interrelated through

$$\Delta[\text{SO}_4^{2-}] = 0 \text{ and } \Delta[\text{H}^+] = -2 \Delta[\text{Cu}^{2+}], \text{ or } \Delta[\text{H}_2\text{SO}_4] = -\Delta[\text{Cu}^{2+}] \quad (22)$$

Table 16

Experimental Conditions and Solution Analyses for Leach-Regeneration

	<u>Run 1</u>	<u>Run 2</u>
Source of Cu ₁ S: Run Nos.	415,420,427	414,513,514,517,518,519
% Cu/Average Composition	67.5% Cu (Cu _{1.05} S)	73.2% Cu (Cu _{1.38} S)
Elapsed Time:		
Temperature/Pressure		
	<u>Hr.</u>	<u>°C</u> <u>psig</u>
	0.0 hr: 20°C/100 psig	0.00 25 100
	0.33 hr: 63°C/117 psig	0.25 40 112
	0.53 hr: 88°C/109 psig	0.33 50 114
	0.67 hr: 103°C/117 psig	0.63 98 108
	0.83 hr: 124°C/110 psig (temperature overshoot)	0.83 110 107
	1.58 hr: 115°C/100 psig	1.21 107 103
	2.08 hr: 100°C/98 psig	temperature and pressure maintained at 100°C, 100 psig
	2.75 hr: 102°C/97 psig	3.25 100 102
	3.58 hr: 100°C/97 psig overnight cooling with continuous stirring	autoclave air quenched

Complete reaction to sulfate can be described as:

For this reaction stoichiometry, the material balance relationships are

$$\Delta[\text{SO}_4^{2-}] = \frac{1}{1+x} \Delta[\text{Cu}^{2+}] \text{ and } \Delta[\text{H}_2\text{SO}_4] = -\frac{x}{1+x} \Delta[\text{Cu}^{2+}] \quad (24)$$

By either chemical route, starting with H_2SO_4 solution and ending with $\text{CuSO}_4/\text{H}_2\text{SO}_4$ solution (i.e., no extraneous solutes introduced), charge balance gives the redundant relationship

$$\Delta[\text{Cu}^{2+}] + \Delta[\text{H}_2\text{SO}_4] = \Delta[\text{SO}_4^{2-}] \quad (25)$$

Material balance on the measured solution compositions gives the results shown in Table 17. It is seen that, within the analytical uncertainty, the $\text{Cu}_{1.05}\text{S}$ precipitate was oxidized predominantly to sulfate in run 1 and that the $\text{Cu}_{1.38}\text{S}$ precipitate was oxidized primarily to sulfur. It is not known to what extent the different precipitate compositions influenced the observed reaction stoichiometries. The more extreme leach conditions in run 1 (higher peak temperature and much longer time at temperature) undoubtedly promoted reaction to sulfate. The elemental sulfur product inferred to form during run 2 could have impeded the pressure leach reaction, leading to incomplete copper solubilization during the time at temperature.

7. Roast Regeneration Test

A single, scoping roast-regeneration experiment was carried out. The precipitate employed was produced in run 520; it contained 72.1% Cu, corresponding to an average composition of $\text{Cu}_{1.3}\text{S}$.

A nominal 5g charge of the washed and vacuum-dried precipitate was roasted for 1 hr at 600°C in an atmosphere of SO_2 and O_2 (partial pressure ratio, ca. 1:6), conditions which would ultimately bring the system into the stability field for CuSO_4 (see Figure 8). The charge of $\text{Cu}_{1.3}\text{S}$ powder was thinly spread over the bottom (ca. 1 cm x 20 cm area) of a porcelain boat, which was placed within a quartz tube of 2-1/2 inch diameter.

Table 17

Material Balance in the Leach-Regeneration Tests

<u>Solution Compositions</u>		<u>Run 1</u>	<u>Run 2</u>
Copper Concentration	initial	-	-
	final	57.4 g/l	34.25 g/l
H ₂ SO ₄ Concentration	initial	1.025 M	1.025 M
	final	0.56 M	0.46 M
Total SO ₄ ²⁻	initial	0.995 M	0.995 M
	final	1.568 M	0.90 M
Solution pH	initial	0.17	0.22
	final	0.47	0.57
Apparent % Cu Solubilized		94.5	52.0
$\Delta[\text{Cu}^{2+}]$		+0.903 M	+0.539 M
$\Delta[\text{H}_2\text{SO}_4]$		-0.465 M	-0.565 M
$\Delta[\text{SO}_4^{2-}]$		+0.573 M	-0.095 M

During heatup of the tube furnace to 600°C, a small flow of nitrogen was maintained through the quartz tube. The nitrogen was then replaced by SO₂, the flow rate of which was measured to be 30 min⁻¹ as determined by a bubble trap at the exit. After a steady SO₂ flow had been attained, O₂ gas was introduced, leading to a total flow rate SO₂ + O₂, of 200 min⁻¹. On this basis, the approximate partial pressures were P_{SO₂} = 0.15 atm and P_{O₂} = 0.85 atm (log P_{SO₂} P_{O₂}^{1/2} = -0.86: region A of Figure 13 in Ref. 9). Total running time for SO₂ was 85 min; for O₂, 65 min; for combined SO₂ and O₂ flow, 50 min.

During reaction, a dark film was observed to condense on the cool walls of the quartz tube projecting beyond the tube furnace. The change in weight of the contents of the sample boat over the run was 1.243g (4.993g, initial → 6.236g, final). Full sulfation of the charge (Cu_{1.3} → 1.3 CuSO₄), containing 3.60g Cu, would have resulted in a weight gain of 81% or 4.04g, while conversion to oxide would have resulted in a weight loss of about 0.9g. The appearance of the roasted charge, mainly a dark sinter with some efflorescent gray areas, indicated that oxidation and sulfation had taken place.

Extraction of copper from the roast residue was effected by the following sequence:

Water soluble copper	= 1.31g (in 100 ml)
1M H ₂ SO ₄ soluble copper	= 1.01g (in 100 ml)
Hot 1M H ₂ SO ₄ soluble copper	= 0.34g (in 150 ml)
Copper unextracted by above (as determined by dissolving residue in hot, conc'd HNO ₃)	= 1.09g
Total Cu (104% recovery)	<u>3.75g</u>

The water soluble copper was undoubtedly present as the sulfate (CuSO₄ or various hydrated forms). The copper dissolved by cold dilute H₂SO₄ was probably the oxysulfate, CuOCuSO₄. The predominantly orange-red color of the residue at this stage suggested that its composition was

mainly Cu_2O (cuprous oxide), without major percentages of CuO (cupric oxide) or unreacted Cu_xS . However, treatment with hot dilute H_2SO_4 extracted only a further 0.34g of copper. If, as likely, the source of this copper was Cu_2O , an equivalent quantity of copper would have been converted to elemental copper. The basis for this statement is the instability of cuprous sulfate toward disproportionation to Cu^0 and Cu^{2+} :

Digestion of the final residue with HNO_3 resulted in some globules of sulfur. Elemental sulfur would not likely have been carried over from the original precipitate, because the temperature of the furnace was more than sufficient to volatilize sulfur out of the heated zone (600°C). Accordingly, the source of the sulfur in the HNO_3 leach was probably unreacted sulfide. Assuming the prevalent copper compounds in the unroasted precipitate to be CuSO_4 , CuO , Cu_2O and $\text{Cu}_{1.3}\text{S}$, the percentage of unreacted sulfide in its initial charge is computed to be 18%.

The indication of incomplete sulfation and oxidation of the sulfide in the scoping experiment is not disconcerting, because the experimental arrangement employed did not approach the surface accessibility of a fluidized-bed roaster but, instead, led to a sintered calcine. In practice, reasonable percentages of unreacted Cu_xS precipitate can be returned to the scrubber (slurry recirculation loop) without significant process difficulty or economic penalty. Moreover, any portion of the Cu_xS that is converted to the oxide rather than to the sulfate would also be active in removing H_2S from geothermal steam, owing to the strong driving force for reactions such as

Note that the formation of CuS and Cu_2S by reaction of H_2S with copper oxides does not result in the formation of acid in the scrubber solution.

The process for H_2S removal by scrubbing the geothermal steam with an aqueous copper sulfate/sulfide slurry has the flexibility of accepting a recycle stream consisting of a mixture of products from a roast-regeneration step. This has a favorable impact in that regeneration process equipment and control can be much simpler than otherwise. In addition, it is known from current practice that conditions during roasting can be adjusted to yield a product mix that is most favorable in terms of internal acid balance.

VI. PLANT DESIGN AND COST ESTIMATE

1. Process Conditions and Field Data

The data available from limited field testing on flashed brine from Niland, though incomplete, suggest that the steam and noncondensibles - mainly CO_2 - flashed at the well head contain approximately 250 ppm each of NH_3 and H_2S .

Thermodynamic calculations predict that these vapors, condensed at 160 psig and subcooled to 300°F , will produce a vent gas containing 96% of the incoming H_2S and 20% of the incoming NH_3 , 830 and 190 ppm, respectively. The high CO_2 partial pressure, 5.6 atm, fixes most of the ammonia in the inlet steam as NH_4HCO_3 at pH ~ 6.1 in the condensate.

For purposes of this analysis, the following are accepted as nominal process conditions for a 10MW station.

544M pph liquid H_2O
96M pph steam
136M pph TDS
24M pph noncondensibles
at 165 psig and 370°F

The noncondensibles are 96% CO_2 , 1.5% N_2 , the balance H_2 (assumed 1%), CH_4 (assumed 1.5%), etc. The unscrubbed, flashed steam carries 175 ppm TDS and 65 ppm OH^- , while cleaned steam contains 15 ppm TDS, 5 ppm Cl^- .

The flashed vapors (120M pph) pass to a heat exchanger, condense to heat the secondary fluid, are subcooled to 300°F . Noncondensibles are vented at 160 psig.

Liquid from the well-head separator (680M pph) and condensate from the heat exchanger are flash-cooled for further energy recovery, but the greater part of the H_2S ends up in the condenser vent gases.

In field tests at Niland, a sample of the flashed steam was pulled off, let down to atmospheric pressure, condensed and cooled. The following data were recorded:

H₂S content of noncondensibles;
600/1000/1200 ppm, 1000 avg.

Total N (as NH₃) content of condensate;
200/300/400 ppm, 300 avg.

Condensate pH ~8

Condensate TDS ~20 ppm

Condensate temperature unknown,
probably 40-50°C

The H₂S content of the condensate and NH₃ content of the noncondensibles were not measured. These tests were done at the end of a short steam production run and may be indicating higher noncondensable levels than will prevail during sustained production.

2. Analysis of Field Data

The assumed noncondensable composition gives an average molecular weight of 35.4, so that the well-head vapors are 88.7 mole % steam. This leads to a noncondensable partial pressure of 20.3 psig and a water partial pressure of 159.4 psig. At 370°F, water's vapor pressure is 173.4 psig, implying a water activity of about 0.92, which is significantly higher than would be expected above a 20% salt solution. At the expected activity of ~0.85, a noncondensable partial pressure of about 33 psi is required which, in turn, would require a noncondensable molecular weight of 20 (which cannot arise from any gas containing 96% CO₂).

It must be concluded that the stated pressure/temperature, steam quality, or salt contents cannot all be exact. Since, however, the well head conditions do not directly affect the vent gas scrubbing operation, they can be accepted for this study, with the major uncertainty restricted to the specific effect of noncondensable composition on partial pressures (mainly for CO₂) and flow rates in the condenser.

If a sample (100 pph) of the flashed steam were withdrawn and condensed/cooled to 50°C at atmospheric pressure, the following flows would be recorded:

	<u>Vent, Mol/Hr</u>	<u>Condensate, Mol/Hr</u>
CO ₂	0.52 ⁻	TR
N ₂ + H ₂ + CH ₄	0.16	-
H ₂ O	0.094	5.239
H ₂ S	0.75 x 10 ⁻³ @ 1000 ppmw	TR
NH ₃	TR	1.66 x 10 ⁻³ @ 300 ppmw

It is necessary to check the partial pressures of NH₃ above the condensate and liquid compositions corresponding to the given CO₂ and H₂S partial pressures (0.672 and 9.7 x 10⁻⁴ atm, respectively) to determine the total mass of each species in the inlet. This can be done by computing the equilibrium compositions of CO₂, HCO₃⁻, CO₃²⁻, HS⁻, S²⁻, and NH₄⁺ in the liquid phase for the stated pH of 8. Equilibrium constants are listed in Table 2 (p. 15) and the results of the calculation summarized below:

	<u>Vent, Mol/Hr</u>	<u>Condensate, Mol/Hr</u>
CO ₂	0.457	0.001
HCO ₃ ⁻	-	0.062
N ₂ + H ₂ + CH ₄	0.16	-
H ₂ O	0.085	5.248
H ₂ S	0.66 x 10 ⁻³	0.004 x 10 ⁻³
HS ⁻	-	0.076 x 10 ⁻³
NH ₃	0.14 x 10 ⁻³	0.39 x 10 ⁻³
NH ₄ ⁺	-	1.27 x 10 ⁻³

While these calculations show increases in the total flows of H₂S and NH₃, 12% and 8% respectively, they are not internally consistent because of the lack of a charge balance (due primarily to the high concentration of bicarbonate). The charge balance cannot be satisfied at a pH of 8 and at a CO₂ pressure of the order of 0.65 atm. Agreement can be reached at 50°C and high CO₂ pressure at pH ~6.4, which would also show very little (1-2%) additional H₂S and NH₃ in the liquid and vapor phases,

respectively. Alternately, if the condensate were not cooled at 50°C, the water pressure would be higher and CO₂ pressure lower. At pH 8, however, the assumption of 90°C condensate, which only lowers CO₂ pressure by a factor of 3, would show a doubling of NH₃ flow due to a very high gas phase partial pressure and increased total flow.

While the data cannot be fully rationalized under circumstances which are reasonable in light of the reported experimental conditions, it is likely that the mass flows of H₂S and NH₃ beyond those measured directly were not large. For design calculations, a 10% increase in each will be assumed, consistent with the calculations made at 50°C for pH 8.

3. Design Basis for Prototype H₂S Removal System

The material balance for the prototype H₂S removal system will be based on the overall flow rates suggested for the 10MW station. Increasing H₂S and NH₃ flows by 10% results in concentrations in the flashed vapors of 225 and 265 ppm, respectively. It is then necessary to predict their partition between vent and condensate streams at condenser exit conditions. This is done by a trial-and-error procedure involving:

- Assume the overall split of major constituents (CO₂/H₂O/noncondensibles) corresponding to the exit temperature and pressure.
- Assume a pH, i.e., hydrogen ion activity at temperature.
- Compute the distribution of all species at this pH, temperature, and partial pressure consistent with the total material balance for each.
- Check the charge balance and original assumed split of major constituents. If not consistent, adjust assumptions and reiterate.

The results of such a series of calculations is summarized below:

Temperature and pH	150°C, pH 6.13
P _{H₂S} , atm	8.26 x 10 ⁻³
[H ₂ S], molal	2.49 x 10 ⁻⁴
[HS ⁻], molal	6.41 x 10 ⁻⁵
P _{NH₃} , atm	3.89 x 10 ⁻³
[NH ₃], molal	4.89 x 10 ⁻³

$[\text{NH}_4^+]$, molal	12.29×10^{-3}
P_{CO_2} , atm	5.59
$[\text{CO}_2]$, molal	48.08×10^{-3}
$[\text{HCO}_3^-]$, molal	12.08×10^{-3}
$[\text{H}^+] + [\text{NH}_4^+]$, molal	12.29×10^{-3}
$[\text{OH}^-] + [\text{HS}^-] + [\text{HCO}_3^-]$, molal	12.14×10^{-3}

Material balance, equilibrium relationships, and the charge balance requirements are met at a pH of about 6.1. Under these conditions, about 1% of the entering CO_2 remains in the condensate, 20% being in the bicarbonate form. This is sufficient to tie up almost 60% of the entering NH_3 , leaving the remaining 40% split roughly between dissolved and vaporized NH_3 . Most of the H_2S entering the condenser, 96.5%, stays in the vent gas, and 80% of the remainder exits as dissolved H_2S in the condensate.

The result of this is to produce a vent gas which is quite high in H_2S content, 830 ppm, and has an $\text{NH}_3/\text{H}_2\text{S}$ molar ratio of 0.47. This is significantly different from conditions at The Geysers, for instance, and will result in a purge stream from the copper sulfate scrubber which is relatively low in $(\text{NH}_4)_2\text{SO}_4$ and high in acidity.

The material balance and operating conditions for the prototype plant around the first flash condenser are summarized in Figure 21.

4. Process Design

The process flow diagram and material and energy balance for a 50 megawatt prototype plant for the removal of hydrogen sulfide from vent gases of Niland composition are shown in Drawings SB-001 and SB-002. Key process design criteria are summarized in Table 18, and the item list and equipment description and design criteria are presented in Table 19.

The equipment and process design criteria are based on:

- previously calculated steam condition for the Niland site,
- material balance and efficiency conditions for scrubbing demonstrated in the 2" pilot column,

Fig. 21: Material balance and process conditions, first flash condenser, 10 MW flashed-brine geothermal steam.

EIC CORPORATION 55 CHAPEL ST. NEWTON, MASS		
PROCESS FLOW DIAGRAM • REGENERATION SECTION		
SB-0002	REV. 0	SIZE B

Table 18

Key Process Design Parameters
50 MW Prototype Plant

Stream to be Treated

118.9 M PPH Inerts, mol.wt. 35.4
37.6 M PPH Steam
130 PPH H₂S, 830 ppm
30 PPH NH₃, 190 ppm
At 160 PSIG, 300°F

Scrubbing Conditions

>97.5% Removal of H₂S, to ≤20 ppm
>95% Removal of NH₃, to ≤10 ppm
Number of Transfer Units Required, ≥3.8
Scrubbing Medium, pH >1.2
Liquid-to-Gas Ratio = 1

Scrubbing Stoichiometry

$\text{Cu}^{++}/\text{H}_2\text{S} = 4/3$ mole/mole; $\text{H}^+/\text{H}_2\text{S} = 26/9$ mole/mole; $\text{S}^0/\text{H}_2\text{S} = 0$

Regeneration Conditions

>98% Leaching of Cu₂S and CuS
100°C, 4 hr retention time, Oxygen Pressure >15 psia
Leaching Slurry, pH ~2.5
Oxidation of 10% of S⁰ to SO₄⁻⁻

Process Constraints

- Self-sustaining plant adjacent to existing site.
- Soluble impurities scrubbed from steam and volatile salts disposed of by deep-well injection.
- Non-volatile salts and solid wastes impounded in lined tailings pond.
- Cleaned gases available for energy recovery. Disposal by release to the atmosphere.

Table 19

Item List and Design Criteria
50 MW Prototype Plant
Niland Conditions

<u>Item No.</u>	<u>Item</u>	<u>Design Criteria</u>	<u>Equipment Description</u>
C101	Scrubbing Tower	Reduce H ₂ S from 830 - 20 ppm, NH ₃ from 190 - 5 ppm from 156.5 MPPH gas, MW 28.7, at 160 psig. Use cross flow sieve trays with 75% tray efficiency (N = 0.6). Vapor F = 2.0, L/G = 1.	Six ft. diam. T316L SS clad tower, 35 ft. high. Internals consist of 7 trays on 2.5 ft. spacing, 6" wire mesh demister, 1500 gal. sump. 200 psi design.
R201	Neutralization Reactor	Neutralize 6 GPM decopperized waste stream and precipitate nonvolatile salts, raising pH to >5.5. Hold slurry for 24 hrs with circulation for crystal growth and air sparge for CO ₂ removal.	9000 gal. reactor/crystallizer SS construction with draft tube and 10 HP pump mixer/agitator. Atmospheric pressure design.
R202	Pressure Leach Reactor	Regenerate 98% of Cu ₂ S and CuS in 4 hrs retention time at 100°C, 100 psig total pressure. Use 400% XS air, effluent pH <3. 10% oxidation of S ⁰ to SO ₄ ²⁻ .	15,000 gal. T316L SS clad reactor with 50 HP gas dispersion agitator. Vessel 11 ft. diam., 20 ft. agitator shaft. 150 psi design.
X101	Energy Recovery Exchanger	Recover energy/heat makeup to within 10° of column temp. Service U = 130.	360 sq. ft. all T316L SS 2 x 4 fixed tube sheet L/L exchanger.
X102	Makeup Heater	Heat makeup stream to 275°F by condensing required clean steam from column, service U = 170.	350 sq. ft. all T316L SS 1 x 2 fixed tube sheet condenser/heater.
X103	Purge Cooler	Cool purge slurry to 125°F with tower water. Service U = 150.	370 sq. ft. 1 x 2 fixed tube sheet L/L exchanger. T316L SS tube side, C/S shell.
X201	Energy Recovery Exchanger	Recover energy/heat leach slurry to 175°F. Service U = 130.	280 sq. ft. all T316L SS 2 x 4 fixed tube sheet L/L exchanger.

Table 19
(Continued)

<u>Item No.</u>	<u>Item</u>	<u>Design Criteria</u>	<u>Equipment Description</u>
X202	Regenerated Slurry Cooler	Cool regenerated slurry to 120°F with tower water. Service U = 150.	200 sq. ft. 2 x 4 fixed tube sheet L/L exchanger. T316L SS tube side, C/S shell.
X203	Leach Slurry Heater	Heat leach slurry to 200°F by condensing required clean steam from column. Service U = 170.	40 sq. ft. all T316L SS 1 x 2 fixed tube sheet condenser/heater.
T101	Process Water Surge	Provide 8 hr surge for process water/condensate.	6000 gal. T304 SS atm press surge tank.
T102	Scrub Makeup Surge	Provide 24 hr surge for makeup scrub solution.	75,000 gal. T304 SS atm press vertical storage tank.
T103	Purge Slurry Surge	Provide 16 hr surge with agitation for purge slurry.	60,000 gal. T304 SS atm press vertical storage tank with 100 HP turbine agitator.
T104	Acid Trim Control Surge	Provide surge for reagent required for column pH control or other control.	1000 gal. T304 SS atm press tank with 5 HP mixer.
T201	Leach Slurry Repulping	Provide repulping for sulfide solids and 8 hrs surge.	30,000 gal. T304 SS atm press tank with 50 HP turbine mixer
T202	Solids Waste Repulping	Provide repulping for solid wastes and 24 hrs surge for 10% slurry density.	6000 gal. T304 SS atm press surge tank with 10 HP mixer.
T203	Precipitate Cu Dissolving Tank	Dissolve 350 lb/D precipitate Cu in 2 hr batch 1 shift/D.	1500 gal. T304 SS atm press tank with 5 HP mixer.
V101	Raw Gas Collecting Piping	Collect 31.3M PPH raw gas from each of five 10 MW generating stations.	Allow 10,000 ft. of 6" SC 40 C/S pipe plus manifolding.
V102	Ammonia Surge	Provide storage for NH ₃ for column pH control	Standard 10 ton liquid NH ₃ storage cylinder.
V201	Scrap Iron Storage	Provide storage for 30 days requirement of scrap.	100 ft ³ C/S covered storage bin.

Table 19
(Continued)

<u>Item No.</u>	<u>Item</u>	<u>Design Criteria</u>	<u>Equipment Description</u>
V202	Cementation Cones	Recover copper from soluble purge by cementation on detained iron scrap. Operate two cones on 24 hr cycle, 30 min residence time.	Two, 200 gal. SS cones with SS baskets and strainers.
V203	Limestone Storage	Provide storage for 30 days requirement of limestone.	350 ft ³ C/S covered storage bin.
V204	Precipitate Cu ^o Storage	Provide storage for 30 days requirement of copper.	100 ft ³ C/S covered storage bin.
V205	Waste Disposal Piping	Conduct 5.5 GPM solubles purge to disposal well, 4 GPM solids slurry to containment area.	Allow 10,000 ft. 1" SC 120 PVC pipe.
V206	Acid Storage	Provide storage for 30 days requirement of acid.	3500 gal. C/S storage tank.
F201	Purge Slurry Filter	Filter 60 GPM purge stream containing 1.5% solids to 50% solids cake, filtrate solids <10 ppm. Factored filtration rate 150 GPH/ft ² .	36 sq. ft. rotary vacuum filter. T316 SS with PVC trim. String discharge, including receivers, pumps, and piping.
F202	Regenerate Slurry Filter	Filter 55 GPM regenerate stream containing 0.4% solids to 50% solids cake, filtrate solids <5 ppm. Factored filtration rate 60 GPH/ft ² .	75 sq. ft. rotary vacuum filter. T316 SS with PVC trim. String discharge, including receivers, pumps, and piping.
F203	Neutralized Slurry Filter	Filter 24 GPM neutralized slurry containing 4% solids to 50% cake on one shift/day factored filtration rate 90 GPH/ft ² .	25 sq. ft. rotary vacuum filter. T316 SS with PVC trim including receivers, pumps, and piping.
S201	Limestone Feeder	Feed 11.5 ft ³ /D -200 mesh limestone to neutralization.	4" screw feeder with timer and day bin. 1 HP motor.
D201	Disposal Well	Cased disposal well for 8M GPD solubles purge at pH 5.5.	3000 ft. 2" lined well with injection pump.

Table 19
(Continued)

<u>Item No.</u>	<u>Item</u>	<u>Design Criteria</u>	<u>Equipment Description</u>
D202	Containment Pond	Lined tailings pond for 35 MCFY solids settled to 55% density. Provide 5 years storage.	One acre graded area with 5 ft. dikes lined with 50 mil PVC. Includes distribution piping and decant pump.
P101	Circulating Pump	Circulate 225 GPM slurry at 300°F thru tower for scrubbing 70 ft. TDH required.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 10 HP motor.
P102	Process Water Pump	Transfer 11 GPM acid condensate for process water use. 450 ft. TDH required.	Turbine pump with hardened SS casing and impeller, mechanical seal. 5 HP motor.
P103	Makeup Feed Pump	Feed 52 GPM makeup scrub solution to tower. 500 ft. TDH required.	Turbine pump with SS casing and impeller, mechanical seal. 15 HP motor.
P104	Purge Slurry Transfer Pump	Transfer 60 GPM purge slurry to filter. 100 ft. TDH required.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 5 HP motor.
P105	Additive Metering Pump	Transfer up to 5 GPM additive to tower for pH control, 450 ft. TDH required.	Positive displacement SS metering pump, 1 HP motor with variespeed drive.
P201	Filtrate Transfer Pump	Transfer filtrate from purge filter to repulp tank.	Included with F201. Total filter power 10 HP.
P202	Leach Reactor Feed Pump	Feed 54 GPM leach slurry to regeneration reactor, 350 ft. TDH required.	Turbine pump with hardened SS casing and impeller, mechanical seal. 10 HP motor.
P203	Neutralized Slurry Transfer Pump	Transfer 25 GPM neutralized slurry to filter, 50 ft. TDH required.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 1 HP motor.
P204	Leached Slurry Transfer Pump	Circulate slurry through leach reactor and transfer leached slurry to filter. Deliver 1000 GPM at 20 ft. TDH.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 10 HP motor.

Table 19
(Continued)

<u>Item No.</u>	<u>Item</u>	<u>Design Criteria</u>	<u>Equipment Description</u>
P205	Filtrate Transfer Pump	Transfer filtrate from regenerated filter to makeup surge tank.	Included with F202. Total filter power 20 HP.
P206	Filtrate	Transfer filtrate from neutralization filter to injection well pump.	Included with F203. Total filter power 10 HP.
P207	Waste Slurry Transfer Pump	Transfer 5 GPM solid waste slurry to containment pond. Allow 350 ft. TDH.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 2 HP motor.
P208	Makeup CuSO ₄ Transfer Pump	Transfer 5 GPM makeup CuSO ₄ solution to makeup surge tank. 100 ft. TDH required.	Centrifugal pump with hardened SS casing and impeller, mechanical seal. 1 HP motor.
P209	Air Compressor	Compress 400 SCPM air to 150 psi for leach reactor and general process use.	Two-stage centrifugal compressor, 125 HP motor.

- measured liquid/solid separation rates for the sulfide purge,
- sulfide regeneration rates and stoichiometries from leach tests run on laboratory produced solids and information derived from literature data,
- standard and established design criteria and procedures for cementation, neutralization, and other process steps.

Referring to the drawings and Table 19, vent gases from primary condenser coolers are collected in piping system V-101 and introduced into scrubbing column C-101. Hydrogen sulfide and ammonia are removed by countercurrent contact on sieve trays, with liquid circulated by pump P-101. A purge stream containing precipitated sulfides and acid is withdrawn from the circulating stream, passed through exchanger X-101 for energy recovery, and cooled to holding temperatures in cooler X-103 for storage in the agitated surge tank T-103. Makeup copper sulfate solution is transferred from surge tank T-102 by pump P-103 through heater condenser X-102 and exchanger X-101 prior to introduction to the column. Energy for heating the makeup in exchanger X-102 is derived by condensing a portion of the cleaned steam. The drips from this condensation, together with those from other process steps, are collected in tank T-101.

Pump P-101 transfers the required makeup water back to the system as well as to other process water needs. Materials required for trim control of pH are held in tank T-104 and pumped to the system, as required, by pump P-105. Ammonia required for trim control of pH is stored in tank T-102. Solids to be regenerated are transferred from the surge tank T-103 to filter F-201 by pump P-104. The separated solids pass to agitated tank T-201, where they are repulped with a sufficient portion of the filtrate to provide most of the acid required for regeneration. The repulped slurry is transferred by pump P-202 through energy recovery exchanger X-201 and heater X-203 into reactor R-202. Air for oxidation is supplied by compressor P-209 and contacted with the slurry by a high intensity dispersion agitator. Liquid circulation is established through

pump P-204, and regenerated slurry is withdrawn through energy recovery exchanger X-201 and cooled to processing temperature by cooler X-202. Unreacted solids and sulfur generated during leaching are separated from regenerated copper sulfate solution in filter F-202. Filtrate is returned to surge tank T-102, while spent solids drop to repulp tank T-202.

The filtrate from sulfide filter F-201 not required for repulping and recycle for acid balance purges solid impurities from the system. This stream passes through cementation columns V-202, where copper is removed by precipitation on detinned scrap iron. Two columns are used and dumped on a daily cycle. The "precip" copper, together with precip copper purchased for makeup of losses is charged to dissolution vessel T-203 where, with required water and acid, and air supplied by compressor P-209, it is oxidized and dissolved and recycled by pump P-208 to surge tank T-102. Required acid is drawn from storage tank T-206 and transferred by pump P-210 to the dissolution vessel and reactor R-202, where it supplies needs beyond those which can be met by recycling filtrate from F-201.

The decopperized purge stream from cementation column V-202 passes to neutralization reactor/crystallizer R-201. Limestone is fed to the reactor crystallizer by feeder 201, and air from compressor P-209 is sparged through the vessel to strip carbon dioxide from the slurry. This neutralizes excess acid and precipitates iron and copper from the soluble purge stream as basic sulfate salts. Once daily, the contents of the neutralizer/crystallizer are transferred by pump P-203 to filter F-203 with the insoluble sulfates dropping, with unreacted sulfides and elemental sulfur, into repulp tank T-202. Filtrate from the insoluble sulfates filter is pumped through disposal system V-205 to disposal well D-201. Sufficient liquid is withdrawn to repulp the solids slurry in tank T-202. Repulped slurry is transferred by pump P-207 through piping system V-205 to tailings pond D-202 for containment.

High degrees of hydrogen sulfide removal should be possible from the Niland vent gas because of the unusually high inlet concentration of this gas. The high hydrogen sulfide to ammonia ratio would result

in the generation of significant excess acid, which will also favor high ammonia removals by depressing pH's. The high molecular weight of the gases treated results in a relatively low mass flow rate of circulated scrubbing liquid. On the other hand, the high rate of acid production necessitates a relatively large flow rate of purge slurry to maintain pH's at acceptably high levels, with a design minimum of 1.2. With a sump volume fixed solely by consideration of circulating pump needs, the slurry residence time in the system is relatively short - of the order of one-half hour. The energy recovery scheme chosen utilizes steam from the vent gas as a high temperature energy source which, in turn, permits the heat exchange area to be minimized. This would not normally be possible if the steam were destined for direct use in power generating turbines, because of the loss of system efficiency.

While 24-hour surge capacity is provided for makeup scrub solution, only 16 hours is provided for purge slurry, since an additional 8 hours exists in the repulp tank following the sulfide filter. The sulfide filter and, indeed, all filters in the process are so small as to permit their use one shift per day, if desirable, at a nominal increase in capital cost. This might prove desirable if difficulties were encountered in obtaining reliable shift labor. The neutralization reactor and insoluble sulfates filter have been sized to permit operation one shift per day, since the size requirements for continuous operation would involve equipment smaller than normally used commercially. Oxidation pressure leaching has been selected as the regeneration mode of choice in this situation for two reasons: (a) the mass flow of solids to be regenerated is so low, approximately 400 lbs per hour, that the appropriate fluid bed roaster would be smaller than generally used commercially and, hence, relatively expensive; (b) the large excess of hydrogen sulfide over ammonia and the corresponding lack of inherent neutralizing capability favor the disposal of as much sulfide as elemental sulfur as possible, a route favored by leaching.

The soluble purge stream has been arbitrarily fixed at approximately 10% of the total purge, although this results in the requirement for

significant makeup of sulfuric acid to the leach reactor. Since this results in a recycle ammonium sulfate concentration of less than 40g per liter, a significantly higher proportion of recycle, up to 95%, would be possible without building up ammonium sulfate levels so high as to materially affect ammonia scrubbing efficiency. This would reduce not only acid, but scrap iron and lime consumptions as well. The 10% limit was chosen, however, in the absence of detailed knowledge of the effect of buildup of deleterious trace constituents, not presently identified, on the system.

Provision has been made for containment of solid waste in a lined tailings pond, one acre in size, located within one mile of the regeneration facility, and for disposal of soluble waste down a new injection well.

5. Cost Estimates

Capital and operating cost estimates for a self-sustaining 50 megawatt plant are summarized in Tables 20 to 22. Purchased equipment costs were obtained from published cost data checked from at least two sources and updated to current dollars. All items except the scrubbing tower, leach reactor, lined tailings pond and disposal well are essentially standard items of equipment and can be well characterized. Conservative estimates were developed for the tower, reactor, and disposal facilities in view of the undeveloped design component in these major items. These costs represent approximately 40% of the total equipment costs identified for the process. Installation factors for civil work, piping, instrumentation, electrical, etc., were derived from literature sources as appropriate for each class of equipment. An allowance of 20% of total physical plant cost was made for off-sites, which would normally be available in an integrated facility. These would include the development of plant power supply and substations, water supply and cooling tower, and limited administrative and support facilities such as site/yard/land, change house, etc. Engineering and construction and fees allowances amounting to 30% of direct plant costs have been made, assuming that construction proceeds from an established design basis on a well-developed site

Table 20

Physical Plant Cost Estimate
50 MW Prototype Plant

<u>Equipment Class</u>	<u>Purchased Equipment Cost, \$M</u>	<u>Installation Factors</u>			<u>Physical Plant Cost, \$M</u>
		<u>% Civil(1)</u>	<u>% PI&E(2)</u>	<u>\$M</u>	
Towers	150	27	87	170	320
Reactors	210	24	65	190	400
Tanks & Vessels	380	24	45	260	640
Heat Exchangers	130	12	63	100	230
Filters	160	6	44	80	240
Pumps	110	6	66	80	190
Non-Factored(3)	230	-	-	-	230
Total Physical Plant Cost					2,250

(1) Percent of purchased equipment cost for foundations, structures, etc.

(2) Percent of purchased equipment cost for piping, instrumentation, insulation, electrical, etc.

(3) Piping distribution systems and waste disposal facilities.

Table 21

Fixed Capital Cost Estimate
50 MW Prototype Plant

	<u>\$M</u>
Total Physical Plant Cost	\$2,250
Offsites ⁽¹⁾ @ 20% TPPC	<u>450</u>
Direct Plant Cost	\$2,700
Engineering & Construction @ 25% DPC	675
Fees @ 5% DPC	<u>135</u>
Fixed Capital Cost	\$3,510
Contingency @ 25% FCC	<u>890</u>
Total Fixed Capital Cost	\$4,400
	\$/KW 88

(1) Power and water supply, administrative and support facilities.

Table 22

Operating Cost Estimate
50 MW Prototype Plant

<u>Process Materials</u>		<u>\$M/Yr.</u>
Sulfuric Acid	300 Tons/Yr. @ \$33/T	10
Limestone	250 Tons/Yr. @ \$8/T	2
Precipitated Copper	37.5 Tons/Yr. @ \$1600/T	60
Detinned Scrap	45 Tons/Yr. @ \$200/T	9
Miscellaneous, Allowance		<u>19</u>
		100
<u>Utilities</u>		
Power	2200 Mkw @ 25\$/Mkw	55
Fuel	--	--
Water	10,000 M Gal. @ \$0.5M Gal.	<u>5</u>
		60
<u>Labor</u>		
Operating Labor	4 MY @ \$18,000/MY	72
Maintenance Labor	1 MY @ \$20,000/MY	20
Supervision	1 MY @ \$22,000/MY	22
Plant G&A @ 40% Total Labor		<u>46</u>
		160
<u>Capital Charges</u>		
Maintenance Materials and Supplies @ 2% TFC		88
Taxes and Insurance @ 3.5% TFC		152
Interest (1)		<u>--</u>
		240
	Cash Operating Costs	560
	Depreciation, 10-Year Straight Line	440
	Total Operating Cost	1,000
	¢/kwh	0.25

(1) Equity financing.

adjacent to existing facilities. The 25% contingency factor applied to this estimate includes an allowance of 10% for undeveloped design and 15% for estimating contingencies. The total fixed capital cost, in mid-1976 dollars, is estimated at approximately 4.5 million dollars or 90 dollars per kilowatt of generating capacity. While this cost would be a large fraction of the total power generating cost, significant economies of scale can be expected in plants designed to be integrated into larger generating stations. The majority of the major equipment items have cost capacity exponents of the order of 0.6 and, at higher regeneration rates, the use of the less costly roasting alternative would be justified. It is anticipated that at a capacity of 500 megawatts, the unit cost would drop to the order of 50 dollars per installed kilowatt.

Process materials and utilities costs, which are essentially independent of capacity, amount to 0.5 mills per kilowatt hr. It has been assumed that this facility will require an independent complement of operating labor. Thus, labor costs are also relatively high, also amounting to 0.4 mills per kilowatt hr. This cost may be expected to decrease significantly at higher capacities or if the size of the operation of the hydrogen sulfide removal facility were integrated with the power station operation. Capital charges excluding depreciation add an additional 0.6 mills, bringing cash operating costs to 1.4 mills per kilowatt hr. A ten-year depreciation life raises total operating costs to 1 million dollars per year, or 2.5 mills per kilowatt hour. It is estimated that, coupled with the economies of scale possible in operation of a larger facility, decreases in unit labor costs and capital charges would reduce operating costs for a 500 megawatt station to the order of 1.5 mills per kilowatt hr.

It should be noted that these economics do not comprehend the possibility of additional energy recovery from the cleaned vent gases. The hydrogen sulfide and ammonia-free, cleaned gases from a 50 megawatt station could be passed through a power recovery turbine which, exhausting to atmospheric pressure, would permit the generation of at least an

additional 3 megawatts without creating additional atmospheric or ground level emissions. This operation would be foregone, or its economic return severely reduced, with the use of conventional technology for the removal of hydrogen sulfide from the vent gases. This arises because of the high water content, which would require condensation during cooling to the low temperatures used in conventional hydrogen sulfide removal, and the need to find an extremely selective sorbent for the sulfide in the presence of an almost pure carbon dioxide stream.

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APPENDICES

APPENDIX A

THE USE OF PACKED COLUMNS

FOR THE REMOVAL OF HYDROGEN SULFIDE FROM STEAM

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THE USE OF PACKED COLUMNS

FOR THE REMOVAL OF HYDROGEN SULFIDE FROM STEAM

Summary

Scoping calculations for the removal of 90% of the hydrogen sulfide from steam containing 220 ppm at 9.1 atm lead to column configurations which are summarized below.

	<u>Laboratory</u>		<u>Commercial</u>
Column Diameter	2"	6"	17'
Packing Size, inches	$\frac{1}{4}$	$\frac{1}{2}$	2
Packed Height, feet	2.5	7.5	12.5
Pressure Drop, inches of H ₂ O	2.5	1.1	12.5
Steam Mass Flow, lb/hr	25	180	10 ⁶
Contact Time, sec	2.5	9	3.3

While it is not possible to obtain strict similitude in scaling from the laboratory to the commercial size columns, useful engineering information can be obtained on a 2" column. Mass transfer rates can be determined which will be valid within about a factor of two, and fouling and corrosion tendencies can be determined.

Background

The steam is to be contacted by an acid copper sulfate stream containing recycled sulfide solids, which absorbs H₂S from the steam. A slip stream is withdrawn from the circulating liquid which carries the precipitated copper sulfide and ammonium sulfate. Copper sulfate

is regenerated from this stream for recycle, and the sulfur and ammonia removed from the steam ultimately are converted to concentrated sulfate streams for disposal.

The object of the present work is to demonstrate H_2S absorption in acid copper sulfate under process conditions which simulate proposed commercial operating conditions. This is to be done at a relatively small scale, and the question arises as to the proper design for the miniplant equipment. The use of a small (2 inch dia.) packed column has been proposed although it is recognized that other contacting devices may be equally suitable.

It is the purpose of this Appendix to examine the requirements for the design of laboratory and commercial scale packed columns.

Packed Column Design-Hydraulics

Design procedures for packed towers are well established and may be followed with a high degree of confidence over a wide range of conditions, including those proposed for hydrogen sulfide removal. Physical properties used throughout this report are summarized in Table I.

Towers are sized using correlations such as those shown in Figure 1. Note that process conditions (temperature, pressure, compositions, flow rates) fix the abscissa, .068 in this case, which is independent of the scale of operations. Pressure drop, the parameter, is a design parameter and in this case, at high absolute pressures, may be

Table I

Assumed Physical Properties

System Pressure	120 psig
System Temperature	350°F
Steam Specific Volume	3.34 ft ³ /lb
Liquid Density	61. lb/ft ³
Slurry Density	64.7 lb/ft ³
Liquid Viscosity	0.24 centipoise
Surface Tension	45. dyne/cm
Schmidt Number (H ₂ S/Steam)	1.3

L = LIQUID RATE, LBS./SEC., SQ. FT.
 G = GAS RATE, LBS./SEC., SQ. FT.
 ρ_L = LIQUID DENSITY, LBS./CU. FT.
 ρ_g = GAS DENSITY, LBS./CU. FT.
 F = PACKING FACTOR
 μ = VISCOSITY OF LIQUID, CENTIPOISE
 g_c = GRAVITATIONAL CONSTANT = 32.2

Figure 1: Tower Sizing

set at the high end of the range without penalty unless packing heights work out to be excessive from mass transfer considerations. For the design point chosen, 1" H₂O Δp/ft, the ordinate has a value of 0.08 and is a function of both system properties and the specific design proposed. For this case, factoring out the physical properties results in the requirement that

$$G^2 F = 57$$

where G = gas mass velocity, lb/sec/ft² (for this correlation)

F = packing factor, a function of the packing size, shape, and porosity

For a given gas flow rate, the relation between tower diameter and packing geometry is

$$F_1/D_1^4 = F_2/D_2^4 = \text{const.} \quad \text{or } D \propto (F)^{1/4}$$

For a given volume of packing (to a first approximation, for a given mass absorbed) economics usually favor building a tower of as small a diameter as possible, especially at high pressures. Thus, one is driven to select the packing with the lowest value of F for a given mass transfer efficiency. The relation between nominal size and geometry for various packings is shown in Figures 2-5. An "efficient" packing will have a low packing factor for a given area and mass transfer capability. Since most published data are for raschig rings or saddles, they will be used here for reference purposes.

It is obvious that the economic constraints will favor the use of the largest sized packing possible since their packing factors are

Figure 2: Metal Pall Rings*

*Punched Cylinders

Figure 3: Metal Raschig Rings*

*Solid Cylinders

Figure 4: Ceramic Raschig Rings*

*Solid Cylinders

Figure 5: Ceramic Intalox*

*Saddles

lowest. In large columns ($D > 3$ ft) a wide choice is available, but in small columns ($D < 1$ ft) liquid hydraulics set a limit on maximum packing size.

It was determined in the '30's that a ratio of tower-to-packing diameters exceeding about 8-10 ($D/d > 8$) was required to obtain reasonably uniform distributions of liquid across the packing (1). Such a distribution is shown in Figure 6. The spreading of the liquid can be viewed as a random procedure, as streams split when falling, and described by an error law type function

$$L_{\text{point}}/L_{\text{ave}} = \frac{c D^2}{4Z} e^{-c r^2/Z}$$

where L = liquid flow rate

r, D = point radius and tower diameter, in

Z = depth below packing top, ft

c = spreading coefficient (ft/in^2)

Packing spreading coefficients have been determined (2) and range from .2 - .3.

Even with large values of D/d , some non-uniformity is inevitable as liquid distributions change and this is reflected in mass transfer rates which change with depth and radius as shown in Figure 7.

Thus, tests on small scale mass transfer equipment must be done in a way which permits scaling based on the correct:

Process Conditions

Temperature, pressure, composition

Liquid/gas ratios

Liquid distribution in a 6-in. column packed with $\frac{1}{2}$ -in. broken stone packing.

Figure 6: Liquid Distribution

Variation of local mass-transfer coefficients in absorption of carbon tetrachloride from air into dibutyl phthalate.

Figure 7: Local Mass Transfer

Tower Design

D/d

Z/D

Mass flow rates and pressure drops

Mass transfer rates

In general, it is not possible to obtain strict similitude in scale-up unless large packing sizes and, therefore, large tower diameters are used from the outset, as will be shown.

A boiler is available which should be able to deliver about 180 lb/hr steam at the required conditions. This will limit the maximum column size since it is desirable to operate at conditions as close as possible to the proposed commercial column design. Some design options for lab and commercial scale columns are summarized in Table II.

This Table shows that a 6-inch diameter column is about the largest which can be tested with the existing boiler and maintain velocities which are even reasonably close to those possible for the commercial design. Even with this limitation, note that it will not be possible, with $\frac{1}{4}$ " and $\frac{1}{2}$ " packing, to simultaneously scale comparable mass velocities, "F" factors, Reynolds numbers, and pressure drops. This results from the tendency of small packings to flood at relatively low mass velocities. Simply reducing the pressure will not change this conclusion, as shown in Table III, unless very low pressures are used, where mass transfer rates will decrease markedly.

Other than simply obtaining data on a larger size packing, use of the 6" column does not offer significant advantages in the hydraulic sense in view of the boiler limitation. Thus, an experimental strategy

Table II

Tower Design Options

Ceramic Saddles

	<u>Lab Scale</u>			<u>Commercial</u>		
Packing size, inches	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	2	3	$3\frac{1}{2}$ (1)
Tower diameter	2"	6"	8"	17'	15'	14'
Steam rate, pph	25	180	180	10^6	10^6	10^6
Mass velocity, pph/ft ²	1100	920	520	4300	5700	6500
Pressure drop, in H ₂ O/ft	1.0	0.15	0.05	1.0	1.0	1.0
Superficial velocity, ft/sec	1.02	0.83	0.46	3.86	5.1	5.8
"F" factor, ft/sec (lb/ft ³) ^{1/2}	0.56	0.47	0.26	2.17	2.88	3.34
Reynolds number, d G/ μ	640	1060	900	19.8M	39.4M	52.4M
Packing properties						
Packing Factor	600	200	145	40	22	18
Area, ft ² /ft ³	300	190	102	36	28	28
Free area, %	75	78	77	79	80	97

(1) High efficiency Flexirings

Table III

Effect of Pressure on Column Hydraulics

6" Column, ½" Saddles

<u>Pressure psig</u>	<u>Velocity ft/sec</u>	<u>"F" Factor</u>	<u>Reynolds No.</u>	<u>ΔP "H₂O/ft</u>	<u>Inlet H₂S Partial Pressure, psia</u>
120	.83	0.47	1060	.15	1.56×10^{-2}
100	.99	0.50	1060	.2	1.33×10^{-2}
75	1.25	0.56	1060	.25	1.04×10^{-2}
50	1.70	0.66	1060	.35	$.75 \times 10^{-2}$
25	2.76	0.84	1060	.5	$.46 \times 10^{-2}$
5	5.4	1.16	1060	1.5	$.23 \times 10^{-2}$

which makes maximum use of a 2" column is reasonable. Such a unit would still give useful engineering information, such as approximate mass transfer rates and fouling tendencies of various packing types, while permitting rapid economic evaluation of various scrubbing alternatives. Then, should time and funds permit, data could be obtained on a 6" column for conditions determined as "optimum" from scoping tests in the small unit. The utility of the larger column would lie in the ability to obtain data with, perhaps, less inherent experimental uncertainty and on packing which is closer to the anticipated commercial size by a factor of two.

Packed Column Design-Mass Transfer

Design procedures for solving the general mass transfer problem in packed towers are not as well developed as for hydraulic problems, although a large body of data exists, because the rate processes involve functions such as true contact area and true local driving forces (interface partial pressures) which are extremely difficult to measure. And the situation is more complicated in systems with chemical reactions involved, such as this one. Nevertheless, a qualitative prediction at least can be made for certain simplified cases.

In a differential element of the packed bed the mass transfer rate may be expressed as

$$-dn = k_g a_1 \Delta P dv$$

where dn = absorption rate moles/hr

k_g = mass transfer coefficient, moles/hr ft²/atm

a_1 = surface area for mass transfer, ft²/ft³

ΔP = mass transfer driving force, atm

dv = volume element, ft³

Strictly, the driving force, ΔP , is that difference between the local bulk gas phase partial pressure and that at the interface between the liquid and the gas. Much of the literature of mass transfer in packed towers is devoted to determining this and relating it to the operating characteristics of the system, along with the true local area a_1 .

For the absorption of H₂S at low concentrations in steam into an acid copper sulfate stream, certain simplifications may be reasonable. It is well known that at reasonable pH's the sulfide pressure at equilibrium above these solutions is extremely low. Then, if reactions in the liquid phase are rapid, as is likely (and can be measured in other ways) and liquid phase mixing is sufficient (eddy diffusivities being high and viscosities low) the interfacial partial pressure can approach zero. Then, the total driving force is simply the gas phase partial pressure which, following ideal gas laws, is

$$\Delta P \approx P \approx \pi / \Sigma n$$

where π = total pressure, atm

Σn = total moles in the gas = moles of inerts

Then the rate equation reduces to

$$-dn = k_g a_1 \pi \frac{n}{\Sigma n} dv$$

which is integrated

$$- \int_{n_o}^{n_e} \frac{dn}{n} = \int_0^{V_T} k_g a_i \frac{\pi}{\Sigma n} dv \approx k_g a_i \frac{\pi}{\Sigma n} \int_0^{V_T} dv$$

$$\text{or } \ln(n_o/n_e) = k_g a_i \frac{\pi}{\Sigma n} AZ$$

where n_o/n_e = moles of solute entering/leaving

A, Z = column area, packing height

and $\Sigma n/A = G$, gas mass velocity, moles/hr/ft²

It is conventional to call

$\ln(n_o/n_e) = N_G$, the number of gas phase transfer units

and $G/k_g a_i \pi = H_G$, the height of a transfer unit, ft

then $Z = \text{packed height, ft} = N_G H_G$

In this case, for 90% removal, $n_o/n_e = 10$ and $N_G = 2.3$ so the mass transfer problem is reduced to finding the appropriate value for H_G .

Since process conditions fix both π and G , the problem really reduces to determining $k_g a_i$, the product of mass transfer rate and interfacial area.

This parameter is evidently a function of not only the properties of the system but packing characteristics and operating conditions as well. A typical set of values is shown in Figure 8 along with pressure drop and liquid holdup, a measure of a_i , as a function of liquid rate for carbon dioxide in air. Even these values, however, are found to be a function of the extent of carbonate formation, increasing with caustic concentration, and packing size, generally decreasing with increasing size.

Figure 8

**MASS TRANSFER PERFORMANCE
1/2" CERAMIC SADDLES**

Column diameter.....15 inches
Packing height.....5 feet
Packing factor.....200
Liquid rate.....lbs./ft.²/hr. as parameter
Gas rate.....450-500 lbs./ft.²/hr.
Gas concentration.....Ln mean 1%
Liquid concentration.....4% NaOH
Liquid temperature.....75° F.
Carbonate content.....25%
Pressure drop.....Inches water/ft. packing

The earlier approaches to the correlation of mass transfer data were based on the effects of hydraulics only (3), that is, were of the form

$$H_G \propto G^n L^m, \quad n \sim 1/3 \quad m \sim -1/3$$

Little effect of packing size was found, but most data were on 1" to 1½" sizes. It was realized that, based on theoretical argument, H_G should vary systematically with Schmidt Number and exponents on this group ranging from 1/6 to 2/3 have been reported. A potentially more sound approach involves the J_D factor analogy between mass and momentum transfer which leads to correlations of the form (4,5,6)

$$\frac{G}{k_g \pi} = H_{Ga_1} \propto N_{Re}^n N_{Se}^m$$

Typically, $n = 2/3$, $.34 < m < .41$, and the proportionality constant is of the order of 1. Use of this type of correlation, however, requires knowledge of the effects of system properties, operating conditions, and packing characteristics on a_1 . This is a very complex problem and has been the subject of considerable work resulting in a number of correlations for a wide variety of systems (7). Calculated values of the mass transfer coefficients for the 2", 6", and 17' commercial columns are summarized in Table IV.

It is obvious that there is a considerable uncertainty in results calculated this way, but in view of the uncertainties involved in calculating the true driving force for mass transfer, they should be acceptable for scoping estimates. Their use in column sizing is summarized in

Table IV

Calculated Mass Transfer Coefficients

H₂S Removal from Steam

Column	2" lab	6" lab	17' commercial
Packing (Saddles) size, inches	$\frac{1}{4}$	$\frac{1}{2}$	2
Packing area, ft ² /ft ³	300	190	36
Gas, liquid mass velocity, lb/hr/ft ²	1100	920	4,300
Reynolds number	640	1060	19,800
H _G , reference (3), ft	.88	.88	.85
H _G , reference (4), ft	16.9/a ₁	20.8/a ₁	70/a ₁
H _G , reference (5), ft	12.5/a ₁	14.8/a ₁	-
H _G , reference (6), ft	11.3/a ₁	13.3/a ₁	38.1/a ₁
a ₁ for water ⁽⁷⁾ , ft ² /ft ³	18.7	8.4	12
a ₁ this system/a ₁ water ⁽⁷⁾	.61	.59	.69
a ₁ for this system ⁽⁷⁾ , ft ² /ft ³	11.3	5.0	9.0
H _G , ft, reference (4), (5), (6)	1.5, 1.1, 1.0	4.2, 3, 2.7	7.8, -, 4.2
k _g a ₁ , mole/hr ft ³ atm, reference (4), (5), (6)	4.5, 6.2, 6.8	1.4, 1.9, 2.1	3.3, -, 6.2
k _g , mole/hr ft ² atm, reference (4), (5), (6)	0.4, 0.55, 0.6	0.28, 0.38, 0.42	0.37, -, 0.69

Table V. These results can be confirmed, to a sufficient degree of accuracy to support more detailed economic calculations, on the 2" or 6" columns.

Other Engineering Considerations

Considerations other than column diameter and packing height could strongly influence the final absorber design.

It is possible that precipitating sulfides will badly foul the packing, ultimately causing flooding, or ceramic packing may or may not foul more rapidly than metallic units. The response of the column to long term operation should be monitored to determine both the rate and extent of build up if any. The commercial tower would precipitate of the order of $\frac{1}{2}$ ft³ of finely subdivided sulfide per ft³ of packing per month which must be continuously flushed out of the tower.

The columns should be designed with enough flexibility to permit at least a preliminary evaluation of the suitability of other types of internals. Specifically, columns containing only a few sieve trays would be appealing if found suitable. Contact times in the proposed packed towers range from 2.5 to 9 seconds, rather longer than likely in a few trays, but bubble areas could be made higher per unit volume if trays don't prove prone to fouling.

It is also possible that the type of contacting device will influence the size distribution of the sulfide product which would have significant impact on the downstream, regeneration steps. Determination of this effect will also require long term testing.

Table V

Column Configurations

H₂S Removal from Steam

Column Diameter, D	2"	6"	17'
Packing size, d, inches	$\frac{1}{4}$ "	$\frac{1}{2}$ "	2"
D/d	8	10	100
H _G , ft	1.1	3.3	5.5
Packed height, (1) Z, ft	2.5	7.5	12.5
Z/D	15(2)	15(2)	.75(3)

-
- (1) 90% removal. 99% removal would require double the depth.
(2) Pack in 3 sections of Z/D = 5
(3) Too shallow for good distribution. More packing would be provided.

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APPENDIX B

THE USE OF TRAYED COLUMNS FOR THE
REMOVAL OF HYDROGEN SULFIDE FROM STEAM

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THE USE OF TRAYED COLUMNS FOR THE
REMOVAL OF HYDROGEN SULFIDE FROM STEAM

Summary

Scoping calculations for the removal of 90% of the hydrogen sulfide from steam containing 220 ppm at 9.1 atm lead to column configurations which are summarized below.

	<u>Laboratory</u>	<u>Pilot</u>	<u>Commercial</u>
Column Diameter	2"	5.5'	15'
Tray Spacing	12"	24"	36"
Number of Trays Required	4-10	2-5	1-4
Steam mass flow, lb/hr	58	10 ⁵	10 ⁶
Contact Time/Tray, sec	1/40	1/5	1/3

While testing on pilot scale equipment will be required to obtain scale up data on mass transfer efficiencies, hydraulics, and fouling tendencies in this system on commercially available tray designs, trays can be used in a 2" column to obtain preliminary information on fouling and foaming tendencies and efficiencies. Detailed calculations illustrating tray hydraulics determination are summarized at the end of this Appendix.

Background

The design bases for the use of packed columns in the removal of H_2S (and NH_3) from geothermal steams at the laboratory, pilot plant and commercial scales have been reviewed in a previous report (1). It was pointed out that engineering considerations other than tower diameter and/or packing type and height might dictate the final design. In particular, the use of a tower containing only a few sieve trays would be an attractive alternative, since costs would be comparable to packed towers (the reference case) and the trays might prove less sensitive to fouling and be easier to clean if fouled.

It is the purpose of this report to examine the requirements for the design of laboratory and commercial trayed columns.

Trayed Column Design-General

Trayed columns, and in particular columns with bubble cap trays, have been widely used in the chemical process industries for many years. Bubble cap trays are so widely used that, while they are currently being displaced by more efficient, economic designs, there exists a wide body of information on their performance (2), and design methods have been well documented (3). Industry groups currently sponsor both extensive in-house development programs and the efforts of such groups as Fractionation Research Incorporated, whose finding on the influence of system properties, operating conditions, and tray designs are held confidential.

Trayed towers differ from packed ones, fundamentally, in that mass transfer occurs in a stagewise manner, in discrete increments on the

individual trays, instead of in a continuous manner as liquid and gas pass countercurrent to each other through the interstitial spaces in a packed section.

The design problem then reduces to consideration of two questions:

- How large should the tower diameter be, and what detailed tray layout is required, to permit effective vapor/liquid contact on the trays for good mass transfer while providing stable operation without "weeping" or excessive entrainment?
- What is the tray efficiency under the design conditions, and how many trays are required to obtain the desired degree of mass transfer?

Trayed Column Design - Hydraulics

Vapor and liquid must pass countercurrent to each other in the column with velocities and tray spacings chosen to control the amount of liquid entrained from a given tray to the one above. The entrainment represents a backmixing of liquids and thus reduces overall efficiency and, in the limit, can result in flooding by preventing liquid from descending through the column.

The parameter used most often to correlate column hydraulics is the superficial vapor "F Factor" defined as:

$$F = V(\rho_g)^{1/2} = G(v_{og})^{1/2} = .000354 \text{ PPHv } (v_{og})^{1/2}/D^2$$

where

$$F = \text{F Factor, ft/sec (lb/ft}^3)^{1/2}$$

V	=	Vapor Velocity, ft/sec
ρ_g	=	Vapor Density, lb/ft ³
v_{og}	=	Vapor Specific Volume, ft ³ /lb = $1/\rho_g$
G	=	Vapor Mass Velocity, lb/sec/ft ²
PPHv	=	Vapor Flow Rate, lb/hr
D	=	Tower Diameter, ft.

The F factor is really just $(2g_c)^{1/2}$ times the square root of a velocity head, and permits one to think in terms of velocity directly, not velocity squared. Typically, values of F are of the order $1 < F < 3$, with the higher values leading to higher levels of entrainment.

One correlation for entrainment as a function of operating rates and the approach to flooding conditions (roughly, tray spacing less froth height) is shown in Figure 1. Clearly, low velocities and wide tray spacings reduce the approach to flooding and therefore entrainment, but increase tower costs. Studies (4) have indicated that entrainment levels as high as 0.2 lb liquid/lb vapor are "optimum", subject to pressure drop and flooding constraints.

Figure 2 shows the relation between F factor at flooding, expressed as a capacity factor C, tray spacing and operating conditions. Note that the abscissa is fundamentally the same as that used in packed tower design (Figure 1, Reference 1) and the capacity factor C is related to the F factor by:

$$F = C \times (\rho_l - \rho_g)^{1/2} \times (\sigma/20)^{.2}$$

FIGURE 1

**ENTRAINMENT AS A FUNCTION OF
FLOW RATE RATIOS AND APPROACH TO FLOODING**

FIGURE 2
FLOODING CAPACITY FOR SIEVE AND BUBBLE TRAYS
AS A FUNCTION OF
FLOW RATE RATIOS AND TRAY SPACING

where ρ_1 = liquid density, lb/ft³
 σ = surface tension, dyne/cm

This correlation is based on the performance of non-foaming systems. Designs are usually based on velocities calculated to be less than 80% of flooding; with foaming systems, less than 70% is used.

The detailed tray design - the layout of holes for vapor passage, liquid travel and descent, weir heights, etc., is fixed by considerations of tray hydraulics. The fundamental problem in the scale up of tray hydraulics is summarized in Table 1, where it is shown that liquid cross flow velocities (weir overflow rates) increase with diameter at a constant vapor velocity (F Factor), since the former is a function of D while the latter depends on D². Since not only entrainment but tray efficiency are evidently functions of liquid rates, caution must be used in taking results from small columns and using them directly in large ones. As is the case with packed towers, system efficiency can not be evaluated independently of system hydraulics.

Typically, detailed tray design efforts involve a trial-and-error procedure in which a configuration is assumed and the hydraulic response is then checked using established correlations. Once proper hydraulics have been obtained, mass transfer efficiency is then checked using models which comprehend the effects of physical properties as well as the imposed hydraulic conditions.

A typical sequence of calculations for establishing a detailed layout for cross flow sieve trays is summarized below and illustrated with numerical

TABLE I

LIQUID FLOW RATES AS A FUNCTION OF

COLUMN SIZE AT CONSTANT VAPOR VELOCITY

Column Diameter	2"	6"	5'	15'
F, ft/sec(lb/ft ³) ^{1/2}	1.5	1.5	1.5	1.5
Vapor Flow, PPH ⁽¹⁾	65	580	57,900	521,000
Liquid Flow, GPM ⁽²⁾	.13	1.16	115.8	1042
Weir Length ⁽³⁾	1.5"	4.5"	45"	135"
Weir Overflow Rate, GPM/ft	1.04	3.09	30.9	92.6

(1) Steam at 120 psig

(2) For L/G = 1, liquid specific gravity=1.

(3) For 12% downcomer area, segmental downcomer.

examples in Table IV:

- Determine the column traffic (liquid and vapor rates).
- Assume a tray spacing, typically 24" - 36" in large columns.
- Given flow rates, densities, and spacing, determine tower capacity factor and correct for surface tension effects.
- Assume a downcomer area and tray arrangement, e.g., use cross flow, return flow, double cross flow, etc. Note that counter flow trays (no downcomers) and proprietary designs can be used to extend capacity ranges.
- Select an operating rate as a percent of flooding velocity; typically, 70-80% is used.
- Determine the level of entrainment for the assumed configuration and verify its suitability. If too high, increase tray spacing and/or decrease velocities.
- Assume a hole layout, hole diameter, pitch, % free area.
- Calculate hole velocities and hole pressure drop. Hole velocities will be limited to prevent "jetting".
- Assume an overflow weir height, typically 1-3".
- Calculate the pressure drop due to surface tension effects (which is typically quite small).
- Calculate the height of clear liquid overflowing the downcomer weir using a modified Francis formula.
- Determine the tray aeration factor or froth density which should be $.55 < \beta < .9$.

- Determine the total pressure drop by summing the individual contributions.
- Check for instability due to weeping by comparing calculated orifice and surface tension pressure drops with those predicted at the onset of weeping. Higher hole velocities (low % free areas) retard the onset of weeping.
- Check for instability due to priming by comparing calculated foam heights with assumed tray spacing. Enough clearance must be left to allow for disengagement of entrainment.
- Calculate the tray hydraulic gradient (which should be quite small unless liquid rates are very high).
- Assume a clearance under the downcomer apron, typically equal to or less than the weir height, and calculate pressure drop in the downcomer.
- Calculate the back up pressure drop in the downcomer by summing tray and downcomer components.
- Check the downcomer back up to insure that it is less than downcomer height. If too high, lower pressure drops and/or higher tray spacing are required.
- Check downcomer residence times to insure that adequate vapor/liquid disengaging time is provided.

The calculations show, for the plate designs chosen, that reasonable configurations leading to good contact (high froth heights) and stable operation (no weeping, low entrainment) will be possible for field pilot and commercial size columns, at least for non-foaming systems. They also

show the influence of liquid hydraulics; a weir overflow height of 3" is rather high for the 10^6 PPH case, and a double cross flow tray might be used effectively. For the lab scale operations, with fixed boiler capacity, the tray configurations (% open area) tend to be outside those generally used commercially, while pressure drops, entrainment levels, and froth heights are relatively low and contact times are shorter than those in the commercial columns. Thus, all else equal, one would expect significantly different mass transfer results at comparable vapor capacities in the pilot and commercial scale columns.

Trayed Column Design - Efficiency

The number of trays required in a given application is determined by the number of ideal stages required and the actual trays' approach to ideality - the tray efficiency.

The number of ideal stages required is determined by the vapor liquid equilibria in the system, the degree of composition change required (inlet/outlet composition), and the system mass balance (liquid/gas flow rate ratios). The number of stages may be determined analytically for certain simplified cases, for example at total reflux with constant relative volatility by the Fenske equation. The McCabe - Thiele approach is graphical, plotting the equilibrium curve and the operating line - which is an expression of the overall mass balance in the system given the selected L/V and terminal compositions - and "stepping off" the number of equilibrium stages which join equilibrium and operating lines. However, some definition of tray efficiency is needed to relate theoretical stage and actual tray requirements.

The usual approach is to attempt to determine point or local efficiencies on the tray. These should be a function of tray hydraulics (bubble size, liquid/vapor contact time, degree of local turbulence, etc.) and system physical properties (diffusivities, viscosities, partial pressure driving forces, etc.). Then point efficiencies are related to an overall tray efficiency by considering the effects of entrainment, which decreases efficiency, and fluid mixing on the tray (and in the gas phase) which may increase or decrease efficiency.

Entrainment is estimated using correlations such as Figure 1 and "dry" plate efficiencies converted to "wet" plate efficiencies using the relation:

$$E_a = E_{mv} / (1 + eVEmv/L)$$

where

E_a is the tray efficiency corrected for entrainment.

E_{mv} is the calculated (dry) tray efficiency.

V, L are vapor and liquid mass flow rates.

e = entrainment, mass of liquid/mass dry vapor.

The effect of liquid hydraulics on the relation between point (E_{og}) and tray efficiency depends on the model chosen to describe liquid flow as well as the system equilibrium relationships. For plug flow of liquid across the tray (not a good assumption), the problem can be solved analytically; a graphical solution is shown in Figure 3. Various mixing models can be constructed to estimate the effects of backmixing, the usual approach being to define a Peclet number using an eddy diffusivity or

FIGURE 3

RELATIONSHIP BETWEEN POINT AND TRAY EFFICIENCY

FOR PLUG FLOW ON THE TRAY

backmixing coefficient which would be determined experimentally. The solution of one such approach is shown in Figure 4.

Three important considerations arise from using these models:

- Entrainment has a more pronounced effect in designs with high efficiency than with low.
- Both the plug flow and backmix models presented (Fig. 3,4) show tray efficiencies always higher than point efficiencies. This may not be so if, for instance, there is short circuiting of liquid on the tray.
- For systems in which the slope of the equilibrium line is zero, point and tray efficiencies will be equal.

The relationships between system properties, tray hydraulics, and point efficiencies are obviously the keys to determining tray efficiencies. The greatest body of experience in this area on trays of commercial size is not generally available, being considered proprietary information by industrial users and tray manufacturers. Even in interpreting available laboratory data, however, two distinct approaches are possible: the classic two-film resistance approach and one based on penetration theory. In either case, the object would be to relate observed mass transfer rates to tray hydraulics and system properties.

The use of the two-film approach is best illustrated by considering the procedures developed for bubble cap trays (3). The number of transfer units on a tray is determined formally in the same way as for packed towers (1). The $k_g a$ term is now evidently a function of tray hydraulics and the

FIGURE 4

RELATIONSHIP BETWEEN POINT AND TRAY EFFICIENCY

WITH BACKMIXING ON THE TRAY

characteristic length, z , a function of froth height. As with packing, the number of transfer units can be defined using interface or overall composition driving forces. Then, if the liquid is completely mixed and the vapor is unmixed vertically, the local mass transfer equation can be solved analytically and the solution cast in terms to relate the transfer units obtained to efficiency by the relation:

$$E_{og} = 1 - \exp(-N_{og})$$

where

$$E_{og} = \text{point efficiency based on gas phase compositions.}$$

$$N_{og} = \text{number of overall gas phase transfer units.}$$

and

$$1/N_{og} = 1/N_g + mV/LN_1$$

where

$$N_g \text{ and } N_1 \text{ are gas and liquid phase transfer units.}$$

m is the slope of the equilibrium line.

V, L are vapor and liquid mass flow rates.

If all mass transfer resistance is in the vapor phase, $N_{og} \equiv N_g$. This implies negligible resistance in the liquid phase, negligible liquid phase concentration differences, a high value of N_1 , and a low value for m since at equilibrium only a low concentration of the diffusing species can exist above the liquid of interest.

The values of the number of gas phase transfer units and point efficiencies for the gas phase controlling case are summarized in Table II for the tray designs postulated in Table IV. These values are indicative only of general trends since the specific correlations were

TABLE II
POINT EFFICIENCIES⁽¹⁾ AS A FUNCTION OF
TRAY HYDRAULICS⁽²⁾

Column Diameter	2"	4"	6"	5.5'	15'
Steam Flow Rate, PPH	58	180	180	10 ⁵	10 ⁶
h_w , Weir Height, inches	1/2	3/4	1	2	3
Fv_a , Active Area Vapor F	2.03	1.38	.62	2.78	3.76
Q, Liquid Flow Rate, GPM	.13	.36	.36	200	2000
W_a , Ave Liquid Flow Width, ft.	.15	.29	.44	4.84	13.2
$N_g^{(3)}$, No. of Transfer Units	.22	.42	.63	.95	3.31
E_g , Point Efficiency	.20	.34	.47	.61	.96
E_g at the Limits of the Correlation	.30	.40	.46	.50	.55

(1) Calculated using a correlation for bubble cap trays, reference (3).

(2) For details of the tray design and hydraulics, see Table IV.

(3) $N_g = (.766 + .166 h_w - .29 Fv_a + .0217 Q/W_a)/(N_{sc})^{.5}$ $N_{sc} = 1.3$

developed for small, bubble cap trays, not sieve trays. The point efficiencies would also represent overall tray efficiencies in this case, since m is taken to approach zero, in which case liquid mixing is unimportant (Figures 3,4). The higher efficiencies predicted for the larger columns is a reflection of the dominating influence of liquid flow rate. The calculated efficiency at the limit of the correlation restricts the values of the parameters to those actually tested, which are significantly lower (for F_{va} and Q/Wa) than those calculated for the trays chosen.

The prediction of point efficiency from mass transfer rates using penetration theory is not as well documented as the two-film resistance approach. Assumptions are generally made with respect to the rate of new surface formation or exposure time and the overall mass transfer rates obtained by integrating the assumed distribution functions over all possible times. These approaches lead to a dependence of mass transfer rate on $(\text{diffusivity})^{1/2}$, not directly on diffusivity as in the two-film resistance approach. It has been suggested that the penetration approach may be more sound where contact times are short relative to a characteristic time defined in terms of diffusivity (5). The results of an efficiency calculation using a correlation (6) based on this approach are summarized in Table III. These predicted efficiencies are of the same order as those based on the two-film resistance approach, and predict the same type of response to variations in tray hydraulics.

TABLE III
POINT EFFICIENCIES⁽¹⁾ AS A FUNCTION OF
TRAY HYDRAULICS⁽²⁾

Column Diameter	2"	4"	6"	5.5'	15'
Steam Flow Rate, PPH	58	180	180	10 ⁵	10 ⁶
h, ⁽³⁾ Liquid Depth, cm	1.5	2.2	2.8	8.3	15.2
E _g , ⁽⁴⁾ Point Efficiency	.46	.55	.61	.82	.89
N _g , No. of Transfer Units	.62	.80	.94	1.71	2.21

(1) Calculated using a correlation derived from penetration theory, ref. 6.

(2) For details of the tray design and hydraulics, see Table IV.

(3) Liquid depth = weir height + weir overflow height.

(4) $E_g = 1/(1 + 3.7M/h\rho T)$ M = mol wt, ρ = density g/cc, T=Temp °K

General Considerations in Trayed Column Design

Carrying out the exercise of developing detailed tray designs for steam rates from one hundred to one million pounds per hour illustrates the design problems involved and suggests the range at least, of commercial design possibilities. These calculations (Tables I, II, III, IV) show:

- At the commercial and pilot scales, trayed and packed tower diameters will be comparable.
- At the commercial and pilot scales, it is reasonable to expect to obtain of the order of .5-2.5 transfer units per tray. Thus, for 90% removal, only one to five trays should be required.
- It is to be expected that lower efficiencies will be measured on lab scale equipment, unless the tray designs are chosen to maintain high liquid hold ups. This would require weir heights which are quite high in relation to column diameters.

These considerations will apply equally as well to any of the proprietary tray designs available (valve trays, counter flow sieve trays, bubble cap trays, etc.).

Other types of trays might also be considered, such as disk-and-donut or shower trays, for special purposes, and specific design methods must be used to determine hydraulics and efficiency. In general, these (and other) types of devices trade an advantage in a given area, e.g., low pressure drop, with a disadvantage in another, e.g., low efficiency.

It is likely that in this case, where apparently only a few conventional trays would be required, the final tray design will be selected to minimize operational problems. That is, a design which proves

resistant to fouling, is easily cleaned if fouled, and/or minimizes foaming would be chosen in preference to a more efficient, higher capacity design with limited operating cycles between cleaning. While indications of tray operability can be obtained in the lab, a final selection of commercial tray designs will require pilot testing on a relatively large scale and for extended periods of time.

TABLE IV
SUMMARY OF TRAY DESIGN CALCULATION

TASK	FUNCTION CALCULATED	SOURCE, METHOD, OR PROCEDURE	REF	Lab 2" Dia.	Lab 4" Dia.	Lab 6" Dia.	Field Pilot	Commer cial
1	Steam flow rate, L/V, operating temp. & press, liq., and gas density, viscosity, surface tension.	Problem definition: Flow rate L/V=1 T=350°F, P=120psig $\rho_v=0.3 \text{ lb/ft}^3$, $\rho_l=61 \text{ lb/ft}^3$ $\mu_l=.24 \text{ cps}$, $\sigma=45 \text{ dyne/cm}$.		as req.	as req.	as req.	10 ⁵ pph	10 ⁶ pph
2	Tray spacing, H_t , inch.	Design parameter.		12"	12"	12"	24"	36"
3	Flow parameter, $L/V(\rho_v/\rho_l)^{1/2}$	To establish flooding capacity.		.07	.07	.07	.07	.07
4	Capacity parameter C.	Function of velocity at flooding, graphical corre- lation.	7	.21	.21	.21	.34	.45
5	F factor at flooding, correct for surface tension.	$F_{\text{flood}} = Cx(\rho_l - \rho_v)^{1/2} x (\sigma/20)^{.2}$ based on net flow area.		1.92	1.92	1.92	3.12	4.12
6	Downcomer area.	Design parameter. For 12% area $L/D = .764$ $H/D = .178$.		12%	12%	12%	12%	12%
7	Total area F at 80% flood in net area.	$F_{\text{flood}} \times .8 \times .88$		1.35	1.35	1.35	2.19	2.90
8	Column diameter given flow or flow rate given col dia.	$D = (\text{pph} \times (V_o)^{1/2} / 2827F)^{1/2}$ or $\text{pph} = 2827FD^2 / (V_o)^{1/2}$.		58pph	232pph call 180	523pph call 180	5.4' call 5.5	14.9' call 15'
9	% of flooding.	Based on F_{flood} (Task 5).		80	62	28	.77	79
10	Entrainment parameter $\psi = e/(L+e)$	Function of approach to flooding, graphical correlation.	7	.042	.013	.002	.036	.039

TASK	FUNCTION CALCULATED	SOURCE, METHOD, OR PROCEDURE	REF	Lab 2" Dia.	Lab 4" Dia.	Lab 6" Dia.	Field Pilot	Commercial
11	Tray hole layout hole dia., d_h , and pitch.	Design parameter.		3/16x9/16"	3/16x5/8"	3/16x3/4"	3/8x1"	3/8x7/8"
12	% hole in active area.	Design parameter; Δ pitch.		10.0	8.2	5.7	12.8	16.6
13	Hole F/hole velocity, ft/sec.	Based on hole/col. area. $U_h = F/\rho_v^{1/2}$.		20.3/ 37.1	16.8/ 30.8	10.9/ 19.9	21.7/ 39.7	22.6/ 41.3
14	Dry plate pressure drop h_o , inches.	$h_o = .186(U_h/Co)^2 \rho_v/\rho_l$ orifice coefficient Co determined graphically = .72	8	2.36"	1.67"	0.76"	2.78"	3.00"
15	Weir height.	Design parameter		1/2"	3/4"	1"	2"	3"
16	Surface tension pre- ssure drop h_σ , inches.	$H_\sigma = .04 / \rho_l^{1/2} d_h$		.16"	.16"	.16"	.08"	.08"
17	Outlet weir overflow rate Q/L_w , gpm/ F_t .	Overflow rate = steam flow/500 weir length = .764 x col dia.		1.02	1.41	.94	48	174
18	Outlet weir overflow crest height h_{ow} , in.	$h_{ow} = .48 F_w(Q/L_w)^{.67}$ weir correlation factor F_w by graphical correlation	9	.10"	.12"	.09"	1.28"	2.99"
19	Active area F / velocity.	100/(100-2 x downcomer % area) times total area $F(T7)/$ total area velocity.		2.03/ 3.71	1.38/ 2.53	0.62/ 1.13	2.78/ 5.09	3.76/ 6.88
20	Aeration factor β $\beta = \frac{\psi+1}{2}$ $\psi = \frac{\text{clear liq. ht.}}{\text{foam ht.}}$	β obtained by graphical correlation with active area F .	10	.59	.61	.68	.58	.56
21	Total tray pressure drop ΔH_t , inches.	$\Delta H_t = h_h + h_\sigma + \beta x$ ($h_w + h_{ow}$)		2.87"	2.36"	1.66"	4.76"	6.43"

TASK	FUNCTION CALCULATED	SOURCE, METHOD OR PROCEDURE	REF	Lab 2" Dia.	Lab 4" Dia.	Lab 6" Dia.	Field Pilot	Commer cial
22	Weeping check: $(h_o + h_\sigma)_{calc} (h_o + h_\sigma)$ weeping > 1 for given $h_w + h_{ow}$.	$h_w + h_{ow}$ from (T15) + (T18), $h_o + h_{cal}$ (from (T14) + (T16)). σ Weeping point given $h_w + h_{ow}$ from graphical correlation.	11	12.6	6.1	2.6	4.1	1.8
23	Foam height h_f , in. check $h_f < H_t$	$h_f = \beta (h_w + h_{ow}) / (2\beta - 1)$ H_t from (T2)		1.2"	1.5"	1.4"	11.9"	28"
24	Hydraulic gradient check Δ , inches.	A complex procedure is req., including calculating foam velocities, Reynolds numbers, & friction factor. Magnitude of Δ is usually quite low.	12	.000015"	.000015"	.000015"	.000007"	.000012"
B-24 25	Clearance under downcomer, inches underflow area, F_t .	Design parameter		3/8"/ .001 sq. ft.	1/2"/ .005 sq. ft.	3/4"/ .018 sq. ft.	1.5"/ .525 sq. ft.	2.5"/ 2.39 sq. ft.
26	Downcomer pressure drop h_d , inches.	$h_d = 3 \times 10^{-6} (Q/A)^2$. A is downcomer underflow area, $F_t^2 Q$ from (T17).		.05"	.01"	negl	.44"	2.1"
27	Downcomer backup pressure drop H_d , inches.	$H_d = \Delta H_t + h_w + H_{ow} + \Delta + h_d$		3.52"	3.24"	2.75"	8.48"	14.52"
28	Downcomer backup liquid height; check $< H_t$	Backup $\sim H_d / \beta$ from (T27), (T20), (T2)		6"	5.2"	4"	15"	26"
29	Downcomer residence time, sec. Check > 3 sec.	$= \frac{\text{col area} \times \% \text{ downcomer area} \times H_t \times 4.5}{Q}$ from (T2), (T6), (T17).		9 sec	13 sec	29 sec	4.5sec	5.7 sec

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APPENDIX C

ABSORPTION OF CONSTITUENTS OTHER THAN H₂S IN THE

COPPER SULFATE SCRUBBING PROCESS

APPENDIX C

ABSORPTION OF CONSTITUENTS OTHER THAN H₂S IN THE COPPER SULFATE SCRUBBING PROCESS

SUMMARY

The fraction of a second constituent absorbed may be expressed simply in terms of the fraction of a reference compound absorbed and the two absorption rate constants. For low concentrations and low equilibrium pressures, the relation is:

$$\text{Fraction absorbed second constituent} = \psi_2 = 1 - (1 - \psi_{\text{REF}})^{k_2/k_{\text{REF}}}$$

where the k 's are the absorption rate constants.

This simplification is limited to non-interacting gases for which:

$(1 - \psi) P^\circ / P^* \gg 20$ where P° and P^* are the inlet and equilibrium pressures of the constituents in the scrubber.

Under typical process conditions, 90% removal of H₂S should also result in 94% removal of NH₃.

Determination of Relative Mass Transfer Rates

The differential equation describing the local rate of mass transfer for a constituent j from a gas stream to a scrubbing liquid is (1)

$$dn_j = k_{gj} a_i (P_{gj} - P_{ij}) dV$$

If the mass transfer processes are limited by gas phase resistances, the partial pressure at the interface will be nearly equal to the equilibrium pressure above the solution. That is:

$$P_{ij} = P_j^*$$

Then comparing the rates of mass transfer for two non-interacting constituents from the gas in the same differential element gives:

$$dn_1/dn_2 = k_1(P_1 - P_1^*)/k_2(P_2 - P_2^*) = k_1\Delta P_1/k_2\Delta P_2$$

If these equations are integrated over the entire volume of the scrubber, the sums of the dn_j 's are δn_j 's, the total mass of constituent j absorbed. The integration of the local partial pressure driving forces, ΔP_j 's, leads to definition of an overall driving force expressed in terms of the terminal ΔP 's: the log mean ΔP

$$\Delta P_{1mj} = (\Delta P_j^{\circ} - \Delta P_j^e) / \ln(\Delta P_j^{\circ} / \Delta P_j^e)$$

where:

$$\Delta P_j^{\circ} = P_j^{\circ} - P_j^*, \quad \Delta P_j^e = P_j^e - P_j^*$$

and the superscripts $^{\circ}$ and e refer to inlet and outlet conditions.

Defining the fraction absorbed, ψ_j , as $\delta n_j / n_j^{\circ}$ and noting that P_j^* cancels in the numerator of ΔP_{1mj} , gives:

$$\frac{\psi_1}{\psi_2} = \frac{n_2^{\circ}}{n_1^{\circ}} \times \frac{k_1}{k_2} \times \frac{(P_1^{\circ} - P_1^e)}{(P_2^{\circ} - P_2^e)} \times \frac{\ln(\Delta P_2^{\circ} / \Delta P_2^e)}{\ln(\Delta P_1^{\circ} / \Delta P_1^e)}$$

For lean gases $P_j^e = P_j^{\circ} (1 - \psi_j)$ so that $P_j^{\circ} - P_j^e = \psi_j P_j^{\circ}$ and $P_j^{\circ} = (n_j^{\circ} / \Sigma n) P$. Substituting gives:

$$\frac{\psi_1}{\psi_2} = \frac{n_2^{\circ}}{n_1^{\circ}} = \frac{k_1}{k_2} \times \frac{\psi_1 n_1^{\circ} / \Sigma n}{\psi_2 n_2^{\circ} / \Sigma n} \times \frac{\ln(\Delta P_2^{\circ} / \Delta P_2^e)}{\ln(\Delta P_1^{\circ} / \Delta P_1^e)}$$

so that:

$$\frac{k_2}{k_1} \ln(\Delta P_1^{\circ} / \Delta P_1^e) = \ln(\Delta P_2^{\circ} / \Delta P_2^e)$$

Taking antilogs gives:

$$\frac{P_2^{\circ} - P_2^*}{P_2^e - P_2^*} = \frac{P_2^{\circ} - P_2^*}{P_2^{\circ}(1 - \psi_2) - P_2^*} = \left[\frac{P_1^{\circ} - P_1^*}{P_1^{\circ}(1 - \psi_1) - P_1^*} \right]^{k_2/k_1}$$

or:

$$\frac{1 - P_2^*/P_2^{\circ}}{(1 - \psi_2) - P_2^*/P_2^{\circ}} = \left[\frac{1 - P_1^*/P_1^{\circ}}{(1 - \psi_1) - P_1^*/P_1^{\circ}} \right]^{k_2/k_1}$$

For typical gas compositions expected in geothermal steams, $P_1^o \sim P_2^o \sim 10^{-3}$ atm. The equilibrium pressures of H_2S and NH_3 above the anticipated scrubbing solutions, however, are very low, ranging from 10^{-10} to 10^{-5} atm respectively. Under these conditions P_1^*/P_1^o can be neglected if $1-\psi_1$ is not also small. Under these conditons:

$$1/(1-\psi_2) \approx (1/(1-\psi_1))^{k_2/k_1}$$

or:

$$1-\psi_2 = (1-\psi_1)^{k_2/k_1}, \quad \psi_2 = 1-(1-\psi_1)^{k_2/k_1}$$

Determination of Mass Transfer Co-efficients

A knowledge of the ratio of the mass transfer coefficients of the two constituents is required to determine the relative fractions absorbed. This can be obtained directly experimentally in a simultaneous absorption experiment which would, of course, also give the relative fractions absorbed directly.

In the absence of such an experiment, the ratio can still be predicted based on a knowledge of the physical properties of the system. Correlations have been established for predicting mass transfer coefficients which are of the form: (2)

$$\frac{G}{k_{gj}\Pi} \propto N_{Re}^n N_{Scj}^m \quad n \sim 1/3, m = 2/3$$

Where N_{Re} is the gas Reynolds number, N_{Scj} is the Schmidt number for each constituent, Π is the total pressure, and G is the total gas mass velocity. Taking ratios gives:

$$k_{g2}/k_{g1} = (N_{Sc1}/N_{Sc2})^{2/3} = (D_2/D_1)^{2/3}$$

This approach is valid only for cases in which the components do not interact in the gas phase. Schmidt numbers or diffusivities, D_j , can be estimated by well known techniques (3), and for the process conditions expected here lead to the ratio:

$$k_{\text{gNH}_3}/k_{\text{gH}_2\text{S}} = (1.3)^{2/3} = 1.2$$

Thus, subject to the limitations that $P_j^*/P^\circ \ll 1$ and $1-\psi_j \gg P_j^*/P^\circ$, for 90% removal of H_2S , the fraction NH_3 removed is:

$$\psi_{\text{NH}_3} = 1 - (1 - 0.9)^{1.2} = 1 - 0.065 = 0.935$$

Check on Equilibrium Pressures, H_2S and NH_3

The free energies estimated for the reactions of interest in the removal of H_2S and NH_3 under expected process conditions are:

so for the H_2S precipitation, $K = 600 \times 10^6$ while for NH_3 protonation, $K = 1.4 \times 10^6$.

The partial pressure of the gases above the scrubbing solutions are:

$$P_{\text{H}_2\text{S}}^* = 1.67 \times 10^{-9} (\alpha_{\text{H}^+})^2 / \alpha_{\text{Cu}^{++}}$$

$$P_{\text{NH}_3}^* = 7.19 \times 10^{-7} \alpha_{\text{NH}_4^+} / \alpha_{\text{H}^+}$$

It is anticipated that scrubbing will be carried out in a solution at pH 1-2 with a copper content of the order of 1g/l. If the initial (mass) concentrations of H_2S and NH_3 and scrubbing efficiencies are comparable, and the make-up copper sulfate solution is introduced at high strength + (>50g/l Cu) with low concentrations of $(\text{NH}_4)_2\text{SO}_4$, the concentration of NH_4^+ in the scrubbing solutions will be of the order of 25g/l, assuming $(\text{NH}_4)_2\text{SO}_4$ is completely disassociated. Under these conditions

$$\alpha_{\text{Cu}^{++}} = .016, \quad \alpha_{\text{NH}_4^+} = 1.39, \quad \alpha_{\text{H}^+} = 0.1 \text{ (pH 1)}$$

so that:

$$P_{H_2S}^* \approx 1.0 \times 10^{-9} \text{ atm}, \quad P_{NH_3}^* \approx 1.0 \times 10^{-5} \text{ atm}$$

With inlet concentrations of 210 ppm each of H_2S and NH_3 in steam at 9.1 atmospheres total pressure, the inlet partial pressures are:

$$P_{H_2S}^o \approx 1.0 \times 10^{-3} \text{ atm}, \quad P_{NH_3}^o \approx 2 \times 10^{-3} \text{ atm}$$

Clearly, for H_2S , P^*/P^o is negligible with respect to $1-\psi$ for all degrees of absorption of interest, and a significant deviation from the assumed operating conditions (to pH 0, copper contents of 0.1g/l) will not change this conclusion.

For ammonia, however, $P^*/P^o \sim .005$ for these conditions which is not negligible with respect to $1-\psi$ at high degrees of removal. Furthermore, higher pH's (to say 2) and higher concentrations of $(NH_4)_2SO_4$ (which could result from recycling purge streams or scrubbing streams with unusually high NH_3 contents) could result in the occurrence of an equilibrium ammonia pressure which would be high enough to limit ammonia absorption to relatively low ($\psi < .9$) values.

Thus, the comparison of relative rates of removal of constituents from the gas stream should be checked to insure that equilibrium back pressures do not limit the maximum possible fraction removed for the overall material balance conditions assumed. This type of estimate can be made for any constituent present provided that diffusivities are known (or estimated) and that equilibrium pressures can be estimated above the solutions from known Henry's Law constants or free energies for any reactions involved.

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APPENDIX D

COMPOSITIONS AND STRUCTURES OF SULPHIDES OF COPPER

From "Leaching and Reduction in Hydrometallurgy,"
A. R. Burkin, Ed., The Institution of Mining and
Metallurgy, London (1975), p. 37.

APPENDIX D

COMPOSITIONS AND STRUCTURES OF SULPHIDES OF COPPER

The solid-state phase equilibria in the Cu_2S – CuS region of the phase diagram have been studied by Djurle and by Roseboom by X-ray diffraction methods. The materials described below exist.

Chalcocite

The composition of chalcocite is approximately Cu_2S . The orthorhombic low-temperature form, $\alpha\text{-Cu}_2\text{S}$, has a unit cell containing 96 formula units with $a = 11.881 \text{ \AA}$, $b = 27.323 \text{ \AA}$, $c = 13.491 \text{ \AA}$, and the sulphur atoms in hexagonal close packing. The exact distribution of the copper atoms is not known. The orthohexagonal sub-cell of orthorhombic chalcocite contains four formula units and has $a' = 3.961 \text{ \AA}$, $b' = 6.830 \text{ \AA}$, $c' = 6.746 \text{ \AA}$. The copper deficiency must, according to Roseboom, be less than would give $\text{Cu}_{1.999}\text{S}$ at 25° , or $\text{Cu}_{1.998}\text{S}$ at 180° .

At $103.5^\circ \pm 1.5^\circ$ $\alpha\text{-Cu}_2\text{S}$ changes to a hexagonal form, $\beta\text{-Cu}_2\text{S}$, with cell dimensions at 152° $a = 3.96 \text{ \AA}$, $c = 6.72 \text{ \AA}$, and the sulphur atoms in hexagonal close packing. The copper atoms are distributed statistically between the three kinds of interstitial sites – trigonal, digonal and tetrahedral. The orthorhombic–hexagonal transformation is reversible, and a substructure–superstructure relationship exists between the two unit cells. β -chalcocite exhibits a range of composition from Cu_2S to about $\text{Cu}_{1.988}\text{S}$ at 105° , but the range decreases with increasing temperature and no deviation from the composition Cu_2S could be detected at 180° . β -chalcocite cannot be quenched to room temperature, and it has never been observed as a mineral. It is stable up to about 435° , where it changes to a high digenite of composition Cu_2S .

Djurleite

Djurle reported the composition of djurleite to be $\text{Cu}_{1.96}\text{S}$ and stated that there were three forms – a low-symmetry form, now called djurleite, a tetragonal form, which was probably metastable, and a high-temperature form. Roseboom found djurleite to be stable only below $93^\circ \pm 2^\circ$ and observed that the tetragonal form appeared to be metastable. Between 93 and 350° material with the composition $\text{Cu}_{1.96}\text{S}$ produced a mixture of high digenite and hexagonal chalcocite.

The true composition of djurleite is now said to be approximately $\text{Cu}_{1.93}\text{S}$. The high-temperature tetragonal phase reported for the composition $\text{Cu}_{1.96}\text{S}$ is also stated to be stable between $\text{Cu}_{1.95}\text{S}$ and Cu_2S at 90 – 140° , but the transition to the tetragonal phase was extremely sluggish.

Djurleite is orthorhombic with a unit cell containing 128 formula units, and the sulphur atoms in hexagonal close packing.

Cu_xS

When a crystal of cadmium sulphide was placed in a solution of cuprous chloride, cation exchange occurred and a crystal of copper sulphide was formed. This took place via the formation of chalcocite, djurleite and Cu_xS structures, where x was between 1.96 and 1.8. The last is a

previously undescribed hexagonal or pseudo-hexagonal phase with $a = 15.475 \pm 0.010 \text{ \AA}$, $c = 13.356 \pm 0.010 \text{ \AA}$.

Digenite

At room temperature the composition range of digenite is $\text{Cu}_{1.765}\text{S}$ to $\text{Cu}_{1.79}\text{S}$. The low-copper limit is not affected by temperature, whereas the copper-rich limit changes to $\text{Cu}_{1.83}\text{S}$ at 83° , at which temperature it inverts to high digenite. Digenite of composition $\text{Cu}_{1.8}\text{S}$ is unstable below about 50° .

The sulphur atoms in digenite are in cubic close packing, with the copper atoms situated along the diagonals of the cube. The sub-cell dimension is $a = 5.555 \text{ \AA}$ at composition $\text{Cu}_{1.765}\text{S}$ and $a = 5.571 \text{ \AA}$ at composition $\text{Cu}_{1.79}\text{S}$.

By use of single crystal methods four different superstructures have been observed in synthetic digenite. Three of these were metastable and inverted to the stable type after periods ranging from several days to several months.

High digenite

High digenite is formed when digenite is heated to a temperature which depends on the composition of the digenite, but is between 76 and 83° . The reflections due to the superstructure disappear and the remaining reflections can all be indexed by use of a cubic cell of side about $5.56 \text{ \AA}$. The inversion is readily reversed and high digenite cannot be quenched to room temperature. It has not been observed as a mineral.

Covellite

The composition of covellite is CuS with, according to Roseboom, no deviation from that stoichiometry, and it is stable at temperatures up to 507° , where it transforms to high digenite and a sulphur-rich liquid. The hexagonal unit cell contains six formula units, with $a = 3.792 \text{ \AA}$, $c = 16.344 \text{ \AA}$. Two-thirds of both the copper and sulphur atoms occupy positions in sheets parallel to (0001) , these sheets being separated by the remainder of the atoms.

'Blaubleibler' covellite

The accepted name for copper-rich covellite is blaubleibler covellite. Roseboom considered that it remained to be proved whether such material is more stable than a mixture of covellite and sulphur-rich digenite, since he did not observe blaubleibler covellite. It is a well-known phase in mineralogy, however, and, according to Moh, is best represented as Cu_{1+x}S , where x is 0.05 – 0.10 . He reported it to be stable up to 157° ; above this temperature it transformed to a mixture of normal covellite and digenite.

Frenzel found that blaubleibler covellite formed by leaching chalcocite could have a copper excess up to the composition $\text{Cu}_{1.4}\text{S}$. The X-ray diffraction pattern of the mineral resembled that of normal covellite, although the relative intensities of reflections for the two structures differed.

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