CONTROL OF HYDROGEN SULFIDE EMISSION
FROM GEOTHERMAL POWER PLANTS

Final Report

Volume I

Summary of Results

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Prepared for

The United States Department of Energy
under Contract No. EY-76-C-02-2730.*000

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SUMMARY

A program of laboratory and pilot plant tests, detailed process and project engineering work, and process engineering and economic evaluation studies has been carried out in support of the design of a test facility for demonstration of the copper sulfate process for the removal of hydrogen sulfide from geothermal steam at turbine upstream conditions.

A demonstration plant has been designed which is capable of removing 99% of the H_2S , 90% of the NH_3 , and significant amounts of H_3BO_3 and particulates from 100,000 lb/hr of geothermal steam of The Geysers composition. Criteria for the mechanical and process design of the scrubber have been confirmed in field tests of fifty hours duration on an eight-inch diameter scrubber at PG & E's Unit No. 7, The Geysers. Design criteria for other items of equipment and for operations ancillary to scrubbing are based on laboratory-scale tests on solids returned from the 1000 lb/hr field tests or on solutions simulating those expected in the demonstration plant.

Austenitic stainless steels will be passivated by the presence of 1-2 g/l of copper at scrubber conditions if the acidity of the scrub solution is limited to $pH \geq 1$. Since C20Cb3 alloy maintains passivity at higher acidities than T304 or T316, it has been specified as the material of construction for the demonstration plant scrubber and its trim, insofar as possible. However, since all stainless steels are subject to crevice corrosion, titanium has been specified as a back-up material. Type 304 stainless is suitable for all uses up to at least $125^\circ C$, and composites of fiberglass reinforced vinyl esters are suitable for use at temperatures up to at least $50^\circ C$ and for short term exposure up to $100^\circ C$.

The solids precipitated when geothermal steam is contacted with copper sulfate solutions at turbine upstream conditions consist of aggregates of fine particles of non-stoichiometric compounds with a composition Cu_nS , with $n \approx 1.6-1.9$. Copper sulfate can be regenerated by pressure leaching under rather mild process conditions, e.g., 99% regeneration can be obtained in 1-1/2 hours at $125^\circ C$ under an oxygen partial pressure of 100 psi without the formation of elemental sulfur. An agitated pressure leach reactor has been specified for the demonstration plant, which will be suitable for use with either air or oxygen. In addition, a slurry surge tank will be fitted with a gas-liquid contactor which will permit a pre-leaching step to be carried out at near ambient conditions if desired.

As expected, the fine, non-stoichiometric solids also proved to be amenable to regeneration by roasting under relatively mild process conditions, e.g., $400^\circ C$, 10-15 min residence time. The reaction products consist of basic copper sulfate salts which would be redissolved in hot acid prior to recycle. The feed material would require dewatering to at least 50% solids to permit autogenous roasting.

The solid aggregates settle rapidly and filter easily, but low slurry and cake densities are obtained. Cake moisture contents low enough to permit autogenous roasting will require the use of centrifuges. For the lower slurry densities appropriate for regeneration by leaching, a continuous decanter is the most cost effective device and will be used in the demonstration plant. Detention times of two minutes and upflow velocities of 30 ft/hr provide slurry densities up to 10% at overflow clarities of 100 ppm.

The scrubber specified for the demonstration plant will contain a single crossflow sieve tray since this style of contactor was shown to be least costly if high degrees of H_2S removal are required. Spray or shower tray columns or venturi contactor should be operable, and if a single stage venturi can achieve high removal efficiencies, it would be a very attractive alternative to a sieve tray column.

Whatever style of contactor is used, it will be necessary to control the acidity and copper content of the scrub solution to maintain both high degrees of H_2S removal and the passivity of stainless steel. A Teledyne photometric analyzer has proved, in laboratory tests, to be an effective, stable device for measuring the copper concentrations of simulated purge streams and will be used in the demonstration plant to control the flow rate of makeup copper sulfate to the scrubber. A Great Lakes pH analyzer with a suitable internal reference solution will be used to monitor the pH of the purge stream, which will be in the range $1 < pH < 2$.

The process and mechanical design criteria which were used to develop equipment specifications for the demonstration plant and the equipment specifications and descriptions have been assembled in a draft process engineering specifications document. An overall objective for the operation of the demonstration plant will be to verify the assumed criteria or to provide data for modifying them. A draft test plan and operating instructions document has also been prepared which contains information required for plant operations and data reduction and analysis. These draft versions will be updated and finalized when equipment purchases are made and operating experience has accrued.

A process engineering and economic evaluation of the process concept has been carried out for a commercial scale operation under The Geysers conditions. For a power plant consisting of two 55 MW turbine-generators, the system would consist of individual upstream scrubbers, with individual heat exchange and liquid-solid separation components. A common regeneration facility would service the two scrubbers. Regeneration would involve a sequence of near-ambient air preleaching, oxygen pressure leaching, and a polish leaching step to purge insoluble solids from the system. Soluble impurities would be removed following neutralization of the purge stream with ammonia and decopperization by solid ion exchange. The system material balance has been solved, and the results summarized graphically so that impact of operating on streams of differing composition or flow rate can be determined easily.

Equipment descriptions were developed for a 110 MW plant based on its material and energy balance and the design criteria used for the 100,000 lb/hr demonstration plant. Factored capital and detailed operating cost estimates were made, and a preliminary evaluation of the performance and costs of alternative abatement techniques was carried out. Fixed capital investment for a commercial plant capable of obtaining 99% H₂S removal, including removal from steam that is vented during turbine trip-outs, are estimated to be about \$50/kW. Direct operating costs are approximately 0.6 mills/kWh, and total operating costs, including capital recovery charges, are about 1.8 mills/kWh. These costs are significantly lower than for downstream abatement processes at comparable degrees of H₂S removal, since the latter will have to be supplemented by a stand-by vent stream treatment process.

I. INTRODUCTION

This report describes work, carried out for the United States Department of Energy under Contract No. EY-76-C-02-2730.*000, on the development of the copper sulfate process for the Control of Hydrogen Sulfide Emissions from Geothermal Power Plants. In this EIC-conceived process, hydrogen sulfide is scrubbed from the raw geothermal steam upstream of the turbine-generator.

The work, consisting of laboratory and pilot scale experiments and engineering evaluation and design studies, was carried out in two phases. Phase I consisted of laboratory scrubbing tests to demonstrate the feasibility of the process concept and included, in addition to steam scrubbing, brief liquid-solid separation, regeneration, and corrosion tests and a preliminary engineering evaluation and cost estimate for a commercial plant. The results of the first phase of the program are fully documented in the Annual Status Report for the period 1 June 1975 to 31 May 1976 under Contract No. E(11-1)-2730, and only the highlights of that effort will be repeated here.

The results of the program were sufficiently promising that the scope of the work was expanded in order to develop the design of a large, 100,000 lb/hr demonstration facility to be installed and operated in the field. The facility would contain all the essential elements of a complete process, would operate in a closed cycle, and would provide a demonstration of the process concept in sufficient detail to support a decision with respect to commercialization. The results of this second phase of the program, including additional laboratory work at EIC and pilot testing at The Geysers, as well as detailed process and project engineering work, are detailed in this report.

The report consists of three volumes: Volume I summarizes the background of the problem and the technical approach to its solution, the scope and results of the first-phase laboratory testing, the scope and results of the experimental and analytical studies carried out in the second phase, and a description of the configuration of the demonstration plant and the test plan for its operation.

Volume II presents the results, in detail, of the laboratory and pilot scale tests and of the process and project engineering work carried out in each task of the second phase of the program.

Volume III consists of the detailed test plan and operating instructions for the demonstration plant. It also contains the equipment specifications for the demonstration plant and the process and mechanical design criteria used in their selection.

II. BACKGROUND

A. The Hydrogen Sulfide Removal Problem in Perspective

The most common gaseous constituents of geothermal fluids are CO₂, H₂S, CH₄, H₂, and N₂. Ammonia and boric acid are sometimes present. Analyses vary from field to field, but there is also a large variation from well to well within a field, and for a particular well as fluid is withdrawn. In all cases, however, CO₂ is the major constituent of the noncondensable gases. Data for steam at The Geysers are given in Table I.

Table I

Range of Concentrations of Noncondensable
Gases in Steam at The Geysers

(Concentration in parts per million)

<u>Gas</u>	<u>Low</u>	<u>High</u>	<u>Average</u>
CO ₂	884	19,000	3,260
H ₂ S	5	1,600	223
CH ₄	56	1,320	194
NH ₃	56	1,060	194
N ₂	16	638	52
H ₂	18	190	56
C ₂ H ₆	3	19	10
Total	1,200	22,000	4,000

In absolute terms, the total daily discharge of H₂S by a geothermal power plant is appreciable. However, the H₂S 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 H₂S 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 is becoming legally obligatory, to control H_2S emissions in the development of geothermal power.

In any power generation mode operating directly 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 stream - 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 passes through the cooling tower.

If H_2S is not removed from the steam prior to condensation, it must be removed from both vent gas and condensate streams. Processes for removing H_2S from the vent gases, with its high CO_2 and H_2O contents, differ only in degree from those applicable to H_2S removal from the steam. While it is possible to remove H_2S from the condensate, when barometric condensers are used, concentrations are low, due to dilution by cooling water, so that driving forces are low; reagent consumption is high; and liquid-solid separation problems are formidable. Furthermore, reagents used to promote H_2S oxidation inherently cause corrosion in materials of construction used in normal cooling systems. Construction of the cooling loop with corrosion resistant materials is very costly, as is the substitution of surface for barometric condensers.

Furthermore, a very significant contribution to the total H_2S emission occurs during turbine down-time when raw steam is diverted to the atmosphere. A geothermal plant stream factor of 0.85, for example, generally means that the upper limit of H_2S abatement by downstream removal is 85%. In sum, for effective control of H_2S 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.

Current technologies for H_2S removal from gas streams (for example, in coal gasification) are not generally applicable to geothermal plants. For example, the Claus Process, which has been used industrially for many years, is only applicable to gas streams containing at least 20% H_2S . Other methods (e.g., the Rectisol Process) cannot operate in steam since the active reagents are water soluble or have boiling points below $100^\circ C$. Solid absorbents for H_2S (e.g., calcium carbonate (as dolomite), calcium oxide, zinc oxide, and iron oxide) cannot be used, either because of solubility or slow

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

kinetics at operating temperatures. In short, existing techniques are not suitable for removing H₂S from steam in geothermal plants.

B. 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 an alkaline solution is perhaps the simplest means of scrubbing H₂S from the steam, the attendant absorption of CO₂, generally present in large excess over H₂S, makes this a difficult approach. A brief catalog of relevant properties of noncondensable gases commonly found in geothermal steam is given in Table II. Nitrogen, not listed, is essentially inert.

Table II

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).

C. Outline of EIC Approach

The process under development by EIC Corporation is based on scrubbing H_2S from geothermal steam with a solution of a metal salt, the cation of which yields a very sparingly soluble sulfide precipitate. Initial considerations indicated $CuSO_4$ to be the most suitable salt for steam compositions having H_2S present in considerable excess over NH_3 . Where adequate NH_3 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 H_2SO_4 and $(NH_4)_2SO_4$. Carbon dioxide is not absorbed at the prevailing high solution temperature and low pH. The steady-state concentrations of H_2SO_4 and $(NH_4)_2SO_4$ in the recirculating slurry will be determined by the steam composition and 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 $(NH_4)_2SO_4$ 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 H_2S/NH_3 ratio in the steam.

In summary, scrubbing of geothermal steam prior to expansion or heat exchange for power generation is clearly the best and most direct strategy for H_2S emission control. Among potential scrubbing processes, removal and precipitation of H_2S as copper sulfide is the preferred approach. All of the process steps involve known chemistry and can be carried out with existing technology. As confirmed in the present laboratory and field development program, H_2S removal can be rapid and quantitative; furthermore, the small loss of steam enthalpy during scrubbing appears to be acceptable and would be offset by a small increase in system steam factor. The overall process economics appear to be favorable by comparison with proposed alternative control strategies.

OPTIONS:

SULFATION ROAST

OXIDATION LEACH

Fig. 2. CuSO_4 process for control of H_2S emissions.

III. PROGRAM SCOPE

A. General Considerations

The commercialization of new technology, such as that being developed in the effort here reported, required detailed documentation of the criteria by which the commercial system is to be designed and operated. A set of process engineering specifications for a commercial system includes, typically, the following components.

- Design requirements for the system (flow rates to be treated, compositions, required removal rates, etc.)
- Material balance design bases (compositions of key streams, reagents, etc.)
- Energy balance design bases (temperatures and states of key streams, thermodynamic properties, etc.)
- Reference case material balance
- Reference case energy balance
- Process description (a sectionalization of the process describing the objectives and requirements for each processing operation within the integrated system)
- Detailed equipment specifications and their design bases (mechanical and process descriptions for major items of equipment and the laboratory and the field test data which support the rating criteria used)
- System control engineering
- Safety aspects
- Utilities requirements
- System piping and instrumentation diagrams
- Assembly drawings as required
- Other information appropriate to specific installations.

Such a set of process engineering specifications can be used as a basis for executing the detailed engineering required for construction of a unit at a given site. Sufficient data are available to make reasonable extrapolations in composition and removal requirements with certainty.

Flow rates may be extrapolated over an order of magnitude with reasonable confidence. Sufficient information will be available on system operability, so that prudent design factors may be established to insure high stream factors and minimum downtime in a commercial system.

The development of detailed process design specifications requires that data be obtained on a representative system; this implies using equipment of a size suitable for obtaining reasonable data and, also, using working fluids which are representative of those to be encountered in commercial practice. Furthermore, tests must be run of sufficient duration to provide information on effects which may occur over long periods of time, such as corrosion, fouling or scaling of equipment, build-up of trace impurities which may affect reaction rates, etc. It was these requirements which dictated the scope of this program.

B. Demonstration Plant Design Philosophy

The copper sulfate process for removal of hydrogen sulfide from geothermal steam consists of three essential steps operating continuously and in series. They are:

- Scrubbing, i.e., contacting raw steam in a suitable device with a copper sulfate solution to precipitate copper sulfide.
- Liquid-solid separation, i.e., separating the precipitated sulfides from soluble sulfate and other soluble salts scrubbed from the steam.
- Regeneration of copper sulfide by oxidation in slurry form at moderate temperatures, using air or oxygen, or by roasting of the separated copper sulfide to sulfate at higher temperature.

In addition, provisions must be made to purge soluble and insoluble impurities from the process and to render waste streams suitable for disposal.

In general, each of the major process steps (scrubbing, liquid-solid separation, and regeneration) would appropriately be tested at different scales of operation. For instance, valid information on liquid/solid separation rates can be obtained on relatively small batches. Properly done, filter-leaf tests with 0.1 sq. ft. units can give valid information for scaleup; settling rates can be determined in liter-cylinder tests with sufficient accuracy to size thickeners and clarifiers; centrifuges can be designed from small, bench-scale tests. The validity of all liquid-solid separation data, however, is constrained by the nature of the solids; if the test sample is not representative of material obtained in practice, results of small-scale tests will be misleading.

Similarly, valid kinetic data on the aqueous phase oxidation of precipitated sulfides can be obtained in small, i.e., one- or two-liter size,

reactors. Mass transfer data can be adequately scaled based on tests in reactors as small as 50 gal, provided attention is paid to the details of scaleup of agitators and tank baffling. Again, however, results in small scale equipment may be spurious if aging, for instance, alters the nature of solids to be regenerated.

In the present case, a trayed tower is the primary candidate for the contacting device. Proper scaleup of this type of equipment requires that the data be obtained in a unit of a size such that wall effects do not dominate the observed mass transfer results. With trayed internals, hydraulics can be simulated only if the relative flow rates and weir arrangements are scalable. This requires a unit of at least 3 ft in diameter.

It should be noted that useful data on the behavior of some items of equipment and materials can be obtained by installing relatively small equipment at a test site where real steam is available. However, such data will be intrinsically limited since they will not be obtained in equipment of scalable design. In addition, no assessment of system reliability can be made from such tests. To assess system reliability, a large mass of steam must be passed through the system, a correspondingly large amount of sulfide precipitated, and the precipitate regenerated to demonstrate that the system can be operated in a commercial environment at a sufficiently high stream factor and with low enough operating costs to be economically attractive.

Information on materials of construction can be obtained from laboratory tests. However, design confidence in materials of construction found to be suitable in the laboratory can only be obtained from tests with real geothermal steams which are representative of those expected in commercial practice. Such field tests will also establish at least a reference case which may be used to validate future laboratory scale corrosion work with simulated steams of various composition.

In summary, in order to verify the preliminary process engineering specifications produced in this program (Contract No. EY-76-C-02-2730*.000) it will be necessary to execute a test in a field test facility whose key elements are of a size suitable for scaling with confidence to full commercial size. Tests must be of sufficient duration to confirm criteria proposed in the specifications and to yield a measure of process reliability and operability. Off-line test work must also be carried out with materials (e.g., precipitate) obtained in the field tests, for operations which will not be field tested, such as regeneration by roasting, liquid/solid separation by centrifugation, or decopperization by solid ion exchange.

C. Detailed Task Descriptions

Included in the scope of this program, then, are all laboratory and pilot tests and analytical studies necessary to develop preliminary design criteria for a commercial scale process, and the detailed process and project

engineering required to design a demonstration plant whose operation would verify the assumed criteria or provide data to modify them. An 18-month program, consisting of 15 tasks, has been carried out to obtain the required information. The tasks were, in turn, grouped into three subprograms: a laboratory support program, process engineering studies, and process-project engineering work. A summary of the objectives of each task, the procedures used to obtain the required data, and the output of each task are summarized in Table III. The program timing and milestones are depicted graphically in Figure 3.

The objective of the laboratory support studies was to obtain mechanical and process design data needed for developing specifications for the demonstration plant. Preliminary evaluations had been carried out which indicated that the configuration of the demonstration plant, dictated in part by the scale of operation and in part by consideration of operating convenience, would not necessarily be the same as that for a commercial scale of operation. Thus, the objective of the process engineering studies was to obtain data for evaluating the technical and economic feasibility of steps or operations which would not be tested in the demonstration plant. Finally, the objectives of the engineering tasks were to carry out the detailed engineering in support of the design of the demonstration plant, develop the required test plan and operating instructions, and carry out optimization and economic evaluation studies to characterize the process and major alternative process steps at a commercial scale of operation.

Corrosion testing in the laboratory support studies was to be limited to austenitic stainless steels, since preliminary tests on these materials had been encouraging, and to scrubber conditions, which were felt to be the most severe which would be encountered in the process. Emphasis would be placed on coupon testing of plain, welded, stressed, and creviced specimens in solutions with a range of composition which bracketed those expected in an integrated process.

Leach-regeneration studies were to be carried out batchwise in small autoclaves under conditions in which gas phase mass transfer would not limit reaction rates. Reaction stoichiometries would be used to develop the overall process material balance, and the kinetic data would be used to fix process conditions as well as to develop specifications for the regeneration reactor volume and agitator power.

The filtration studies, carried out with an 0.1 sq. ft. test leaf, would be used to obtain solid and liquid filtration rates and cake densities in order to develop specifications for the filtration cycle, filter area, and filter volume required for the demonstration plant.

Some analytical technique development was also required to insure that analytical procedures, sensing elements and control hardware required for operation of the demonstration plant would be available. Of particular concern were the requirements for reliable on-stream analysis and control of the scrubbing solution's copper content and acidity.

Table III

Task Description, Laboratory Support Studies

TASK A.1: Corrosion Studies of Austenitic Stainless Steels

Objective: To determine performance of austenitic stainless steels under scrubbing tower conditions, including stressed and welded materials.

Procedures: Coupon, volt-amperometric and corrosimeter testing in liquid and vapor compositions at conditions of temperature and pressure simulating the scrubbing tower.

Output: Reports of test and specification of materials of construction in the field unit scrubber

TASK A.2: Leach Regeneration Studies

Objective: To determine the rates and product stoichiometries for regeneration of CuSO_4 from Cu_nS precipitated in the laboratory scrubber.

Procedures: Batch autoclave leaching of Cu_nS precipitated in the lab column under various temperatures, oxygen pressures, pH's and salt concentrations.

Output: A report of test and specifications of design criteria for the field unit regeneration reactor.

TASK A.3: Filter-Leaf Filtration Studies

Objective: To determine the filtration rate for purge streams containing Cu_nS precipitated in the scrubber.

Procedures: 0.1 sq. ft. filter-leaf tests, with and without filter aid, on $\text{Cu}_n\text{S}/\text{CuSO}_4/\text{H}_2\text{SO}_4$ slurries produced in the lab column.

Output: A report of test and specifications for the configuration of the field unit filter system.

TASK A.4: Analytical Technique Development for Field Unit

Objective: To determine analytical techniques and procedures for process control and chemical analysis during operation of the field scrubber unit.

Table III
(continued)

Procedures: Instrument and process control studies, vendor contact to set performance specifications, development of analytical procedures, as required, and calibration of instruments on mixtures simulating various process streams.

Output: A report of tests and an analytical and control procedures document for the field test operating manual.

TASK B.1: Materials Testing

Objective: To identify suitable less expensive materials of construction for process equipment other than the scrubber tower.

Procedures: Coupon and corrosimeter testing in liquid and vapor compositions and at temperatures and pressures simulating all key process steps.

Output: A report of test and specifications of materials of construction for other process steps.

TASK B.2: Roast Regeneration Studies

Objective: To determine roasting conditions leading to control of extent of reaction and CuO/CuSO_4 ratio from roasting Cu_nS precipitated in the scrubber.

Procedures: Batch roasting in a laboratory oven under different temperatures and SO_2/O_2 pressures. Determination of roasting rates, CuO/CuSO_4 ratios and rates of solution in batch dissolution tests.

Output: A report of test with recommendations for conditions required in subsequent fluid-bed roasting tests.

TASK B.3: Liquid-Solid Separation Studies

Objective: To predict liquid-solid separation rates in thickeners, centrifuges, and vacuum filters.

Procedures: Liter-cylinder sedimentation tests, bench centrifugation tests, and vacuum filtration tests on $\text{Cu}_n\text{S}/\text{CuSO}_4/\text{H}_2\text{SO}_4$ slurries precipitated in the laboratory scrubber.

Table III
(continued)

Output: A report of test with recommendations for the optimum type of liquid solid separation device for commercial use.

TASK B.4: Scrubber Configuration Studies

Objective: To determine the performance characteristics of alternative scrubbing techniques.

Procedures: Testing of alternative internals (packing and tray types) in a 4" laboratory column and of a venturi scrubber to determine mass transfer efficiency and fouling rates.

Output: A report of test and a technical and economic evaluation of the use of tested alternatives for commercial use.

TASK C.1: Program Definition

Objective: To determine the objectives for the field test unit, fix a site for design purposes, and set program schedules.

Procedures: Coordination and review with DOE personnel and a site operator by EIC Corporation project personnel.

Output: Selection of a test site, establishment of reporting procedures and resolution of interface responsibilities.

TASK C.2: 8" Column Design and Operation

Objective: To design, fabricate, install and operate an 8" scrubber at the field test site so as to confirm laboratory results for the design of the field test facility.

Procedures: Engineering work will be done to specify requirements for the system. A design/fabrication firm will be selected and the system purchased. Supervision will be provided for installation at the selected site, mechanical and process testing, and data reduction and analysis.

Table III
(continued)

Output: Delivery to the selected site of an 8" scrubber unit and its operation for a sufficient time to confirm preliminary criteria obtained from lab data. A report of data obtained from the unit and its relation to lab results and field test unit design.

TASK C.3: Preliminary Project and Process Engineering

Objective: To determine critical operations, steps, design requirements, equipment deliveries, and needs for additional lab work and to develop a preliminary design for a field test facility.

Procedures: Engineering work done to: assemble preliminary design criteria from known practice; prepare preliminary flow sheets and material/energy balances; develop preliminary materials selection; evaluate the impact of alternative site compositions on process conditions.

Output: Preparation of the outlines of a process engineering specifications document with assignment of preliminary values to process design criteria.

TASK C.4: Detailed Project and Process Engineering

Objective: To carry out process and project engineering for the final, detailed design of the field test facility. Preparation of cost estimates and a bid package for the test unit.

Procedures: Engineering work done to review all data, leading to the final selection of materials, definition of final flow sheets and material/energy balances, specifications of all equipment and auxiliaries including piping and instrumentation diagrams, and preliminary definition of safety and operating procedures.

Output: Updating of the process engineering specifications with final criteria. A bid package(s) containing descriptions of all hardware and system requirements for use as a basis for RFP's.

Table III
(continued)

TASK C.5: Test Plan Preparation

- Objective: To develop a test plan for the field test unit to obtain required scale-up information.
- Procedures: Engineering work to develop a detailed test plan for operating the field test unit under a variety of conditions to obtain design and scale-up information. Analysis of the impact of alternative site compositions on system design and operation.
- Output: An operating manual for the field test unit, including test schedules and procedures, safety requirements, analytical procedures, etc.

TASK C.6: Optimization and Economics Studies

- Objective: To determine optimum system configuration for various sites and to develop the economics of the process for commercial use.
- Procedures: Process engineering studies reviewing material/energy balances and design criteria impacts on system capital and operating costs.
- Output: Final updating of the process engineering specifications. Preparation of a formal cost estimate and process description document.

Field Test Facility for the Removal of H₂S from Geothermal Steam

- 1 Preliminary report, recommendations for field unit design. 2 Selection of hardware, construction of test loop. 3 Initial selection of materials for further testing. 4 Completion of testing and report. 5 End of production phase, initial evaluation of alternative internals. 6 Design of 8" column system complete; purchase equipment. 7 Equipment installation. 8 Preliminary evaluation of field test results. 9 Flowsheet frozen, preliminary draft process engineering specifications. 10 Final review of lab and field data; update criteria. 11 Detailed specifications for bid package, formal draft process engineering specifications. 12 Operating manuals issued. 13 Prototype and commercial cost estimates complete. 14 Final Phase I Report; update and summarize preliminary reports and draft process engineering specifications.

Fig. 3. Program timing and milestones

Materials testing in the process engineering studies, using coupon weight loss (gain) and stress-deflection tests, were to be directed towards determining the suitability of various materials under process conditions external to the scrubber. A variety of composite materials and elastomers was to be tested in order to find acceptable low cost alternatives to stainless steel.

A series of roast-regeneration studies was to be carried out to obtain scoping information on process conditions and kinetics. These data would be used as the bases for recommending operating conditions in subsequent small-scale fluid bed roasting tests and for economic evaluation studies. Additional liquid-solid separation studies would also be carried out to obtain design data for types of devices, e.g., centrifuges, not contemplated for use in the demonstration plant but which might prove suitable for use at a commercial scale.

Finally, a series of scrubbing tests would be carried out to determine the performance of alternative types of scrubbers or styles of scrubber internals. These data would be used in technical and economic evaluations to determine the optimum type of scrubber for commercial service.

The first engineering task to be carried out under the program just completed would involve program definitions; a site was to be selected and objectives, criteria, schedules, and interface responsibilities fixed. Then, a small (8" diameter) modular scrubber unit was to be designed, fabricated, and tested at the selected site in order to confirm the preliminary criteria developed from laboratory data by scrubbing geothermal steam.

Data from the laboratory support studies and 8" scrubber field tests were to be used as the bases for the preliminary and then detailed process and project engineering work required for the design of the demonstration plant. Material and energy balances were to be developed, materials selection studies carried out, process flow sheets and piping and instrumentation diagrams prepared, equipment process and mechanical design criteria established, and required site preparation work and services defined.

This information would fully define the proposed demonstration plant in terms of configuration, design bases and mode of operation, and would permit a detailed cost estimate to be developed. The mode of operation would fix the manner in which the test operation would be carried out in verifying the assumed design criteria.

A formal test plan and operating instructions document was to be prepared which would present the scope of the field test, its duration, test and data reduction procedures, start up and shut down instructions, safety requirements, etc. Finally, a series of optimization and economics studies was to be carried out to determine the optimum system configuration(s) at a commercial scale of operation, the impact of operation on streams of differing composition, the estimated capital and operating costs for the process, and its performance vis-a-vis alternative hydrogen sulfide abatement technologies.

IV. PHASE I - LABORATORY PROCESS DEVELOPMENT

A. Equipment and Procedures

The system used in the laboratory studies of H_2S removal by scrubbing with $CuSO_4$ is shown schematically in Figure 4. Its major components include a packaged boiler for generating the required amount of steam, cylinders of "noncondensable" gases, rotameters for metering these gases into the steam, a scrubber column with liquid sump and vapor disengaging sections, scrubbing solution (slurry) circulating pump, a holding tank and pressurized metering system for injecting makeup $CuSO_4$ to the system, a metering pump for injecting solution into the system, and a condenser and condensate disposal system for cleaned steam. All lines and wetted parts were of Type 316 or 304 stainless steel.

A steam pressure regulator at the outlet of the boiler and a manual flow-control valve downstream of the column were set to deliver the required flow rate at the desired pressure. Condensate in the steam was trapped out in advance of impurity gas injection, and the steam passed through an orifice for flow indication. Hydrogen sulfide was introduced to the system as a mixture, with N_2 of certified composition. Superheating to offset the cooling effect of the injected gases was obtained by means of electrical heating tapes wrapped around the steam line.

The active portion of the scrubber column assembly consisted of a 4-foot length of 2" IPS Type 316 stainless steel pipe. A chamber at the top of the column served as a disengagement section and was fitted with nozzles for temperature and pressure instruments, steam outlet, and recirculated scrub solution (slurry) inlet piping. The scrub solution inlet nozzle extended into the chamber and was directed downward along the column centerline. A demister pad was installed above the nozzle.

A chamber below the column served as a steam injection and slurry accumulation section. This sump was tapped and fitted with nozzles for temperature, pressure and corrosion monitoring instruments, a level gage glass, steam inlet, recirculated solution (slurry) outlet and return, makeup $CuSO_4$ and other solution inlets, and sample withdrawal piping. The slurry accumulation section and column proper were heated by electrical heating tapes and insulated with fiberglass batt.

The scrubbing solution, a slurry of precipitated sulfides in copper sulfate solution, was recirculated to the top of the scrubber by a 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. In the majority of runs, one of the two pump heads was used to redirect solution to the column sump in an effort to mix makeup $CuSO_4$ solution thoroughly with the reservoir of slurry.

Fig. 4. Laboratory set-up for H_2S scrubbing.

Makeup CuSO_4 solution was introduced to the column sump by pressurizing the external makeup tank. 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 makeup rate of CuSO_4 .

Scrubbed steam was condensed in a 20-foot section of 3/8" OD stainless steel coiled tube over which cold tap water was passed. The condensate and noncondensibles, including unscrubbed H_2S and NH_3 , were bubbled into a 2-gal plastic container of continuously replenished NaOH solution, which neutralized and removed unscrubbed H_2S . Analysis for H_2S in steam was carried out by sparging a quantity of condensate into ammoniacal CdSO_4 solution and analyzing for unprecipitated Cd^{2+} by EDTA titration. An accurate value for the steam flow rate was simultaneously obtained from the measured weight of condensate collected. Ammonia in steam was determined in an analogous way by collecting condensate in a known quantity of standard H_2SO_4 solution and analyzing for unneutralized H_2SO_4 by NaOH titration.

Rapid Cu^{2+} and pH analyses of solution samples from the scrubber were performed for purposes of process control during operation. Quantitative solution analyses for material balance purposes were performed for Cu^{2+} , NH_4^+ , H_2SO_4 and total sulfate. For copper and sulfide analysis of scrubber solids, weighed samples of the washed and dried material were decomposed in $\text{HNO}_3/\text{NaClO}_3$ until any elemental sulfur produced in this reaction had been dissolved. The final solution was then analyzed for Cu^{2+} and SO_4^{2-} .

This same apparatus was used, with minor changes, for scrubbing tests carried out in the second phase of this program. For this work, the 2" column was replaced with a 4" column section which was fitted with sight glasses, top and bottom, so that the tray action could be observed directly. Makeup $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4$ solution was introduced directly to the column sump using a metering pump, and the external pressurized tank was used as a pulsation damper for the recirculating pumps.

B. Scrubber Configuration Studies

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 (1/4" x 5/8")
- open, high-efficiency Flexirings
- counterflow sieve trays

- shower trays
- sieve-tray with downcomer.

The noncondensibles for these runs were H_2S and N_2 .

Initial tests were run with the column packed with 4 feet of ceramic saddles, at 25 lb/hr steam, or 80% of anticipated flooding. Hydrogen 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 typically decreased, and scrubbing liquid was primed over into the condensate, signifying that the column had flooded. Following these tests, the packing, especially the bottom 6 inches, and packing support plate were found to be fouled with accumulated precipitate.

For the next series of column tests, the small ceramic packing was replaced with 3 feet of 5/8" stainless steel Flexirings, which are much more open and have better hydraulic characteristics. Steam-water tests on clean packing confirmed the normal hydraulic behavior of the packing and column configuration, in that flooding could be induced at the expected velocities. As was the case with the ceramic packing, however, stable operation when scrubbing with $CuSO_4$ 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 was concluded that the flooding phenomenon is associated with surface activity of the freshly precipitated sulfides, leading to formation of a light froth. With small-sized internals, bubble sizes may be of the order of the packing size and, moving as solid bodies, would prevent free liquid passage. The postulated high steam/liquid contact area was also consistent with the high measured values for k_{ga} (about 4 times calculated). The froth hypothesis was subsequently confirmed in runs on columns of larger diameter equipped with sight glass ports.

Following experience with column packing, which showed that near-quantitative H_2S removal is possible provided operability problems can be overcome, various arrangements of trayed internals were tested. One arrangement consisted of a succession of counterflow sieve trays spaced at 12-inch intervals. Initially, each tray contained 15 holes, 3/16-inch dia, giving 15% open area. The onset of flooding was delayed using this arrangement until over 3 hours of operation, during which time H_2S removal efficiency was of the order of 40%, with tray efficiencies of the order of 10%. Post-run inspection revealed an accumulation of loose precipitate together with some nearly spherical pellets on the top tray, where most of the mass transfer had evidently occurred.

Various modifications of the sieve-tray configuration were tested, including 26% open-area trays on the same 12" spacing and 50% open-area trays on 8" spacing. In operation, open trays exhibited significantly improved

efficiencies, up to 35%. However, attempts to increase either L/V or steam velocity to the range of desired values for a commercial installation resulted again in column flooding. Most of the solids accumulation now occurred in the lowest trays. No significant improvement was realized by cutting wedges out of the counterflow sieve trays to enable solids to pass down the column.

Longer run times at higher L/V and velocity were achieved using shower tray internals. The tray cartridge in this case consisted of 60 segmented dishes having 30% of their area removed and spaced at 3/4" intervals. Very high degrees of H₂S removal were achieved, although individual tray efficiencies were low, but vapor velocity could not be increased to more than about half of the desired range without flooding. On the other hand, this open style of scrubber internals resulted in no accumulation of solids. The longer run times achieved led to the observation of reduced scrubbing efficiency below about pH 1 as H₂SO₄ accumulated in the sump solution.

The final, and most successful, contact tray configuration evaluated consisted of a single sieve tray with a downcomer. For the 2" column, the configuration consisting of a 1" dia downcomer projecting 1" above a single 37% open area sieve tray provided the most favorable combination of high scrubbing efficiency and high permissible steam velocities and L/V's. This basic configuration was scaled up for utilization in the 4" laboratory column.

Some results for H₂S scrubbing with the 4" column at 200 PPH steam containing 224 ppm H₂S and for L/V = 1.9 are as follows:

scrub solution copper concentration, g/l	2.5
scrub solution pH	1.4
outlet H ₂ S, ppm	1.7
froth height, in.	24

The pressure drop across the tray during these measurements was 7 in. of water, the indicated substantial froth height accounting for the observed high scrubbing efficiencies.

C. Effects of Scrub Solution Composition

While depletion of CuSO₄ in the recirculating scrub solution resulted in cessation of H₂S removal, no consistent effect on H₂S removal efficiency was perceived on varying the copper concentration from 0.4 to over 5 g/l in these tests. The effects of pH and sulfate concentration on H₂S removal efficiency are interrelated through the agency of bisulfate ionization:

Bisulfate ion becomes a progressively weaker acid as the temperature is raised. Thus, the presence of excess SO_4^{2-} as $(\text{NH}_4)_2\text{SO}_4$, either deliberately added (laboratory) or resulting from co-scrubbing of NH_3 from the geothermal steam (commercial operation), acts as a strong pH buffer at scrubber operating temperature maintaining pH within the desired range. At low values of excess sulfate, the pH of the scrub solution is little affected by temperature. Consequently, H_2S removal efficiency fell off at pH's below about 1.0.

The concentration of sulfate cannot be allowed to increase beyond certain limits, however, due to hydrolysis, leading to precipitation of basic copper sulfate in the makeup CuSO_4 feed system.

D. Characterization of the Precipitates

The physical characteristics of the copper sulfide solids formed in the scrubber are as significant as their chemical behavior in influencing engineering feasibility and process economics. Provision was made for continuous suspension and recirculation of precipitate in the scrubber for the purpose of promoting particle growth and thereby improving liquid/solid separation characteristics. As it turned out, the solids produced under scrubber conditions settled unexpectedly rapidly, especially from hot solution, so that continuous suspension is primarily a convenient means of moving the solids.

Ultimate particle size, however, is very small as one would anticipate for a rapid reaction between a dilute gaseous and a dilute solution constituent. No colloidal dispersions were noted in this work, and the ultimate particles evidently aggregated rapidly to tightly bound clusters as revealed under the SEM (Fig. 5). Particle size analysis of sonically dispersed scrubber slurry revealed the aggregates to have sizes in the 2-20 micron range.

The microporosity of the scrubber solids renders them prone to air oxidation in storage or during drying. The oxidation products, mainly basic copper sulfate, are easily acid soluble. The high specific surface area also results in unusually rapid enrichment with respect to copper by reaction of the initially formed copper sulfide with Cu^{2+} in solution. The end members of the secondary enrichment reactions are CuS and Cu_2S . Under conditions of very short residence times, compositions close to CuS have been observed. For the longer residence (one or more hours) of solids in contact with scrubber solution, as encountered during continuous operations, compositions were close to Cu_2S .

The observed susceptibility of separated scrubber solids to atmospheric oxidation suggested that regeneration of CuSO_4 could be accomplished under relatively mild conditions. This proved to be the case for oxygen/acid pressure leaching and for roasting, as demonstrated in preliminary regeneration experiments of both types.

Fig. 5. SEM photograph of copper sulfide precipitate (Run No. 330). Magnification 500X.

E. Corrosion Test Results

Stainless steels, the preferred corrosion-resistant materials of construction, are aggressively attacked by dilute sulfuric acid under non-oxidizing conditions at scrubber temperature (about 175°C). Consequently, since acid is generated by the metal sulfides precipitation reaction, some oxidizing capacity was required to maintain stainless steels in the passive state. Fortunately, cupric ion provides this capacity, and CuSO_4 appears to be uniquely suited among candidate scrubber salts in terms of sulfide solubility and scrubber corrosion resistance.

Follow-up laboratory corrosion tests confirmed that the corrosion rates of austenitic stainless steels in contact with scrubber solutions were less than 10 mil/year provided that the H_2SO_4 concentration was controlled and the solution was not allowed to become depleted in copper:

V. RESULTS OF PHASE II EXPERIMENTAL AND ANALYTICAL STUDIES

The continuation phase of the development effort for the copper sulfate process required the execution of fifteen tasks. The objectives and procedures for these tasks have been summarized in the chapter defining the scope of the program. Nine of these tasks (A.1-A.4, B.1-B.4, and C.2) are experimental and analytical in nature; one, Task C.6, involved optimization and economics studies; three (Tasks C.1, C.3, and C.4) involved engineering work, the culmination of which is the demonstration plant design presented in detail in Volume III of this report; one, Task C.5, resulted in the detailed test plan and operating instructions document for the demonstration plant, which is also presented in Volume III of this report. The outputs of Tasks C.1 and C.3-C.5 are contained, then, in Volume II.

This volume fulfills the requirements for Task D.1, namely updating of preliminary work to produce a final report. In this section, the results of the experimental and analytical tasks (A.1-A.4, B.1-B.4, C.2 and C.6) are summarized. Complete final task reports are presented in Volume II.

A. Task A.1, Corrosion Studies on Austenitic Stainless Steels

Autoclave testing, utilizing modified Huey procedures, under conditions simulating those anticipated in removing H_2S from geothermal steam by scrubbing with $CuSO_4$ has shown that the higher austenitic stainless steels will be generally useful materials of construction if conditions leading to crevice corrosion can be avoided.

In the presence of $(NH_4)_2SO_4$ at the expected levels of concentration (50-100 g/l) and controlled acidities ($H_2SO_4 < 30$ g/l) a concentration of 1-2 g/l of copper is sufficient to passivate austenitic stainless steels in the "bare metal" state. The effect of acidity on corrosion rate for various alloys is shown in Figure 6. The order of passivity of the alloys tested under simulated process compositions is:

$Ti \gg EB26-1 > C20Cb3 \sim UHB904L > T330 \sim T310 > T304 \sim T316$

These results were confirmed in field test work on an 8-inch scrubbing column system on real geothermal steams, where no corrosion of Alloy 20 pressure parts was observed in short term tests.

In laboratory tests, the wrought alloys appeared to show superior resistance to the corresponding cast versions. While little evidence was seen of stress or weld corrosion or pitting attack, all alloys tested were subject to crevice corrosion, probably due to local depletion of the solution copper content.

Continuous on-line monitoring of the corrosion rate in an operating system with a current measuring instrument (Magna Corporation's Corrator[®], Petrolite Corporation's corrosion rate instruments) will not be feasible due to the cupric/cuprous redox reaction occurring in parallel with the metal dissolution reaction. The use of a resistance measuring instrument (Magna's Corrosimeter[®]) would be possible, however.

Based on these tests, and the limited life requirements of the demonstration plant, it was recommended that the scrubbing column and trim for the 100,000 lb/hr field test facility be constructed of C20Cb3 and Alloy 20 alloys insofar as possible, and that titanium, which is passive under all conditions tested, be considered as a backup material.

B. Task A.2, Leach Regeneration Tests

Pressure leach experiments were carried out on copper sulfide solids produced in the laboratory scrubber and produced during operation of the 8-inch field-test scrubber at The Geysers. The main objectives of this work were to confirm the technical feasibility of the pressure-leach mode of regeneration and to provide data for the engineering and design of the demonstration plant.

Precipitates produced by scrubbing H₂S from synthetic geothermal steam were typically more reactive toward oxygen pressure leaching in acid medium than are synthetic or mineral CuS powders. For the scrubber solids, the preponderant reaction product of sulfide oxidation under the conditions investigated was sulfate rather than elemental sulfur. Accordingly, they could be leached to leave virtually no solid residue. Rates of copper solubilization, corrected for diminishing interfacial area, were approximately first-order in time, on average, but exhibited a wide range of time dependence. Under conditions of vigorous gas dispersal in the solution, the most important parameter determining leach rates was oxygen partial pressure, as illustrated by the data of Figure 7.

The range of temperatures investigated was not sufficiently broad to establish an activation energy with certainty, but its probable value (≤ 7 kcal/mol) is in a range consistent with mass transport rather than chemical reaction control. At a temperature of 140°C, complete reaction could be achieved in about 2 hr (Fig. 8) when the oxygen partial pressure was maintained at 100 psi. These are relatively mild process conditions and confirm the suitability of pressure leach regeneration for small H₂S removal plants.

A brief investigation of oxidative leaching of scrubber slurry by air sparging showed that approximately 50% of the copper sulfide could be solubilized in 10 hr at near ambient temperature. Thus, a pre-leach with air will significantly lower the oxygen requirements in leach regeneration.

Fig. 7. Correlation between time for complete reaction and oxygen partial pressure.

Fig. 8. Oxygen pressure leaching of field test solids (Expt. 15). Conditions: 100 g/l $(\text{NH}_4)_2\text{SO}_4$, 40 g/l H_2SO_4 , 100 psi O_2 .

C. Task A.3, Filter Leaf Test Studies

Copper sulfide precipitates produced by removing low concentrations of hydrogen sulfide from steam by scrubbing with copper sulfate, while composed ultimately of particles less than 1 micron in size, flocculate naturally and settle and filter rapidly. There are no apparent differences in macroscopic properties between material produced in laboratory tests where simulated geothermal steam was scrubbed and precipitates produced during field tests on actual geothermal steams. The solids content of the filter cakes and pulp densities from settled slurries tend to be rather low, 25 and 15% solids, respectively, due to the flocculent nature of the precipitates.

Tight, monofilament filter cloths show excessive tendencies to blind, while multifilament cloths require periodic back washing. Spun fabrics, on the other hand, show little tendency to blind, and they give adequate cake release. Cake specific resistances are low, being approximately equal to media resistances for a 0.5-inch cake. A continuous filter to separate solids from a slurry purged from the 100,000 lb/hr field test unit would be quite small in size, but the size of a batch filter would be controlled by solids retention capacity.

Settling rates for purged slurries are rapid, of the order of 1 ft/min, and compression times are less than one minute. Typical settling rate curves are shown in Figure 9. Flash-cooled solids settle slightly faster and to higher densities than do slurries cooled slowly. Slurries which have been subjected to high shear environments also settle more slowly and to lower pulp densities. The size of a thickener/clarifier for separating purge slurries would be controlled by overflow rate and not by solids settling rates.

Because of its simplicity and flexibility, a continuous decanter will be used in the 100,000 lb/hr field test facility to make the primary liquid/solid separation for producing a concentrated slurry for leaching and a clear solubles purge stream for disposal.

D. Task A.4, Analytical Technique Development

Laboratory testing on simulated purge streams and on purge slurry returned from operation of the 8-inch scrubber on geothermal steam have demonstrated that on-line monitoring of pH and monitoring and control of copper content are feasible in this process. It was demonstrated that a Swirlklean by-pass filter will remove precipitated sulfide solids from the sample purge stream very effectively. A minimum amount of backflushing - once a day - will maintain high filtration rates.

A Teledyne photometric analyzer is effective, stable, and accurate in measuring the copper content of a filtered purge stream in the presence of ammonium sulfate and sulfuric acid and will generate an output signal which can be used for process control to maintain the desired copper content. The absorbance of the purge solution is a strong function of temperature,

Fig. 9. Settling Rates of Solids Produced from Real Geothermal Steam

x Flash cooled to 105°C
O Slow cooled to 55°C

as shown in Figure 10, as well as of concentration, so that sample temperature control or a calibration for temperature will be required to obtain precise concentrations.

A Great Lakes Analyzer with a differential electrode can serve to monitor the pH of the purge stream. However, modification of the standard probe by replacing the internal pH reference solution with one more suitable for this system is required to obtain linearity of response in the range pH 1-2. Typical response of the instrument in streams of varying acidity is shown in Figure 11. Periodic recalibrations will probably also be required to maintain accuracy within ± 0.1 pH unit.

Both instruments will have to be modified for field use. In particular, the Teledyne Analyzer will have to be enclosed in a purged housing to protect its electronics from deterioration due to ambient H_2S . Replacement of the span adjustment potentiometer will enable more precise control to be obtained. Similarly, the span control for the Great Lakes Analyzer will have to be replaced to insure adequate range if respanning to pH 1.0 is required routinely.

E. Task B.1, Materials Testing

A series of tests has been carried out to determine the resistance to corrosion and the stability of various materials under conditions which simulate operation of process steps other than steam scrubbing. A variety of alloy materials, composites, and elastomers was selected for testing based on information on their suitability derived from the open literature and provided by manufacturers.

As expected, austenitic stainless steels were found to be suitable for use under all conditions tested at temperatures up to at least $125^\circ C$. Type 304 would be the preferred alloy in terms of cost and general availability.

Elastomers such as Viton and EPR and fluorinated polymers such as Teflon will also provide excellent service up to the maximum temperatures recommended by the manufacturers.

A series of weight gain and stress-deflection tests was carried out on two types of composite materials: fiberglass reinforced vinyl esters and chlorinated polyesters. Both were found to be dimensionally stable, although the latter type showed some tendency towards wicking at elevated temperatures. Both have demonstrated their suitability in long term testing at $50^\circ C$ as shown in Figure 12. The vinyl esters, such as Derakane® and Duracor®, have shown excellent stability and retention of strength for shorter term exposure at the normal boiling point.

An additional series of tests carried out in an attempt to determine the mechanisms important in the initiation of crevice corrosion was incon-

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Fig. 11. Calibration of Great Lakes Instruments pH Analyzer.

Fig. 12. Weight gain of samples at 50°C.

clusive. Results indicated that high ratios of cathodic-to-anodic areas and high bolting pressures on gasketed joints would minimize the possibility of the onset of this type of corrosion, but no effect attributable to gasket material or solution velocity could be found. Since these two conditions were present in the 8-inch (field) and 4-inch (laboratory) scrubbing column systems, where very little crevice corrosion was observed, the results suggest that it may be possible to design around the problem in a commercial system.

F. Task B.2, Roast Regeneration Studies

Sufficient laboratory work had been carried out under Task B.2 to characterize the broad technical features of the roast-regeneration of copper sulfide scrubber solids. Both wet and dry roasting give oxidation products which are soluble in sulfuric acid to form a copper sulfate solution suitable for makeup to the scrubber. Partial acid neutralization for the overall hydrogen sulfide removal process can be effected by dissolving the roasted solids in scrub solution.

Wet roasting, whereby a thin bed of solids is moistened while being heated in air, can be made reasonably rapid, i.e., reaction times in the range 3-6 hr, at temperatures above about 150°C. However, the reaction is much slower if water, rather than acid, is used for moistening. Moreover, the ammonium sulfate present in scrub solution retards the reaction. When sulfuric acid or scrub solution is used for moistening the solids, thermal decomposition of sulfuric acid or ammonium sulfate, respectively, occurs. These adverse features, together with the substantial energy requirements for continuously vaporizing water make wet roasting a relatively unattractive alternative.

Dry roasting was studied with thin fixed beds at temperatures of 200, 250, 300 and 400°C. While the rate is slower at 200°C than for wet roasting under optimum wet-roast conditions at the same temperature, the temperature coefficient of the dry-roast rate is much higher. Thus, the activation energy for dry roasting is about 20 kcal/mol (chemical reaction control) as compared with about 4 kcal/mol (mass transfer control) for wet roasting. Consequently, scrubber solids can be dry roasted in short times (less than 1 hr) at temperatures of 300°C and above.

The most significant factor in determining the extent of reaction at the higher range of temperature is the accessibility of the solid particles to the air. For a very thin fixed bed, the roast reaction at 400°C was essentially complete within 15 mins, the shortest time tested. Chemical analysis of the products revealed the predominant reaction to be oxidation of Cu_2S to $\text{CuO} \cdot \text{CuSO}_4$ without loss of sulfur (as SO_2 or SO_3), thereby eliminating the need for secondary gas scrubbing. Figure 13, summarizing results expressed as percent weight gain vs. percent reacted, confirms the overall chemistry of the roast reaction in air. The favorable features of dry as compared with wet roasting are offset by the need in roasting to dewater the solids.

Fig. 13. Collected dry roast data. ○ = 200°C, ⬡ = 300°C, □ = 400°C.

G. Task B.3, Liquid-Solid Separation Studies

Liquid-solid separation rates of copper sulfide solids, produced by removing low concentrations of hydrogen sulfide from steam by scrubbing with copper sulfate, have been measured in a continuous laboratory scale decanter and in a laboratory batch centrifuge. Tests were carried out on solids yielding liter cylinder settling rates which varied by more than an order of magnitude.

The continuous decantation tests confirmed the preliminary design criteria, developed in work carried out in Task A.3, used for the decanter for the 100,000 lb/hr demonstration facility. In addition, the work indicates that stable operation will be possible over a wide range of total flow rates, percent decanted, and feed-solids contents.

Batch centrifugation tests demonstrated that the solids settled rapidly to approximately 50% solids density at 1600 G as shown in Figure 14. Settling rates were not greatly affected by pH or temperature within the ranges tested. A centrifuge would be used for regeneration by autogenous roasting, where rather high degrees of water removal are required.

At a commercial scale of operation (50 MW) on 10^6 lb/hr steam containing 220 PPM H_2S , a continuous decanter is the preferred type of liquid-solid separation device when regeneration of copper sulfate is to be carried out by leaching.

Continuous (vacuum) filters and thickeners are alternatives in these two regeneration cases, respectively; batch filters would be significantly more costly and labor intensive.

H. Task B.4, Scrubber Configuration Studies

The performance of shower-type trayed columns, a spray column, and a venturi contactor has been evaluated in laboratory tests to determine their effectiveness as scrubbers for the removal of H_2S from geothermal steam. All are possible alternatives to the use of a crossflow sieve-tray scrubber in this service.

It was found that all devices tested were acceptable from an operability point of view: they did not foul or retain solids and had wide ranges of stable operation. However, while it proved to be relatively easy to obtain H_2S removal efficiencies in the 80-90% range, near quantitative removal was not achieved under any conditions tested. Extrapolation of the data that were obtained indicated that high scrub liquid flow rates, low vapor velocities, or multi-staged operations would be required to obtain very high degrees of H_2S removal.

Laboratory data and equipment scale-up laws and correlations were used to scope the configuration of each type of scrubber at a commercial

Fig. 14. Rate of settling under centrifugal force, solids Run 809.

scale of operation. Costs were estimated for both 80-90% and high degrees of H_2S removal and are summarized in Table IV. A crossflow sieve-tray scrubber would be cost effective for either degree of H_2S removal required, but the alternative types would be significantly more costly if near quantitative removal is required.

The minimum size of all alternatives evaluated is fixed by the demister design assumed and the requirement to hold an adequate inventory of copper in the system. If the assumed criteria can be relaxed, system costs can be reduced significantly. Also, if the required degree of H_2S removal could be obtained in a single venturi contactor at low scrub liquid flow rates, this configuration would represent a simple, compact, inexpensive scrubber system.

I. Task C.2, Eight Inch Column Design and Operation

Nearly quantitative removal (cleaned steam < 0.7 ppm H_2S) of hydrogen sulfide from geothermal steam was obtained, with no major operating problems, by scrubbing with copper sulfate solution in an 8-inch scrubbing column containing a single crossflow sieve-tray. The system and auxiliaries are shown schematically in Figure 15.

In a run of thirty hours duration, at Unit No. 7, The Geysers, an average removal efficiency of 98.9% was obtained (cleaned steam average H_2S content 2.6 ppm) at a pressure drop of 0.5 psi. The log of percent H_2S removal for this run is shown in Figure 16. The scrub solution averaged about 3 g/l Cu, 60 g/l $(NH_4)_2SO_4$, 15 g/l H_2SO_4 and had a pH (room temperature) of 1.4. Approximately 80% of the ammonia and boron in the incoming steam were also removed under the process conditions tested.

No fouling of the scrubber internals due to deposition of solids or accumulation of large agglomerates was observed. Entrainment of copper from the scrub solution into the cleaned steam was negligible, being below the limit of detection (< 0.05 ppm).

The predominant solid species formed under the prevailing scrubber conditions (3-1/4 hr solids residence time at $175^\circ C$) was close to chalcocite, with a composition of $Cu_{1.9}S$. Under these conditions, approximately 10% of the incoming sulfide was oxidized to elemental sulfur and was steam-stripped into the cleaned steam condensate and 15% was oxidized to sulfate. The copper sulfide solids produced had essentially the same macroscopic properties as those made in lab-scale tests on simulated geothermal steam and settled rapidly.

J. Task C.6, Optimization and Economics Studies

A process engineering and economic evaluation was carried out to determine the optimum configuration for the copper sulfate process at a commercial scale and the effect on process economics of varying steam composition and treatment rates.

Table IV
Characteristics of Various Types of Scrubbing Devices
in a Commercial Scale Operation⁽¹⁾

Type of Scrubber Used	80-90% H ₂ S Removal Required				High Degrees of Removal Required			
	Sieve Tray Column	Shower Tray Column	Spray Column	Venturi (one)	Sieve Tray Column	Shower Tray Column	Spray Column	Venturis (two)
Scrubber Description	16' Dia 25' Shell 1 Tray	20' Dia 40' Shell 6 Trays	16' Dia 35' Shell	3' Throat Disengage in 16' Dia 20' Shell	16' Dia 30' Shell 1 Tray	22' Dia 60' Shell 12 Trays	16' Dia 40' Shell	Same as One Plus 14' Dia 10' Shell
Liquid Circulation Rate, GPM	2000	2000	2000	2000	2000	2000	4000	4000
46 Pressure Drop, Incl. In/Out Losses, psi	0.7	0.8	0.5	3.5	1.2	0.9	0.5	7.0
Cost of Scrubber Shell, \$M	350	700	450	350 ⁽²⁾	400	1,150	500	675 ⁽²⁾
Internals and Auxiliaries, \$M	75	125	75	25	75	175	75	50
Scrubbing Liquid Services, \$M	75	75	75	75	75	75	125	125
Total Cost, \$M	500	900	600	450	550	1,400	700	850

(1) Nominal 50 MW. 10⁶ lb/hr steam, 250 ppm inlet H₂S.

(2) Venturi proper, vapor-liquid disengagement, and interconnecting piping.

[illegible]

Case No. 17	9/17/76	17	1976-17
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Fig. 16. Percent removal of H_2S , Run 1214/1215.

A trayed scrubber with a single crossflow sieve tray is the most cost-effective type of device if high degrees of H_2S removal are required. Regeneration by oxygen pressure leaching is less costly than roast regeneration, at least for plant sizes of 110 MW or less, so that liquid-solid separation is most advantageously carried out by continuous decantation. A preleach operation at near ambient conditions followed by an oxygen pressure leach will provide 99% regeneration of sulfide precipitates at minimum cost. A polish leaching step would be used to separate refractory sulfides from rock dust and other inerts purged from the systems. Because solids disposal costs are high at the Geysers, purge stream neutralization with ammonia is preferred over lime neutralization. Since purge stream decopperization by solid ion exchange can effectively utilize a stream whose pH has been adjusted by ammonia, the two steps can be combined at a minimum overall cost. The process configuration and material balance for a 110 MW plant is shown in Figure 17.

The overall process material and energy balance is a function of the amount of steam to be treated, its composition, and the stoichiometry of the scrubbing and regeneration reactions. The reaction stoichiometries have been presented graphically, as in Figures 18 and 19, over the range of compositions of interest so that the impact of operation at different sites on system configuration can be determined easily. Scrubber size is determined by the flow rate of steam to be treated, but the size of the regeneration system is fixed by the amount of sulfide which is scrubbed and the system acid balance. The amount of soluble impurities removed from the steam and the system water and acid balances determine the volume of the solubles purge stream and the size of the decopperization step.

Capital costs for a commercial scale plant have been estimated by a factoring technique. Two-thirds of the total equipment costs is for the two large scrubbers required for a 110 MW system consisting of two 55 MW turbines. All other costs account for the remaining one-third. Thus, the estimated total investment of approximately \$50/kW is dominated by the installed cost of the scrubbers. Total operating costs were estimated from the process material and energy balance and projected manning table. Direct costs are less than 0.6 mills/kWh, and capital charges raise total costs to about 1.8 mills/kWh.

A preliminary technical and economic review of alternative approaches for H_2S abatement indicates that the iron catalyzed air oxidation system, although relatively inexpensive, will not be capable of achieving high degrees of H_2S removal. The use of surface condensers with Stretford plants supplemented by a standby upstream steam cleaning system and the use of H_2O_2 to oxidize residual H_2S in the plant condensate is probably capable of highly effective abatement but is likely to be very costly as shown in Table V.

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STREAM NUMBER	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
TEMPERATURE °C	175	175	175	95	95	25	80	100	130	110	25	25	110	50	50	50	50	70	40	25	25	30	30	30	95	110	40	90
PRESSURE ATM.	92	92	92	9	3	2	1	7.8	8.8	6.8	7.8	1	2	1.5	1.5	1.5	2	102	1.5	7.8	1	92	2	92	2	6.8	2	3
TOTAL FLOW GPM.			2M	18	57	1.5M	26M	110	110	108			2	26	8	26	8	61				10	4	10	2	2	1	450
LB/HR.	1mm	1mm									500								110	9	4							
SCFM											5																	
SOLIDS FLOW LB/HR.	20	10	21M	1	775			925	40												4				1	40	20	

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FIGURE 17
PROCESS FLOW DIAGRAM
COPPER SULFATE SCRUBBING
PROCESS

REMOVAL OF H₂S FROM
GEOTHERMAL STEAM AT
THE GEYSERS CONDITIONS

DWG NO. SC-0023

Fig. 18. Relation between ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed from steam and purge stream composition.

Fig. 19. Effect of ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed and scrubbing reaction stoichiometry on purge requirements.

Table V

Capital and Operating Cost Estimates for H₂S Abatement Processes

110 MW Capacity, 220 PPM H₂S in Steam

<u>Process</u>	<u>Upstream Scrubbing with Copper Sulfate</u>		<u>Iron Catalyzed Air Oxidation Downstream</u>		<u>Surface Condensers- Stretford Plants</u>	
<u>Approximate % H₂S Removal Obtained(2)</u>	<u>Fixed Capital Investment \$/kW</u>	<u>Operating Cost(1) mill/kWh</u>	<u>Fixed Capital Investment \$/kW</u>	<u>Operating Cost(1) mill/kWh</u>	<u>Fixed Capital Investment \$/kW</u>	<u>Operating Cost(1) mill/kWh</u>
85(3)			25	1.4	70	2.0
90(4)			45	2.0	90	2.6
95(5)			not achievable		75	3.2
99	50	1.8	not achievable		95	3.8

(1)

Includes direct costs plus capital charges. Based on 7500 hr operation.

(2)

From steam to plants plus steam vented during trip-outs.

(3)

Approximately 90% abatement in the plant, no control of preplant vent.

(4)

Approximately 90% abatement in the plant, vent abatement with "iron oxide box".

(5)

Approximately 99% abatement in the plant, no control of preplant vent.

VI. DEMONSTRATION PLANT DESCRIPTION, TEST PLAN, AND KEY PROCESS
PARAMETERS TO BE VERIFIED

A. Description of the Demonstration Plant

The system designed for obtaining the field test data required to confirm the process engineering specifications for the copper sulfate scrubbing process is described in Dwgs. SD-0012 through SD-0016.

The minimum sized equipment which can be used to derive data that can be used to scale to commercial size systems with confidence requires a steam flow rate of at least 20,000 lb/hr (1 MW). A facility designed to process 100,000 lb/hr of raw steam (5 MW) will yield information at a higher degree of confidence: not only will process equipment be closer to commercial scale, but more raw steam can be processed in a test campaign of fixed duration.

Material and energy balances carried out for a facility designed to process 100,000 lb/hr of steam result in a purge stream from the scrubbing tower of approximately 7 gal/min for the removal of 25 lb/hr of hydrogen sulfide from the steam. This stream, carrying of the order of 90 lb/hr of precipitated sulfides, is too small to treat conveniently in a continuous manner and to yield data on the scale-up of the regeneration step. At this purge rate, a rather intensive labor input would be required to monitor a continuous operation. Such an effort would be incompatible with the scale of attention required for the operation of a continuous scrubbing system.

In addition, it may be desirable or necessary to utilize the components of this system at different sites or under conditions which differ significantly from those assumed in the reference case design during supplemental testing or during runs at alternate sites. Thus, based on the equipment limitations dictated by the scale of operation and on the requirement for developing a system with a maximum degree of flexibility, the field test facility is configured so as to consist of continuous scrubbing and liquid-solid separations and batch regeneration.

The system may be conveniently described as consisting of three modules: a scrubbing and liquid-solid separation module, a regeneration module, and a service module. The first module, shown in Dwg. SD-0012, consists of a system for the continuous removal of hydrogen sulfide from geothermal steam, an energy recovery operation, and a liquid-solid separation step. Fresh scrub solution is transferred from tank T102 by pump P102 through energy recovery exchanger HX101 to the scrubbing tower. Hydrogen sulfide is removed from the steam in the scrubbing tower C101 by counter-current contact with scrubbing fluid made up of fresh precipitant solution and recycled slurry transferred by pump P101.

The flow rate of steam to the system is controlled by a steam flow rate recorder controller loop FC101. The flow rate of recirculated

H₂S REMOVAL FROM
GEOTHERMAL STEAM

SCRUBBING SECTION

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scrubbing solution is controlled to obtain the required mass transfer results by flow recorder controller FC103 operating off the scrubbing tray's pressure drop recorder DPR103. The proper amount of regenerated solution is made up to the system by maintaining composition control, i.e., the copper content, in the slurry purge stream using composition recorder controller AIC105. Material balance control will be achieved within the tower by maintaining the proper level in the tower sump with purge slurry flow controller FC107. Tower operations will be monitored by observing pressure drops through the scrubbing and demister sections with pressure drop indicators DPR103 and 104.

The purge stream from the tower will be passed through energy recovery exchanger HX101 and cooled further in cooler HX102, if required. Liquid-solid separation on the purge slurry will be carried out in the continuous decanter C102, with sufficient clear liquid purge withdrawn by flow control FR108 to maintain the concentration of soluble components in the system at a desired level. The decanted solution passes to neutralizing tank T302, while the thickened slurry passes to surge tank T101.

Makeup water for process use will be obtained from the cooling tower sumps, filtered, and held in surge tank T304. It will be transferred by pumps P304 and P305 to serve as demister wash water and as seal coolant and flush water for the pumps, as required.

The scrubbing tower C101 is of sufficient size and height to require permanent, load-bearing foundations. The pumps, piping, and equipment associated with the slurry circulating pumps P101, energy recovery and liquid-solid separation operations (heat exchangers HX101-HX103, decanter C102), and service water pumps and tanks T304, P304 are of sufficient size to permit them to be prepped in fabricators' shops and assembled as components on Skids No. 1, 2, and 5 respectively.

The regeneration module, shown on Dwg. SD-0013, will be operated in a batch fashion one shift per day. The purge slurry will be held in suspension in surge tank T101 by agitator A101. Trim control of the slurry density can be obtained by stopping the agitator and decanting liquid, if required. The temperature of the slurry can be raised prior to introduction to the regeneration reactor by steam-heated exchanger HX201. The purge slurry will be transferred by pump P103, in two or three batches per day, to regeneration reactor V201. Addition of makeup copper and acid or ammonia, if required, would be made to the regeneration reactor prior to initiation of a leach run. In addition, preleaching of the slurry can be carried out at near ambient conditions, if desired, by circulating it through a contactor.

The precipitated copper sulfides are suspended in the sulfate solution in the reactor by agitator A201, and sufficient air is sparged through the reactor from compressor P401 to reoxidize the precipitated sulfides

ISSUE	REVISION	BY	DATE
P-1	PRELIMINARY	RM	7/5/77
-	INITIAL SKID COPS	RM	8/6/77
A	ADD TO PRELIMINARY	RM	12/6/77

to copper sulfate in a two-hour reaction cycle. The required oxygen partial pressure is maintained in the reactor by the pressure control loop PRC205. The reactor is held at the required temperature by the temperature control loop TRC202, which controls the flow rate of coolant through the reactor jacket. When leaching with high purity oxygen instead of air, oxygen will be made up to the reactor through flow recorder FR207 at a rate sufficient to maintain the desired total system pressure by pressure controller PRC205.

At the completion of the regeneration cycle, the reactor contents - regenerated copper sulfate solution containing unreacted solids - are transferred from reactor V201 through filter F201 and cooler HX202 by the autogenous pressure within the reactor. The filtrate, containing the regenerated copper sulfate solution, will be returned to tank T102 following sampling and pH adjustment, if required. Off-gases from the regeneration reactor V201 will be passed through scrubber V202 to eliminate acid mist.

The final module, shown on Dwg. SD-0014, consists of the required service equipment. This includes a sulfuric acid supply tank and transfer pump T303, P303, neutralization and general purpose tanks and transfer pumps T301, T302 and P301, P302 and liquid ammonia and liquid oxygen storage tanks and vaporizer T305, and T306.

Because of their size, storage tanks T101 and T102 and regeneration reactor V201 will require permanent load-bearing foundations, as will liquid oxygen and ammonia storage tanks T305 and T306 and surge and storage tanks T301, T302, T303 and compressor P401. Slurry and regenerated copper sulfate solution transfer pumps P103 and P201 and cooler HX202 will be preassembled on Skid No. 3, and pumps and tank P301, P302, and T301 will be located on service Skid No. 4.

An instrument control and alarm panel will be provided and analytical support activities will be carried out in a trailer located adjacent to the test area.

Drawing SD-0016 shows the arrangement of equipment at The Geysers Unit No. 7. A process schematic and material balance for the demonstration plant is shown in Dwg. SD-0017.

Specifications for all items of equipment shown on these drawings are contained in Volume III of this report.

B. Test Plan Outline

Development of a test program for demonstrating the process design criteria must be carried out in the face of conflicting requirements. On the one hand, the tests must be carried out at a stable operating condition for a sufficiently long period to demonstrate unequivocally the appropriateness

ISSUE	REVISION	BY	DATE
P-1	PRELIMINARY	RAY	3/30/77

SCALE: 1/4" = 1'
 DRAWN: 3/30/77

NOTES:
 1. REFERENCE DNG. EIC # SD-0015 FOR TANK HEIGHTS & DIMENSIONS.
 2. REFERENCE: TOPOGRAPHIC MAP BY MASSACHUSETTS INC. FOR PLOT AREA DATED MARCH, 1977 SURVEY NO. 1096-77

H ₂ S REMOVAL FROM GEOTHERMAL STEAM PRELIMINARY PLOT PLAN	EIC Corporation NEWTON, MASS. DNG NO. SD-0016
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of the preliminary design criteria; on the other hand, for reasons of economy, the test program must be limited, and a wide range of processing conditions must be investigated to demonstrate system operability over potential ranges anticipated in commercial service. In response to these needs, the demonstration plant test campaign will be carried out in four phases:

- Water test phase.
- Open circuit scrub, liquid/solid separation, and regeneration tests.
- Closed circuit, short term testing over a wide range of operating conditions.
- Closed circuit, long term testing at "optimal" operating conditions.

The measurements to be made during the test program, the information derived from them, and their impact upon scaleup are summarized in Table VI. It should be emphasized that there are limitations inherent in the proposed facility. While scrubbing and liquid-solid separation will be demonstrated with equipment of scalable design in a continuous manner, regeneration will be carried out batchwise. Since it is anticipated that the liquid-solid separation and regeneration equipment chosen for the demonstration plant will not necessarily be appropriate for all possible commercial uses, additional off-line test work is included to obtain design parameters appropriate for alternative approaches for these steps. This can be done with a high degree of confidence since representative copper sulfides will be available; however, these steps may not be demonstrated for a long period of time on equipment types required for commercial service.

Water Tests. In the first phase of testing, geothermal steam will be passed through the scrubbing tower, but "scrubbing" will be done with water containing neither acids nor copper sulfate. The objectives of this test are to demonstrate system mechanical integrity with a minimum of safety hazards or operational problems and to obtain data on the system in a clean condition. System behavior when clean will be used as a reference condition, since it is anticipated that fouling may occur when precipitated sulfides are circulated through the system. Barring mechanical difficulties, it is anticipated that the duration of this phase will be relatively short, less than a month; it will be extended only if required for training operators or modifying equipment.

Open Circuit Tests. The second phase of testing will involve open circuit demonstration of scrubbing, liquid-solid separation, and regeneration. Open circuit testing on the scrubber module, for instance, will entail use of makeup scrub solution derived directly from purchased copper and ammonium sulfates and continuous purging of depleted scrub solution without

Table VI

Summary of Demonstration Plant Measurements and Operational Information

<u>Measurements Made</u>	<u>Information Derived</u>	<u>Impact on Scaleup</u>
Steam and scrub solution flow rates, column pressure, ΔP (water flow tests).	Pressure drops as a function of operating conditions for clean service.	Establish a reference case for column hydraulics, against which performance in service will be rated.
Steam, scrub, makeup, and purge flow rates. Steam quality (water flow tests).	Column material balance.	Establishes column material and energy balance.
Exit steam quality, steam flow rates, L/G ratio, scrub rate (water flow tests).	Entrainment level as a function of operating conditions, demister design.	Determines extent of copper loss by this mechanism, as well as potential impact on generating equipment stream factor.
Purge, makeup flow rates and temperatures (water flow tests).	Energy balance on recovery exchangers and cooler.	Establishes clean service heat-transfer coefficients for comparison with calculated values and as a reference for determining the rate of fouling.
Steam flow rate and compositions, makeup and purge flow rates and compositions.	System material balances for S^o , NH_3 , $SO_4^{=}$, Cu, B, solids in steam, etc., as a function of operating conditions.	Determines rates and extents of removal of NH_3 , H_2S , and other impurities as a function of operating conditions (and internals designs, if tested). Confirms rate data established on lab columns and influence of pH, and $CuSO_4$ content on scrubbing effectiveness. Determines influence of velocities, L/G ratio, temperature, etc., at a scale of internals design which permits reliable extrapolation to commercial scale.
Tray and demister ΔP as a function of time. Visual inspection of tray and demister condition.	Relation between extent of fouling and column hydraulics. Rate of fouling.	Determines operability of various internals designs Establishes service requirements and provides information on the effects of operating conditions on the rates of fouling. Determines effectiveness of use of ΔP as a control variable for commercial operation.

Table VI
(continued)

Measurements Made	Information Derived	Impact on Scaleup
Composition and size distribution of precipitated sulfides. Trace constituents and "modifier" composition.	Process chemistry. Influence of operating conditions, system composition on nature of products formed.	Determines extent to which column operation may be manipulated to influence process conditions in the subsequent regeneration steps. Provides information on impurities effects as influencing design for other installations. Permits correlation between form and composition of precipitated and scrubbed solids and rate of fouling of tower internals.
Test coupon weight loss, corrosimeter reading. Build-up of precipitated solids in the tower.	Rate of corrosion for test materials as a function of operating environment. Propensity of various materials to foul.	Confirms laboratory tests establishing suitability of materials of construction. Provides information on the influence of trace constituents on corrosion rate. Information on the rates of fouling of various materials will be generated, as influencing operability.
Rates-of-change of flow rates, pressure drops, temperature/pressure, etc. (water tests).	Column dynamic response to upsets in controlled variables. Limits of stable operation.	Confirms suitability of proposed system-hydraulics control philosophy, in view of expected magnitude of fluctuations of steam rate and pressure and required delivery condition.
Rates-of-change of steam, makeup, and purge compositions and rates.	Scrubbing system dynamic response to upsets in controlled variables. Influence of operating conditions on stability.	Determines capacity of proposed system to meet removal requirements in view of expected magnitude of fluctuations of steam rate and composition, and operating requirements necessary to insure compliance with performance specifications.
Flow rates and temperatures of makeup and purge streams.	Energy balance on recovery exchangers and cooler under process conditions.	Determines rate of fouling of heat transfer surfaces. Provides information on the influence of temperature, velocity, composition, materials of construction, and solids characteristics on fouling.

Table VI
(continued)

Measurements Made	Information Derived	Impact on Scaleup
Extent of buildup of solids. Loss of metal in pumps, valves, meters, lines, tanks, etc.	Extent and rates of fouling and corrosion of system components under operating conditions.	Confirms laboratory tests determining suitability of materials of construction. Provides information on the influence of velocity and compositions on corrosion-erosion-buildup. Indicates suitability of control hardware.
Test coupon weight loss and buildup of precipitated solids in holding tanks.	Rates of corrosion and fouling for test materials in these operating environments.	Confirms laboratory tests determining suitability of materials of construction for auxiliary equipment. Provides information on the effects of trace constituents.
Change in solids size distribution and character in storage.	Effect of storage temperature and time on solids properties.	Determines influence of holding conditions on subsequent process steps. Provides information on the influence of trace constituent and "modifier" composition.
Solids contents of over and underflow streams from decanter.	Settling rate and overflow clarity for scrub solution produced under varying conditions and at various flow rates.	Defines scale-up parameters for a continuous decanter. Indicates stability of system to upsets caused by varying over- and underflow rates and inlet solids densities and purge solution compositions, temperature, etc.
Off-line tests on liquid/solid separation and wash rates on various test devices.	Solid and liquid filtration rates in 0.1 sq. ft leaf tests, wash efficiencies. Solid settling rates and compression points in liter cylinders, influence of flocculants. Rates of solids settling at high G's.	Determines filtration behavior on real slurries. Results can be scaled up to determine commercial-scale requirements for other types of liquid/solid separation devices, e.g., rotary drum filters, clarifiers, centrifuges, etc.

Table VI
(continued)

Measurements Made	Information Derived	Impact on Scaleup
Filtrate composition.	Influences of operating conditions - characteristics of solids, type of L/S separation device, use of aid/floc, etc. - on clarity.	Determines non-soluble copper loss at the liquid/solid separation step (done for both on- and off-line tests). Solution composition also largely fixes soluble copper losses, wash efficiency, fixes effectiveness of NH_3 purge. Indicates necessity of subsequent treatment steps, e.g., neutralization, prior to disposal, as well as possible methods.
Separated solids physical properties: density, pumping limit, cohesion/stickiness, etc.	Influence of operating conditions on external properties for fresh/aged/wet/dried solids.	Will determine how separated solids will be transferred from separation to regeneration steps at commercial scale. Data derived from both on- and off-line tests.
9 Regeneration reactor slurry composition, temperature, pressure, O_2 /air flow rates, vent gas composition, agitation conditions.	System material balance for S^{--} , S^0 , SO_4^{--} , Cu, and others as a function of operating conditions. Rate and extent of regeneration of precipitated sulfides.	Confirms laboratory data on the rates and stoichiometry of aqueous sulfide oxidation and influence of solution composition. Establishes influence of agitation on mass transfer in equipment of scalable size. Provides information on the effects of trace constituent and "modifier" composition.
Test coupon weight loss and buildup of solids in reactor/agitator.	Rate of corrosion and fouling for test materials in these operating environments.	Confirms laboratory tests determining suitability of materials of construction. Determines operability of various internals and agitator designs. Provides information on the effects of operating conditions on rates of fouling.
Off-line tests on sulfide oxidation by other techniques.	Rate and extent of oxidation and formation of insoluble copper compounds during roasting in air. Rate and stoichiometry of aqueous oxidation at high temperatures and pressures.	Determines suitability and obtains preliminary design information for scaleup of regeneration step to commercial scale on representative materials for alternate techniques. Provides information on the effects of operating conditions and compositions.

Table VI
(continued)

Measurements Made	Information Derived	Impact on Scaleup
Leached slurry flow rate and temperatures (water flow tests).	Energy balance on cooler.	Establishes clean service heat transfer coefficients for comparison with calculated values and as a reference for determining the rate of fouling.
Leached slurry flow rate and temperatures.	Energy balance on cooler under process conditions.	Determines rate of fouling of heat transfer surfaces. Provides information on the influence of operating conditions on the rate and extent of fouling.
Leached solids size distribution and character.	Effect of regeneration operating conditions, system properties, cooling rate, etc., on solids properties.	Determines influence of regeneration conditions on subsequence process steps. Provides information on the influence of trace constituents and "modifier" composition.
Liquid/solid separation behavior; polish filters flow rate, pressure drop.	Same as for liquid/solid separation of precipitated sulfides.	Same as for liquid/solid separation of precipitated sulfides. Data required on rates, wash efficiencies, solids and filtrate properties and compositions, etc. Both on- and off-line testing will be carried out.
Waste solids composition and properties.	Physical and chemical stability of process solid wastes. Influence of process conditions on fresh/aged/wet/dried solids.	Determines how waste solids will be transferred from separation to disposal steps at commercial scale as well as possible methods of disposal. Information required on properties of solids generated in off-line tests as well. Provides data on the effects of operating conditions on waste properties.
Makeup copper and acid addition rates.	Material balance on Cu and SO_4^{--} requirements.	Confirms overall system material balances based on other stream composition measurements.

Table VI
(continued)

Measurements Made	Information Derived	Impact on Scaleup
Rates of water addition to process streams at all points of the system.	System water balance.	Fixes liquid waste purge requirements at commercial scale and the relationship to operating conditions, e.g., heat loss, demister wash requirements.
Power input to all motors.	System operating power requirements.	Determines process power requirements, especially for leach reactor in gassed and ungassed conditions.
Rate of removal of Cu from purge stream with H ₂ S, Fe.	Materials consumption, degree of recovery of Cu.	Defines loss of Cu in purge streams for these recovery techniques, indicates need for further treatment.

regard to the requirements of separation and makeup. The objective of this test will be to demonstrate stable operation of the scrubber under carefully controlled conditions. In addition, a limited but systematic investigation of the effects of process conditions (temperature, pressure, liquid-to-gas ratios, copper content, pH, etc.) on mass transfer efficiency will be carried out. Finally, a determination of tower dynamics will be made in a mode of operation uncoupled to liquid-solid separation and regeneration to ease control problems. These tests will be interrupted, as required, by intervals of water testing to permit makeup of fresh scrub solution and disposal of purge solution.

Open circuit liquid-solid separation tests will be carried out in conjunction with open circuit scrubbing tests, subject only to the constraints of timing and availability of copper sulfides. The object of these tests will be to determine the behavior of the solids produced by the scrubbing tower in the separator selected for the demonstration plant. The liquid-solid separation behavior will be related to tower and decanter operating conditions, such as temperature, slurry density, underflow density, etc. In addition, off-line testing will be carried out to determine basic data on filtration and settling rates appropriate to other types of filtration equipment, for example, continuous rotary vacuum filters, and settling equipment, such as thickeners and clarifiers. These data will be related to operating conditions in the scrubbing tower e.g., aging times and temperature of precipitated solids, influence of habit modifiers and conditioning agents, effects of trace elements, etc.

Solids produced during the open circuit separation testing will be used to determine the basic parameters for operation of the regeneration reactor. The effects of temperature, pressure, excess air, pH, residence time, and agitation on reaction rates and stoichiometry will be determined for solids produced under varying conditions in the tower and subject to various aging cycles. This information will be used to confirm the overall process stoichiometry and thereby define the overall material balance. Effects of reactor operating conditions on the nature of the residues produced and their liquid-solid separation characteristics will be determined.

Off-line testing of alternate regeneration schemes, such as roasting, oxidation under continuous conditions with limited oxygen supply, and oxidation under conditions favoring complete conversion of sulfide to sulfate, will be carried out with solids produced in the open circuit separation tests. It is anticipated that some of this testing will be carried out in laboratory scale equipment at EIC Corporation or in vendor shops.

Following the open circuit tests, the plant will be run for a short duration in the water test mode to determine the rate of fouling, and will then be cleaned and flushed prior to initiation of continuous, closed circuit testing.

Closed Circuit, Short Term Tests. Closed circuit, short term testing will be carried out to demonstrate plant operability and dynamics under integrated conditions. Operational procedures will be confirmed during this period to insure that longer periods of testing, scheduled to follow, can be carried out in an orderly manner. The plant will be operated at the extremes of anticipated operating conditions in order to demonstrate operability and obtain scoping data for subsequent test work. The plant will be operated in a closed circuit mode for a sufficient time (approximately one month) to systematically explore the effects of operating parameters on overall performance. An object of this phase of the program will be to obtain data which may be used to extrapolate operation to conditions not considered "optimum" for the site chosen, as well as to obtain copper sulfides in significant quantities for evaluation in off-line liquid-solid separation and regeneration testing. Water testing will follow integrated closed circuit short term testing, and the plant will then be inspected, cleaned, and modified as required.

Closed Circuit, Long Term Testing. The final four months of the test program will be devoted to a long term, continuous test under conditions controlled about the point determined as "optimum" for operation at the test site. The objectives of this test will be to demonstrate plant operability, confirm design criteria, and measure rates of fouling under steady conditions; i.e., without ambiguities introduced by operation under a variety of test conditions.

The data to be gathered, summarized in Table VI will provide overall material and energy balances for the process as well as a compilation of information on the operating characteristics of key elements of the system, viz., the scrubbing tower C101, decanter C102, and regeneration reactor V201. Flow rates, temperatures, and pressures will be measured by instrumentation provided as a part of the test facility equipment package. Samples will be withdrawn from the process streams, as appropriate, and analyzed in equipment installed at the site to provide information for process control and interpretation of results. Analytical instrumentation, including portable corrosion meter, spectrophotometer, gas chromatograph, and required wet chemistry hardware, will have been calibrated in the laboratory. Suitable experimental procedures will also be determined prior to use in the field. Specialized analytical procedures, such as petrographic examination of precipitated sulfides, will be carried out off-site.

A detailed description of the tasks required to achieve these objectives, including procedures for start up, shut down, operation, and data collection, reduction and evaluation is presented in the Test Plan and Operation Instructions document, Volume III of this report.

C. Key Process Parameters to be Verified

The demonstration plant's description, its capabilities, anticipated mode of operation, and the proposed test plan for its operation have been

summarized in the preceding sections. The immediate objectives of its operation are to demonstrate the process concept and verify the assumed process and mechanical design criteria in equipment of scalable design.

The laboratory and pilot scale test work which has been carried out to date allows a more confident definition for some of the assumed criteria than for others. Furthermore, the consequences of a revision to more conservative criteria, e.g., halving maximum allowable velocities, would be more significant for some items than for others because of their relative cost and process significance. Doubling the required decanter area, for example, would cost little, but increasing the scrubber diameter by forty percent would be very costly. On the other hand, doubling the required froth height, to obtain the equivalent contact time at a fixed scrubber diameter, would not impose an unacceptable cost increase. The key criteria to be verified in the field tests, possible problems, and design alternatives are summarized in Table VII. The order in which they are listed is, roughly, the order of their importance from the economic and process operability point of view.

Because the key process objective is to obtain both high degrees of H₂S removal and high reliability, criteria which affect the scrubber design and operation are of critical importance. In particular, it will be important to demonstrate that the scrubber can operate with stability for long periods of time with a minimum of attention, maintain a high degree of H₂S removal efficiency during process upsets, and respond to control point changes necessitated by varying steam compositions or flow rates.

The scrubber and its trim components must show adequate resistance to failure by corrosion, whether from ambient H₂S or from process fluids, and prove not to be prone to operability problems brought about by fouling. In addition, operation of the leach regeneration and purge stream decopperization steps must be shown to be effective under a wide variety of process conditions, so that the results can be extrapolated to continuous operation at a commercial scale with confidence.

It is possible to envision design alternatives which would rectify any potential operation problem brought about through the use of inappropriate design criteria, although some changes would have an adverse effect on process economics. The design of the demonstration plant has been carried out in such a way as to permit maximum flexibility in its operation. It is anticipated that if unforeseen operating problems do occur, they can be rectified quickly or the necessary plant design changes made with a minimum additional cost and loss of time.

Table VII

Key Process Parameters to be Verified

<u>Criteria</u>	<u>Potential Problems</u>	<u>Design Alternative</u>
Scrubber and Trim Materials of Construction	Crevice corrosion of C20Cb3.	Redesign to eliminate crevices. Specify use of lining material or Ti.
Scrubber Tray Design	Fouling, lower than expected efficiency, narrow operating range	Revise tray layout, downcomer area, froth height, operating conditions. Specify alternative scrubber type.
Process Control Concept	Narrow operating range, on-line analytical difficulties, intermittent operability problems.	Specify alternative hardware. Revise control philosophy.
Demister Specification	Fouling, high pressure drop, inefficient operations	Revise washing schedule/technique. Specify lower velocity, alternative style. Redesign for external separator.
Regeneration Reactor Effectiveness	By-passing of solids, low conversion efficiency, low gased density/frothing.	Redesign internals, reduce agitation intensity. Specify staged vessels or solids recycle.
Purge Decopperization Efficiency.	Poisoning by trace elements, poor chemical/mechanical stability.	Revise operating conditions. Remove trace elements. Specify alternative resin or alternative decopperization technique.
Trim Components Mechanical Integrity	Seal failure, erosion/corrosion.	Specify alternative styles, materials.
Heat Exchangers Fouling Factor	Rapid fouling.	Revise operating conditions. Forego energy recovery.