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Sulfur Dioxide Emission Control by Hydrogen Sulfide Reaction in Aqueous Solution

The Citrate System

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7774

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The Citrate System

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SULFUR DIOXIDE EMISSION CONTROL BY HYDROGEN SULFIDE REACTION IN AQUEOUS SOLUTION

The Citrate System

by

J. B. Rosenbaum,[1] W. A. McKinney,[2] H. R. Beard,[3] Laird Crocker,[4] and W. I. Nissen[5]

ABSTRACT

Prolonged laboratory and limited pilot plant tests have shown that the Bureau of Mines buffered SO_2-H_2S process is capable of removing 95 to 99 percent of the SO_2 from industrial waste gases. Most of the SO_2 is converted to elemental sulfur; only about 1 percent converted to sulfate. The process comprises (1) washing the flue gas to remove particulates and SO_3, (2) absorption of the SO_2 in citric acid or other carboxylate solution, (3) reaction of the loaded solution with H_2S in a closed vessel to precipitate the absorbed SO_2 as elemental sulfur, and (4) separation of the sulfur from the regenerated solution by oil flotation and melting. Two-thirds of the molten sulfur is converted to H_2S for use in the sulfur precipitation step by reacting sulfur vapor with natural gas and steam in the presence of an alumina catalyst.

The chemistry and mechanism of the process are described, initial laboratory and pilot plant data are summarized, and second-generation laboratory operation and pilot plant design are reviewed. Preliminary cost estimates are presented for recovering sulfur from copper smelter gas, powerplant flue gas, and Claus plant tail gas.

INTRODUCTION

The Bureau of Mines buffered SO_2-H_2S process for removing SO_2 from waste gas developed as a spin-off from research on recovering sulfur from H_2S. We were searching for a technique that would be more manageable on a laboratory scale than the Claus process for reacting H_2S with SO_2. Initial experiments confirmed information in the technical and patent literature (1, 8)[6] that H_2S and SO_2 can be readily reacted in many organic liquids to recover sulfur. Furthermore, the ease and completeness of the reaction suggested that if H_2S

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[6] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

were available or could be readily generated, the technique might be applicable for removing SO_2 from a dilute combustion gas or smelter gas. Subsequent laboratory investigations with dilute SO_2-air mixtures showed a very high SO_2 removal and sulfur recovery efficiency, but also disclosed that losses by volatilization of the high-boiling organic liquids tested would be excessive when treating dilute SO_2 gas streams.

Attention was then turned to the use of inorganic and mixed organic and inorganic solutions. Organic acids such as acetic, citric, lactic, malic, glycolic, succinic, and others were mentioned by Keller (10) for the H_2S-SO_2 reaction. After screening many possible reagent combinations, a solution of sodium citrate and citric acid was selected as being suitable for further development of the process. Among the factors affecting the choice of citrate were chemical stability, low vapor pressure, adequate pH buffering capacity, and the purity and physical character of the precipitated sulfur. Other carboxylates we tested such as maleic anhydride and glycolic acid were about as suitable as citric acid and cost less, but in the closed system projected, with slight solution or decomposition loss, the carboxylate price seemed relatively unimportant. Acetic acid buffered well but volatility losses were high.

Findings of the initial research were reported in 1970 and 1971 (7, 13). As first conceived, the process was comprised of gas cleaning and cooling, absorbing SO_2 in citrate solution, reacting the absorbed SO_2 with H_2S, washing the precipitated sulfur, and reacting two-thirds of the sulfur with natural gas and steam to form the needed H_2S.

Subsequently, the integrated process was studied in a laboratory apparatus processing up to 15 cfm of gas at SO_2 concentration of 0.3 to 2.0 percent. An important difference from the initial process concept was that in lieu of washing for citrate removal, the precipitated sulfur was filtered and melted to give substantially complete separation from occluded citrate. Preparation of H_2S from recycled sulfur was separately examined, but bottled H_2S was used in the integrated laboratory apparatus.

In November 1970, a scaled-up plant to process up to 300 cfm of reverberatory furnace gas was placed into operation jointly by the Bureau of Mines and Magma Copper Co. at the San Manuel smelter in Arizona. Sulfur conversion to H_2S was omitted as being premature. Intermittent operation of the pilot plant over a 6-month period was troubled by failures of the gas cleaning system, pump breakdowns, and plugging of flow lines by precipitated and melted sulfur. Useful data on consumption of citric acid and other reagents were not obtained, but the SO_2 absorption and regeneration system proved to be readily manageable for removal of 90 to 99 percent of the SO_2 from the smelter gas.

To obtain firm data on chemical, capital, and operating costs for process evaluation, a second-generation integrated laboratory apparatus was assembled and operated as a prototype of a pilot plant to be constructed at the Bunker Hill lead smelter, Kellogg, Idaho. Removal of sulfur from the dilute citrate slurry by oil flotation has worked well in the laboratory and is a potential major improvement to the process that will be tested in the pilot plant. A contract for detailed design and construction of the Kellogg pilot plant with

a nominal capacity of 1,000 cfm of 0.5 percent SO_2 gas has been awarded by the Bureau of Mines. Initial operation by the Bureau of Mines and Bunker Hill is expected in the fall of 1973.

A pilot plant to test the process on coal burning powerplant flue gas was announced by a consortium composed of Arthur G. McKee Co., Peabody Engineering, and Pfizer Chemical (5). Startup of their pilot plant to handle 2,000 cfm of 0.25 percent SO_2 gas was slated for the spring of 1973.

This Bureau of Mines report describes the chemistry and mechanisms of the buffered SO_2-H_2S process, summarizes the initial laboratory and pilot plant data, and reviews the second-generation laboratory operation and pilot plant design. Preliminary estimates of capital and operating costs for recovering sulfur from copper smelter gas, powerplant flue gas, and Claus plant tail gas are presented.

GENERALIZED PROCESS DESCRIPTION

As shown in figure 1, the buffered SO_2-H_2S process is comprised of the following steps:

1. The SO_2-bearing gas is cooled to between 45° and 65° C and cleaned of H_2SO_4 mist and solid particles.

2. The SO_2 is absorbed from the cooled and cleaned gas by a solution of sodium citrate, citric acid, and sodium thiosulfate.

3. Absorbed SO_2 is reacted with added H_2S precipitating elemental sulfur and regenerating the solution for recycle.

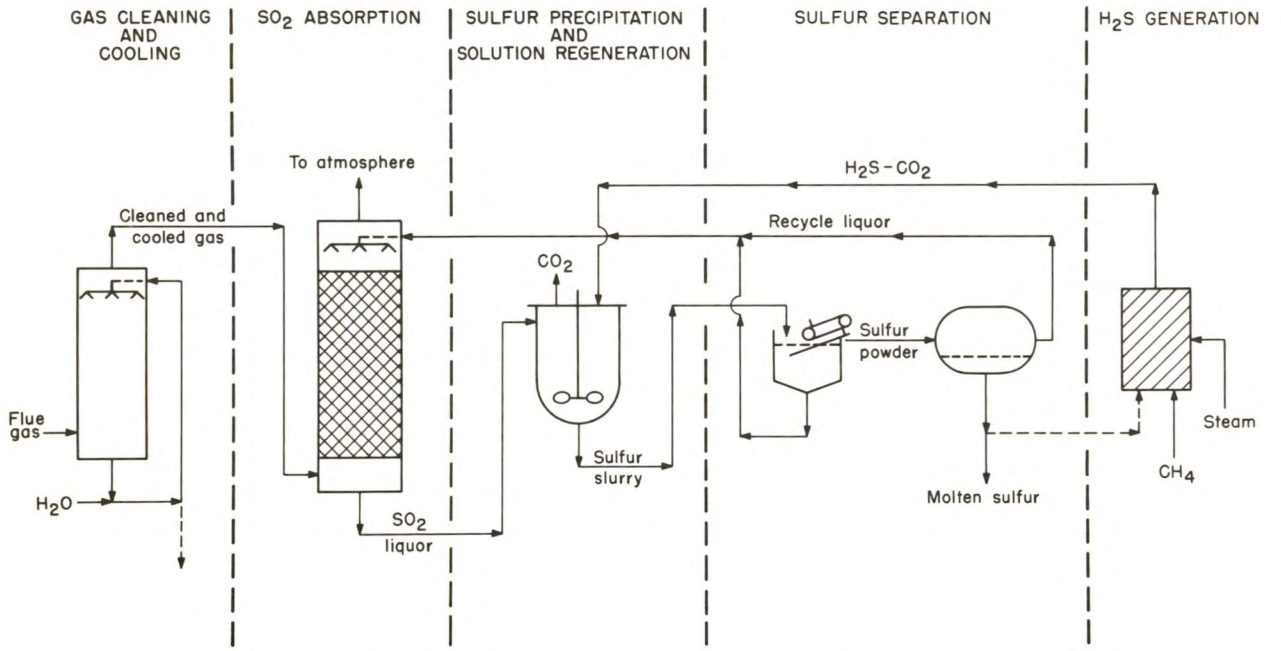

FIGURE 1. - Generalized citrate process flowsheet.

4. Sulfur is separated from the solution by oil flotation and melting.

5. The H_2S for step 3, if not otherwise available, is made by reacting two-thirds of the recovered sulfur with natural gas and steam.

Variations of the process that may be suitable for local conditions stem from ability to steam strip a part of the loaded SO_2. Depending on the solution loading, about two-thirds of the SO_2 can be stripped using 3 to 5 pounds of steam per pound of SO_2. Residual SO_2 in solution would be reacted with H_2S to obtain elemental sulfur and regenerated solution for the absorption step. The SO_2 obtained by steam stripping could be used for enriching a lean SO_2 gas to make it suitable for feed to a H_2SO_4 plant. Alternatively, the SO_2 could be reacted with methane to make H_2S for regenerating the partly stripped solution.

CHEMISTRY OF THE PROCESS

Absorption of SO_2 in aqueous solution is pH-dependent, increasing at higher pH. Because dissolution of SO_2 forms H_2SO_3 (sulfurous acid) with resultant decrease in pH, the absorption of SO_2 in aqueous solution is self-limiting. However, by incorporating a buffering agent in the solution to inhibit pH drop during SO_2 absorption, substantially higher SO_2 loadings can be attained. The principal function of citric or other organic acids is as a buffering agent during SO_2 absorption. Thiosulfate ion serves a major role in complexing absorbed SO_2, thus inhibiting oxidation to sulfate. Hydrogen sulfide for the process may be made by reacting sulfur, methane, and steam in a catalytic converter. Regeneration of the absorbent solution by removing all SO_2 enables substantially complete SO_2 removal from gaseous emissions.

ABSORPTION AND REGENERATION

Sulfur dioxide and H_2S react in aqueous solutions at ambient temperature and atmospheric pressure to form sulfur and water according to equation 1.

$$SO_2 + 2H_2S \rightarrow 3S^\circ + 2H_2O \qquad (1)$$

The overall stoichiometry involves 1 mole of SO_2 and 2 moles of H_2S, but the chemistry is believed to be more complex. Thiosulfate and polythionates are found in solution at equilibrium concentrations after several SO_2-absorption and H_2S-regeneration cycles. Among the important reactions that are believed to occur are the following:

$$SO_2 + H_2O \rightleftarrows HSO_3^- + H^+ \qquad (2)$$

$$HSO_3^- + S \rightleftarrows S_2O_3^= + H^+ \qquad (3)$$

$$H^+ + HSO_3^- + S_2O_3^= \rightleftarrows (SO_2 \cdot S_2O_3)^= + H_2O \qquad (4)$$

$$(SO_2 \cdot S_2O_3)^= + 2H_2S \rightleftarrows 3S^\circ + 2H_2O + S_2O_3^= \qquad (5)$$

Reaction 2 shows the formation of bisulfite ion, which is about 95-percent complete at a pH from 3.5 to 4.5. Reaction 3 shows formation of thiosulfate, and reaction 4 shows a probable complex formed from hydrogen, bisulfite, and thiosulfate ions. Reaction 5 shows how the complex might react with H_2S to form elemental sulfur and thiosulfate ions. To assure satisfactory operation of the system on startup, the initial absorbing solution is made at least 0.3 M in sodium thiosulfate.

Kodak Research Laboratories has reported the formation of the $(SO_2 \cdot S_2O_3)^=$ complex (3). As further evidence of such a complex, we found that when a citrate solution containing SO_2 and $S_2O_3^=$ is loaded on an anion exchange resin and eluted with 1 M NaCl, only about 30 percent of the absorbed SO_2 is eluted. If the same solution without $S_2O_3^=$ is treated similarly, all the SO_2 is eluted.

Small concentrations of polythionates found in the recycling solution could be formed and decomposed by the following reactions:

$$H^+ + H_2S + 3HSO_3^- \rightleftarrows S_4O_6^= + 3H_2O \quad (6)$$

$$2H^+ + 4HSO_3^- + S_2O_3^= \rightleftarrows 2S_3O_6^= + 3H_2O \quad (7)$$

$$S_3O_6^= + S^\circ \rightleftarrows S_4O_6^= \quad (8)$$

$$S_4O_6^= + S^\circ \rightleftarrows S_5O_6^= \quad (9)$$

$$S_5O_6^= + HSO_3^- \rightleftarrows S_4O_6^= + S_2O_3^= + H^+ \quad (10)$$

These are probably the major reactions involving polythionates. Tetrathionate ($S_4O_6^=$) stays nearly constant throughout the system. Reactions 6 and 7 are slow compared with the rate of reaction 5, and only small amounts of $S_4O_6^=$ are formed in the reactor where both sulfur and bisulfite are present. According to reactions 7 and 8, the $S_3O_6^=$ decreases in the reactor where sulfur is formed and increases during absorption of SO_2 where sulfur is absent and HSO_3^- is maximum. Pentathionate ($S_5O_6^=$), as shown in reactions 9 and 10, behaves contrary to $S_3O_6^=$; thus, the net effect of reactions 8, 9, and 10 is to maintain a uniform level of $S_4O_6^=$.

Thiosulfate forms in the reactor according to reactions 3 and 10. At a system pH of 3.5 to 4.5, the $S_2O_3^=$ concentration stabilizes at approximately 33 grams per liter (0.3 M).

OXIDATION OF SO_2 AND pH CONTROL

When using an aqueous solution for absorbing SO_2 from flue gas containing oxygen, some of the absorbed SO_2 is oxidized with formation of H_2SO_4 in accordance with reaction 11.

$$2HSO_3^- + O_2 \rightarrow 2SO_4^= + 2H^+ \quad (11)$$

Dissolved metals such as iron or copper, which may be derived from the flue gas or from corrosion of equipment, generally catalyze the oxidation of

SO_2 (12). In the buffered SO_2-H_2S process, oxidation of SO_2 in the aqueous solution is sharply depressed by complexing of SO_2 by $S_2O_3^=$ and complexing of metal ions of valence 2 or higher by citrate. Accelerated oxidation tests using a gas containing 4 percent SO_2 and 16 percent oxygen and a citrate solution of pH 4.5, without thiosulfate, showed about 1 percent of the SO_2 was converted to H_2SO_4. When the gas contained 7.5 percent oxygen, about 0.5 percent of the SO_2 oxidized to H_2SO_4. The presence of 0.5 M thiosulfate in the solution depressed SO_2 oxidation fivefold.

Although oxidation of SO_2 in the absorption step is a small source of H_2SO_4, some H_2SO_4 pickup occurs because of incomplete H_2SO_4 mist removal from the feed gas, and some sulfate is formed in the solution present during melting of the sulfur, possibly in accordance with reaction 12.

$$3HSO_3^- \rightarrow 2SO_4^= + S + H^+ + H_2O \qquad (12)$$

Reaction 12 is pH-dependent and is very slow above pH 4.5. Control of pH may be effected by the addition of Na_2CO_3 to neutralize any H_2SO_4 absorbed or formed. Refrigeration of a small side stream would remove sulfate as Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) without removing citrate or thiosulfate. At a sulfate concentration of 50 grams per liter, 60 percent of the sulfate would be removed by cooling to 4° C.

HYDROGEN SULFIDE GENERATION

Generation of H_2S on an industrial scale by reacting hydrogen, usually from reformed methane, with sulfur is routine practice (6). An alternative procedure that may be more economical bypasses methane reforming and directly reacts methane with sulfur and steam as shown in reaction 13.

$$CH_4 + 4S + 2H_2O \rightarrow CO_2 + 4H_2S \qquad (13)$$

This approach is a modification of the commercial process for producing carbon disulfide, in which sulfur and methane are reacted according to equation 14 (2, 14).

$$CH_4 + 4S \rightarrow CS_2 + 2H_2S \qquad (14)$$

By adding steam as shown in equation 13, the CS_2 formed in equation 14 is hydrolyzed to $CO_2 + H_2S$. Reaction 13 yields a gas containing 20 percent CO_2 and 80 percent H_2S. A side reaction between CS_2 and H_2O as shown in reaction 15 results in the product gas

$$CS_2 + H_2O \rightarrow H_2S + COS \qquad (15)$$

containing around 0.1 percent of undesirable carbonyl sulfide. The carbonyl sulfide, along with CO_2, is inert in the regeneration reaction by which SO_2 and H_2S react to form sulfur.

Carbon monoxide may be reacted with sulfur to produce CS_2 (11), or with sulfur and steam to produce H_2S as shown in reaction 16.

$$CO + S + H_2O \rightarrow CO_2 + H_2S \quad (16)$$

The product gas contains 50 percent H_2S.

Sulfur dioxide gas, which may be obtained by steam stripping a part of the SO_2 from an absorbing solution, can be made to react with methane to form H_2S by reaction 17.

$$3CH_4 + 4SO_2 \rightarrow 3CO_2 + 2H_2O + 4H_2S \quad (17)$$

After condensing the water, the product gas contains 57 percent H_2S.

Base metal sulfides can be reacted with H_2SO_4 or HCl under reducing conditions to yield H_2S. Also molten copper matte (a mixture of copper and iron sulfides) can be reacted with steam to yield H_2S. Another procedure, with roots in commercial practice (4), is to reductively roast copper sulfide concentrate with lime to produce a calcine containing calcium sulfide, that upon subsequent reaction with water and carbon dioxide yields H_2S.

LABORATORY AND PILOT PLANT TESTS AND PLANS

Findings from initial laboratory and pilot plant testing of the SO_2-H_2S process have been summarized (13). During most of the early work the aqueous solution was composed of 1 M citric acid and 1.5 M NaOH and had a pH of 3.8 to 3.0. Thiosulfate was not added, and although its presence in the cycling solution was known, the role of thiosulfate in complexing SO_2 was not fully recognized. In fact, SO_2 complexing was attributed to the citrate ion, and hence, citrate was used as the name of the process. Sulfur was precipitated, and the solution regenerated, using tank H_2S in a single stirred reactor. Sulfur was separated from the slurry by filtration or thickening and centrifuging, and subsequently melted batchwise in the laboratory, and continuously in the San Manuel pilot plant.

Second-generation laboratory work in preparation for the Bunker Hill pilot plant test has used solution containing a higher ratio of caustic to citrate (0.5 M citric acid and 1.0 M NaOH) with a resultant higher pH range of 4.5 to 3.8. Also the starting solution was made 0.3 M in sodium thiosulfate. A lower citrate concentration of 0.5 M was selected as appropriate for 0.5 percent SO_2 stack gas to be treated at the Bunker Hill smelter as compared with over 1 percent SO_2 in the stack gas treated at San Manuel. An 80 percent H_2S-20 percent CO_2 gas has been used for sulfur precipitation in a series of three reactors arranged for countercurrent flow of gas and solution. Sulfur separation has been by oil flotation and the flotation product at about 50 percent solids pumped through a heat exchanger for melting and periodic discharge from a pressurized settler.

Pertinent developments, findings, and plans are reviewed for the several unit steps in the process. Figures 2 and 3 are photographs of the first- and

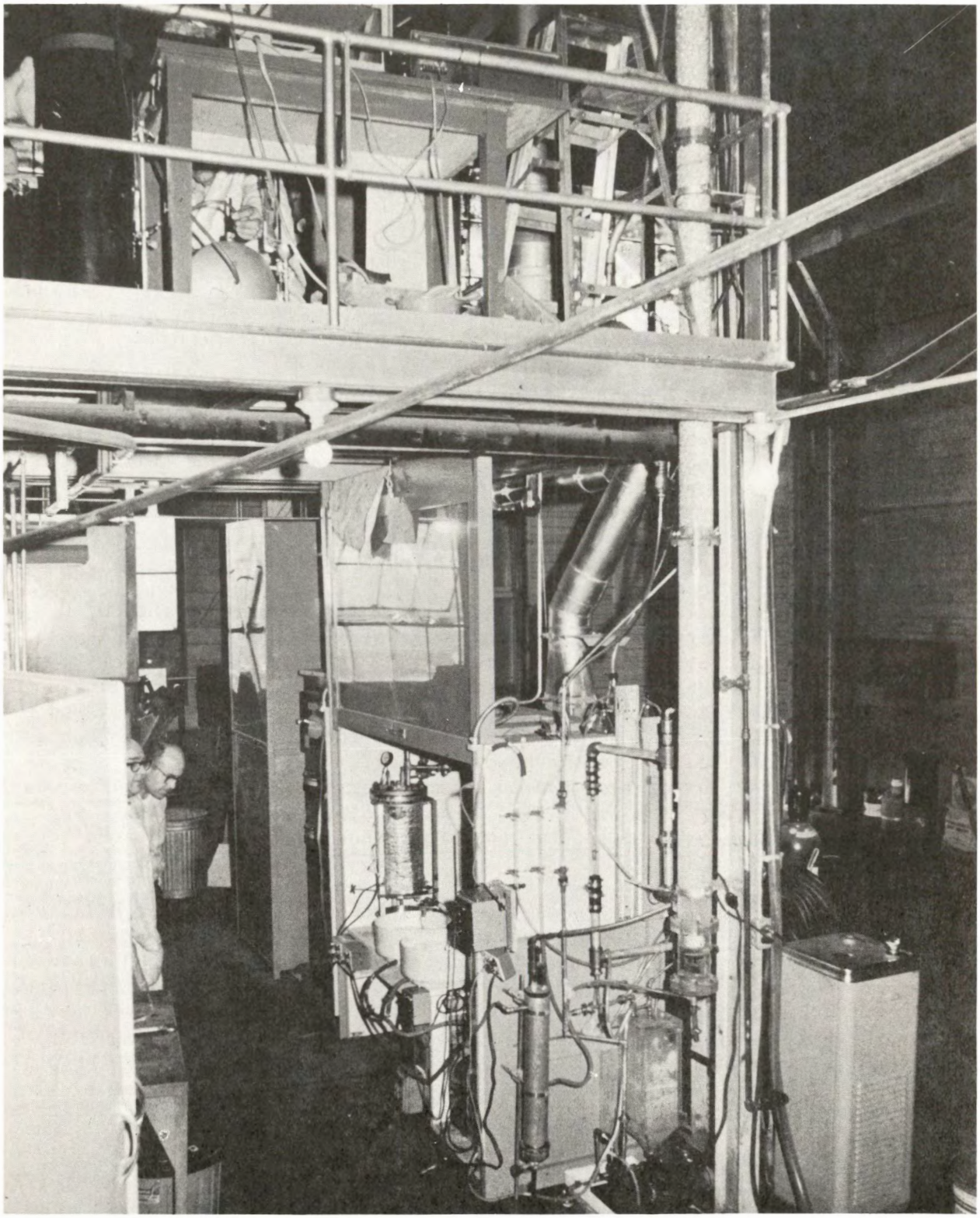

FIGURE 2. - First-generation laboratory assembly.

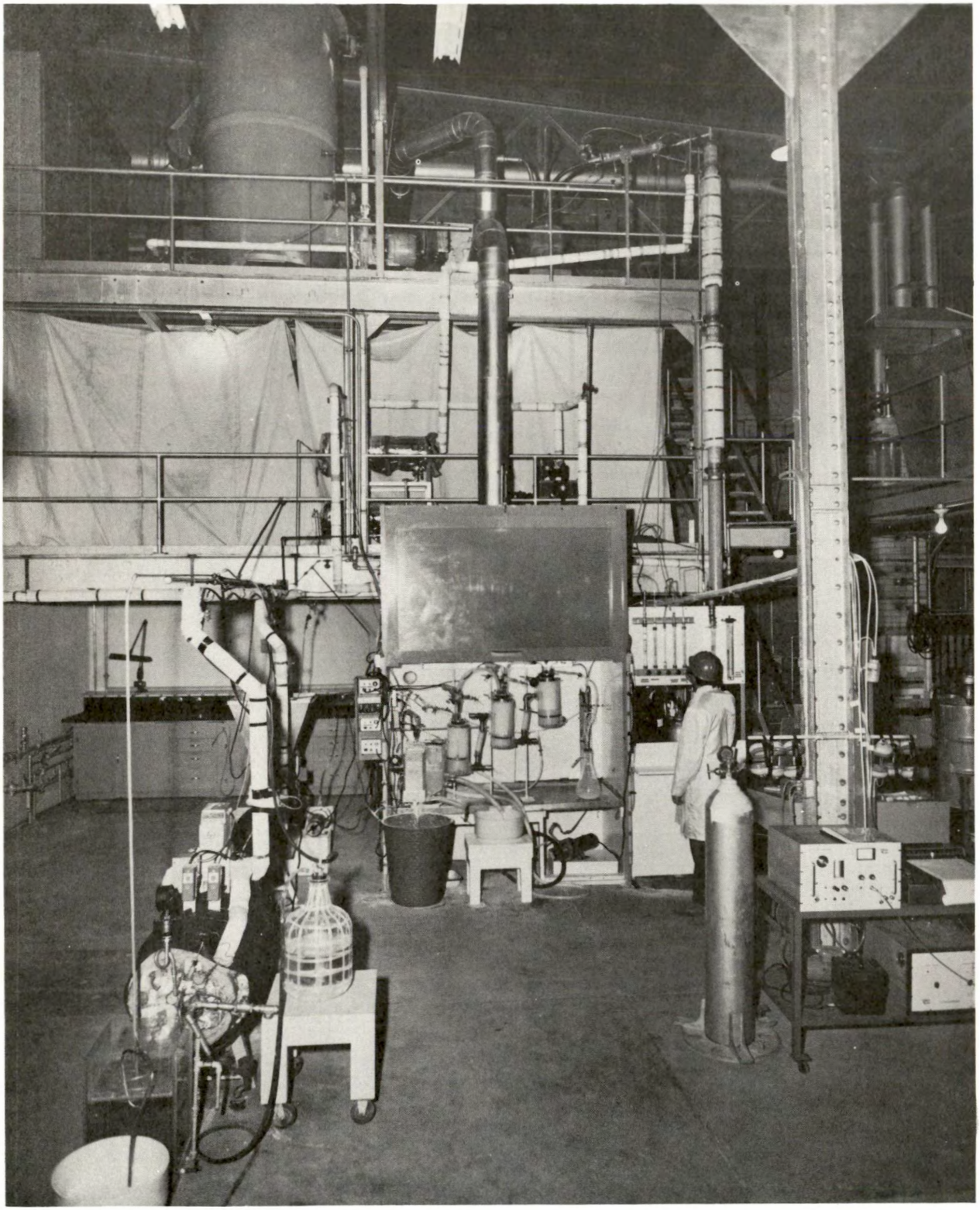

FIGURE 3. - Second-generation laboratory assembly.

second-generation laboratory test assemblies. A 4-inch-diameter by 12-foot-tall packed column used for SO_2 absorption in both assemblies is shown at the right in each photograph. Figure 4 is the flowsheet, and figure 5 is a photograph of the San Manuel pilot plant. Figure 6 is a block diagram of the scheduled Bunker Hill pilot plant.

Operation of the test plant at Bunker Hill will start on cleaned gas diverted from the lead smelter acid plant and diluted with air to 0.5 percent SO_2. Hydrogen sulfide at startup will come from a tank trailer. After several weeks of operation, when mechanical and chemical shakedown has been completed, gas-cleaning and H_2S-generation sections of the pilot plant will be activated, and smelter sinter plant tail gas will be used as pilot plant feed. The sinter tail gas contains dust, acid mist, and about 0.5 percent SO_2. One of the goals in the test plant operation is to determine the minimum gas-cleaning requirement compatible with the SO_2-H_2S process.

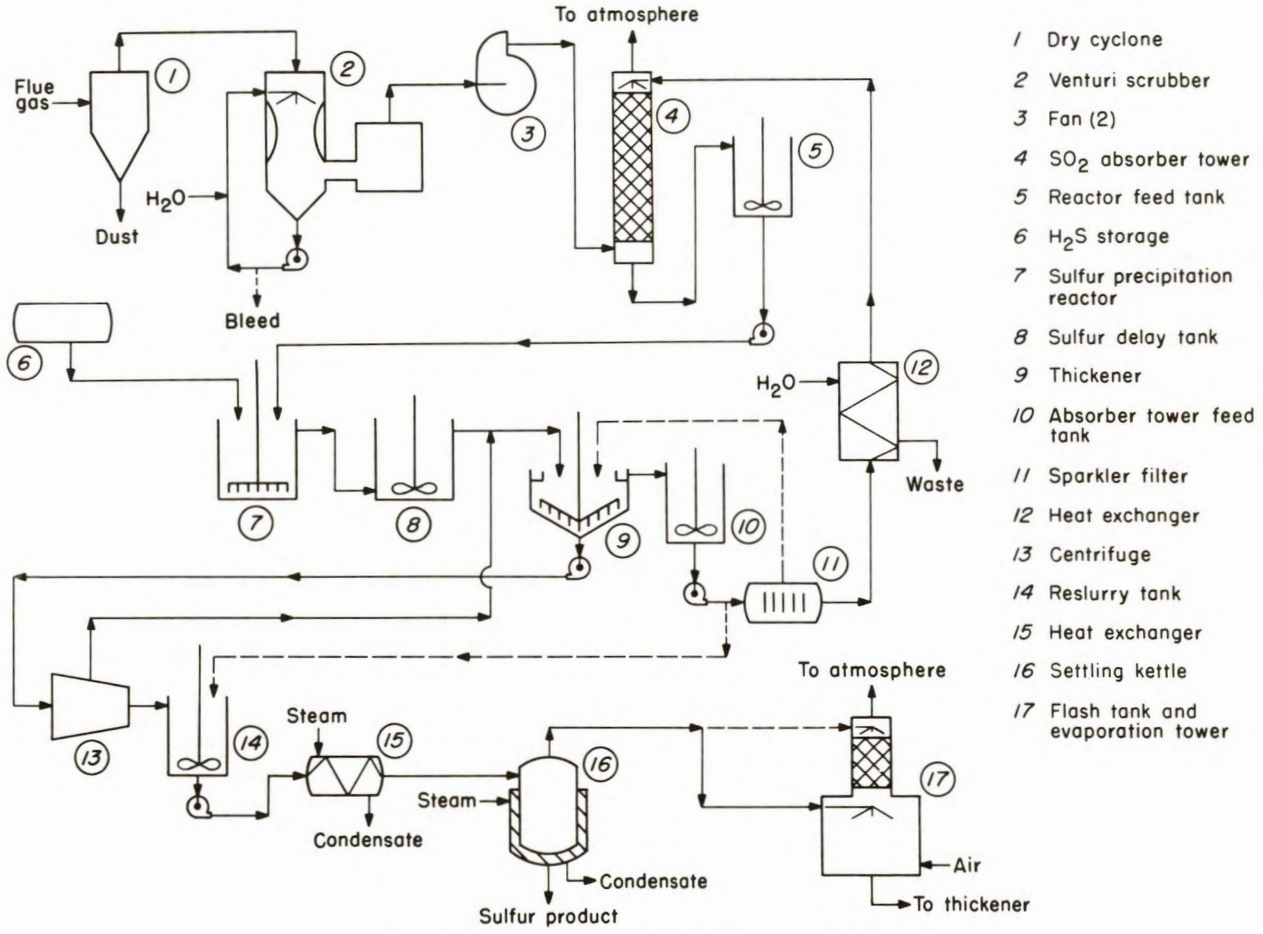

FIGURE 4. - San Manuel pilot plant flowsheet.

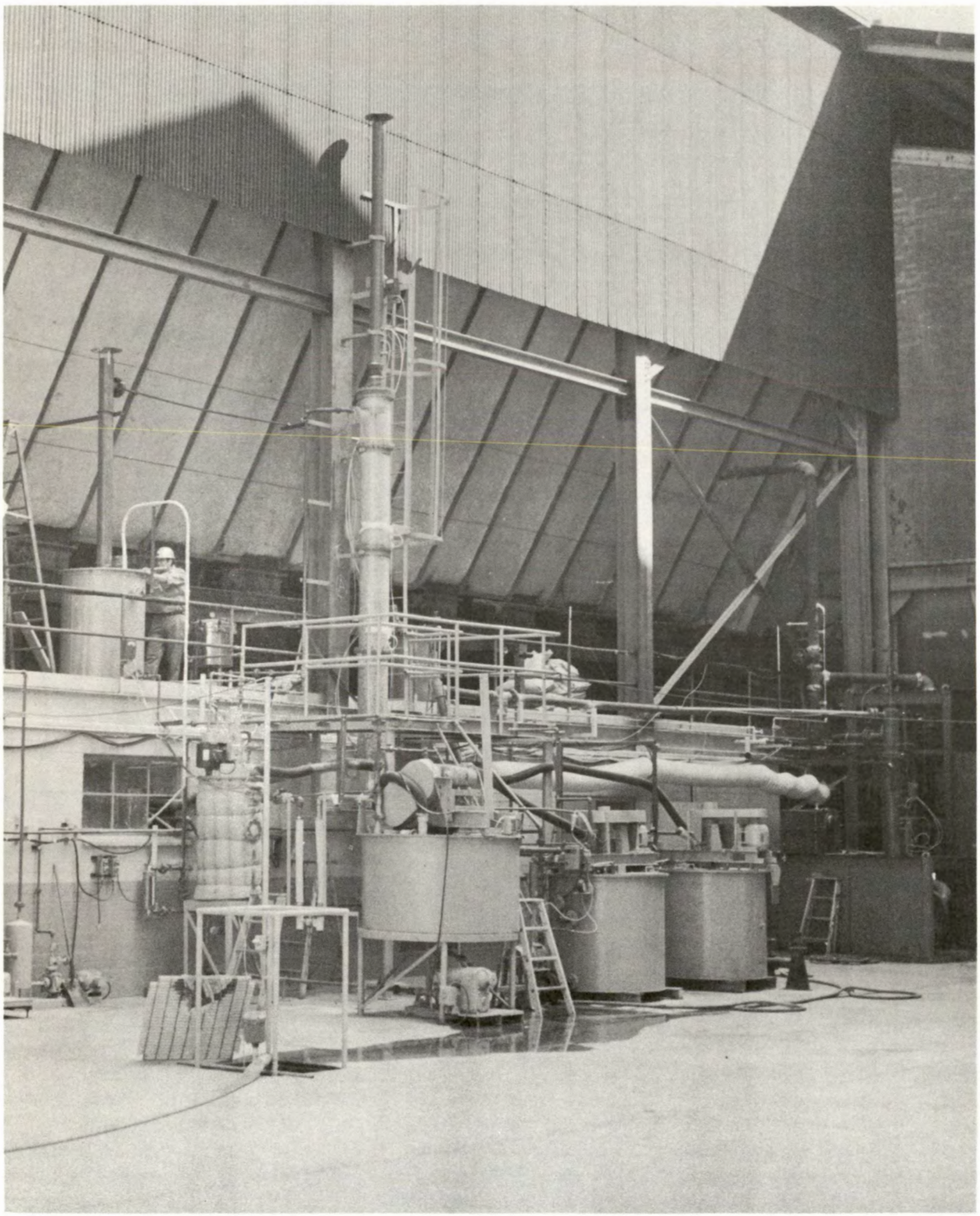

FIGURE 5. - Pilot plant at San Manuel smelter.

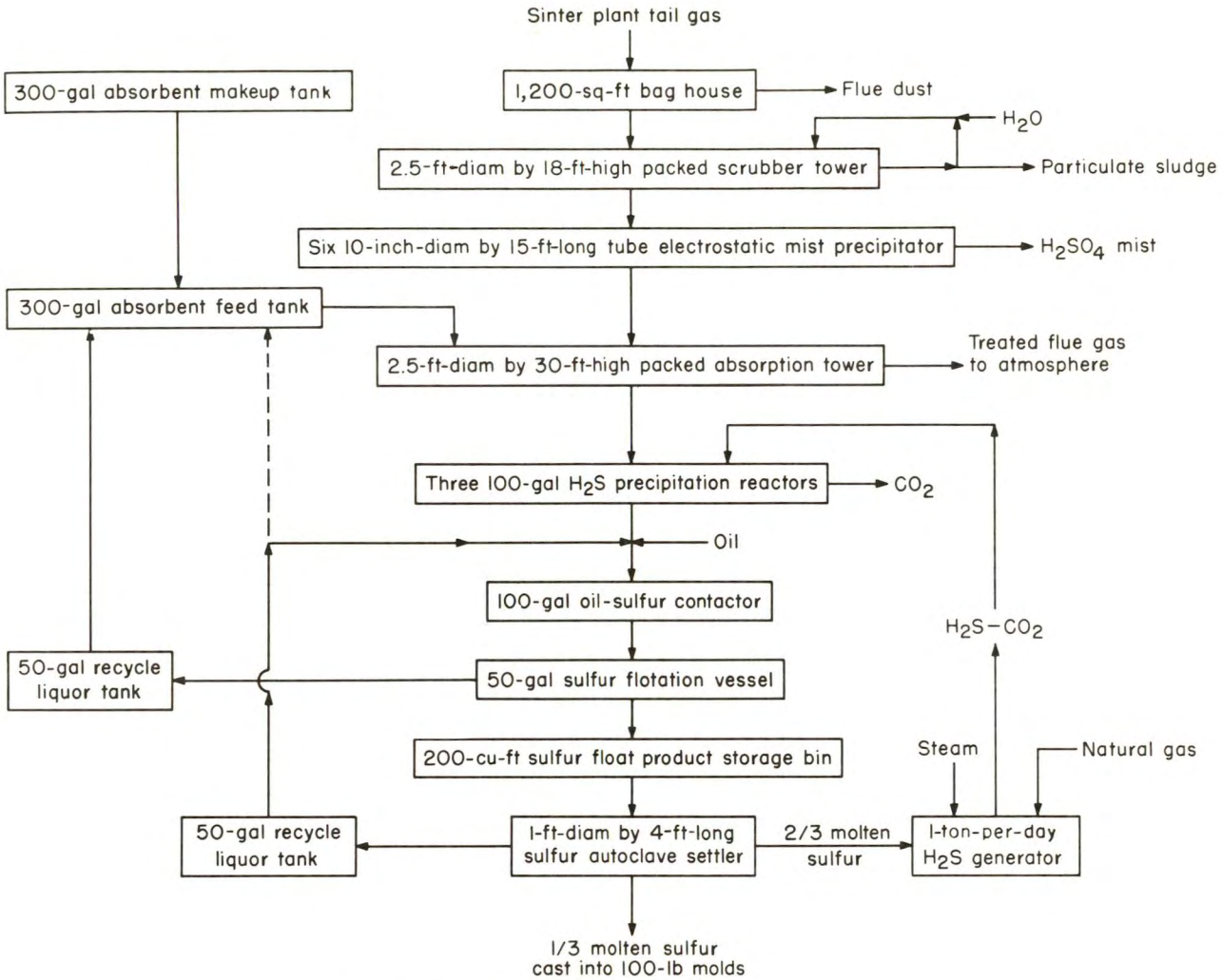

FIGURE 6. - Proposed Bunker Hill pilot plant.

GAS COOLING AND CLEANING

Gas cooling and cleaning requirements are probably comparable with those used in preparing smelter gas for a contact H_2SO_4 plant. If H_2SO_4 mist is not removed, a part of the mist will dissolve in the absorber solution necessitating neutralization of the H_2SO_4 and periodic treatment of the absorber solution for removal of sulfate. Solid particles in the absorber feed gas would tend to plug the absorber, and contaminate the sulfur product and solution. Standard gas cleaning and cooling practice for acid plants includes gas treatment in a dry electrostatic precipitator, adiabatic cooling and more dust removal in a spray chamber, further cooling by passage through a water-cooled heat exchanger, and finally, removal of H_2SO_4 mist and traces of particulate matter by passage through a wet electrostatic precipitator. In the laboratory tests, gas from fluid-bed roasting of sulfides was satisfactorily cooled and cleaned in a venturi scrubber operating with recycled dilute acid solution.

In the San Manuel pilot plant, up to 300 scfm of feed gas containing 1 to 1.7 percent SO_2 was drawn from the waste heat boiler of the reverberatory furnace at about 370° C. The gas was cleaned and cooled to between 40° and 50° C by passage through a dry cyclone, followed by passage through a venturi scrubber. A portion of the recycling venturi scrubber solution was replaced with fresh water for control of the cooled gas temperature.

The initial gas cleaning and cooling procedure using a venturi scrubber employed two 10-horsepower, high-speed turbo fans placed in series behind the scrubber. The pressure drop through the venturi scrubber was approximately 50 inches water gage and, under these conditions, most of the H_2SO_4 mist and essentially all of the dust were removed from the gas. Condensation in the fans, however, caused corrosion of the cast iron impellers at a more rapid rate than replacement impellers could be obtained. To replace the venturi scrubber, a packaged replacement unit was installed incorporating venturi and impingement scrubbing and electrostatic precipitation. This scrubber unit was unsatisfactory for removal of either particulate matter or sulfuric acid mist.

For the Bunker Hill pilot plant, a baghouse, packed scrubber, and electrostatic mist precipitator are being provided for cleaning and cooling about 1,000 scfm of feed gas. The dust loading is estimated at 3.5 grains per cubic foot.

ABSORPTION OF SO_2

Absorption of SO_2 from the cooled and cleaned gas is by countercurrent contacting with regenerated citrate solution in a packed absorption tower. Other gas-liquid contacting techniques may also be applicable. Efficiency of SO_2 removal from the feed gas is influenced by the effectiveness of the absorption equipment and the SO_2 absorption capacity of the solution at the operating temperature.

The effect of SO_2 concentration in the gas and of temperature on equilibrium loading of SO_2 in solution for different citrate concentrations are shown in figures 7-8. The solutions used in these tests contained a molar ratio of NaOH to citric acid of 2, and 0.2 mole thiosulfate. The effect of SO_2 concentration in the gas and the solution pH when loading 0.5 M citrate solution at 45° C is shown in figure 9. A molar ratio of NaOH to citric acid of 2 gave a pH of 4.6, and a ratio of 1.5 gave a pH of 4.1. The decrease in pH corresponding to SO_2 loading in solutions of different citrate concentration is shown in figure 10.

Sulfur dioxide absorption is shown to be favored by increased SO_2 concentration in the gas, increased pH and buffer content of the solution, and decreased temperature. The maximum operable pH of about 5.0 is determined by limitations in the regeneration, rather than in the absorption step. To minimize reagent costs, the lowest citrate concentration compatible with the SO_2 content of the gas and requisite solution flows would be preferred. The preferred operating temperature must represent trade-offs between higher SO_2 loading in the solution at lower temperature and the cost of cooling.

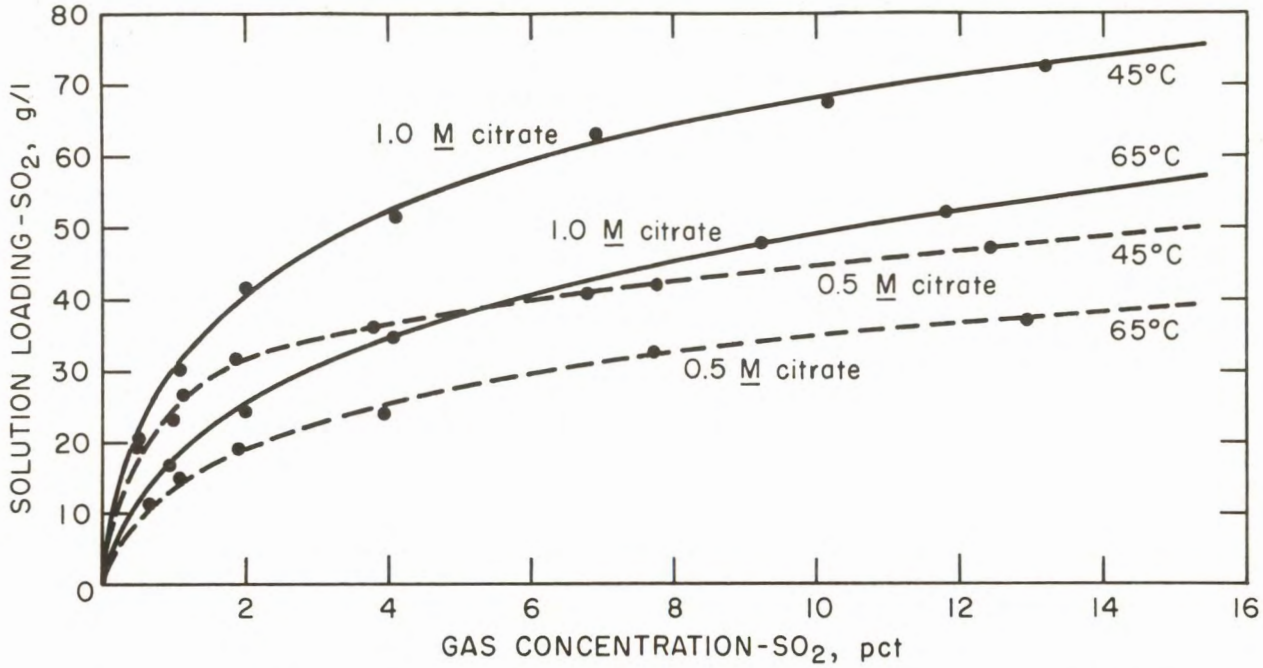

FIGURE 7. - Effect of gas concentration, solution temperature, and citrate concentration on SO_2 absorption.

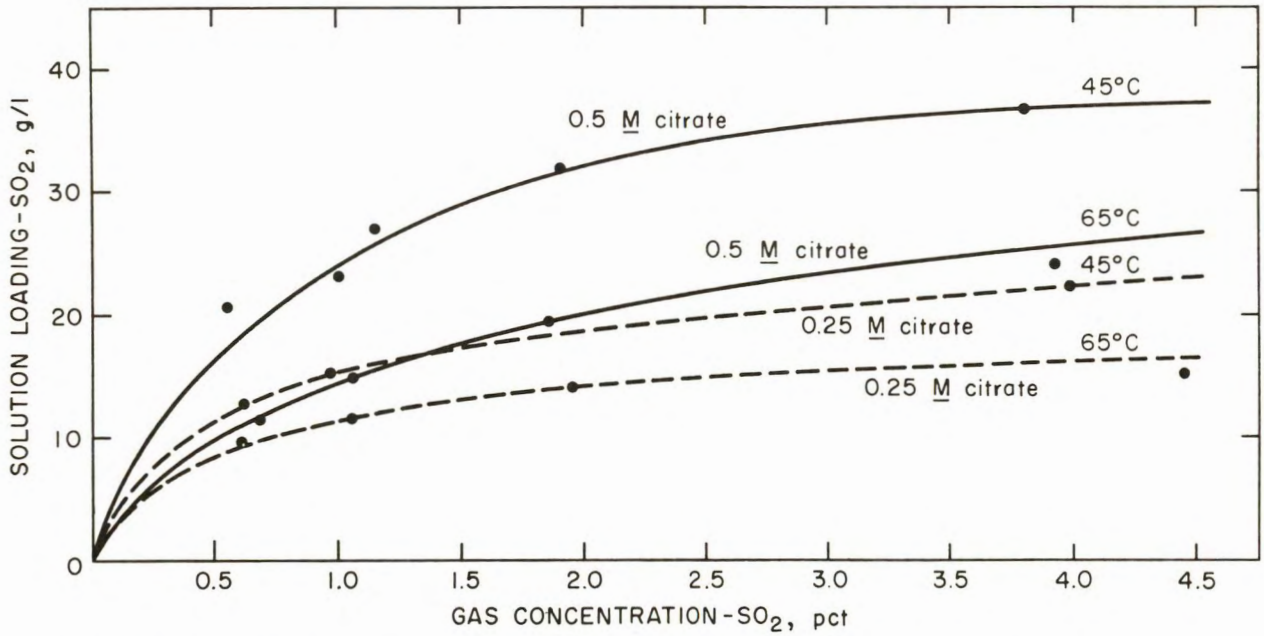

FIGURE 8. - Effect of gas concentration, solution temperature, and citrate concentration on SO_2 absorption.

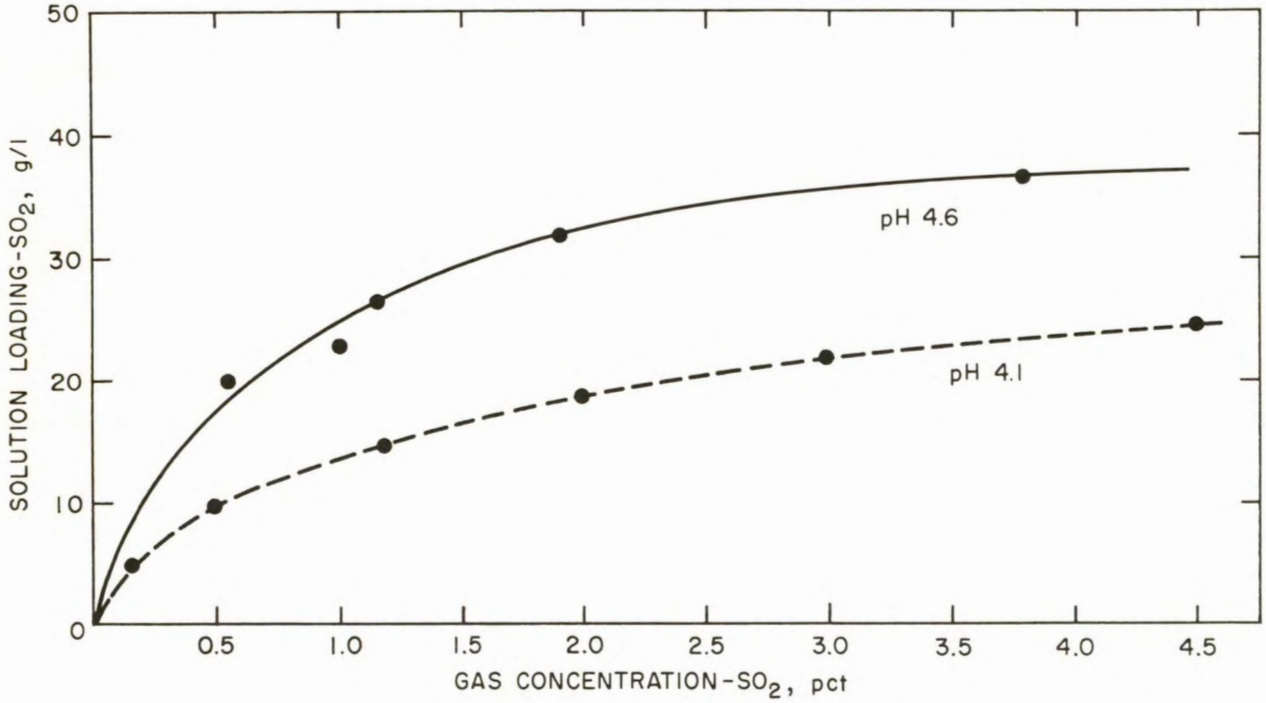

FIGURE 9. - Effect of initial pH on SO_2 absorption in 0.5 M citrate solution at 45° C.

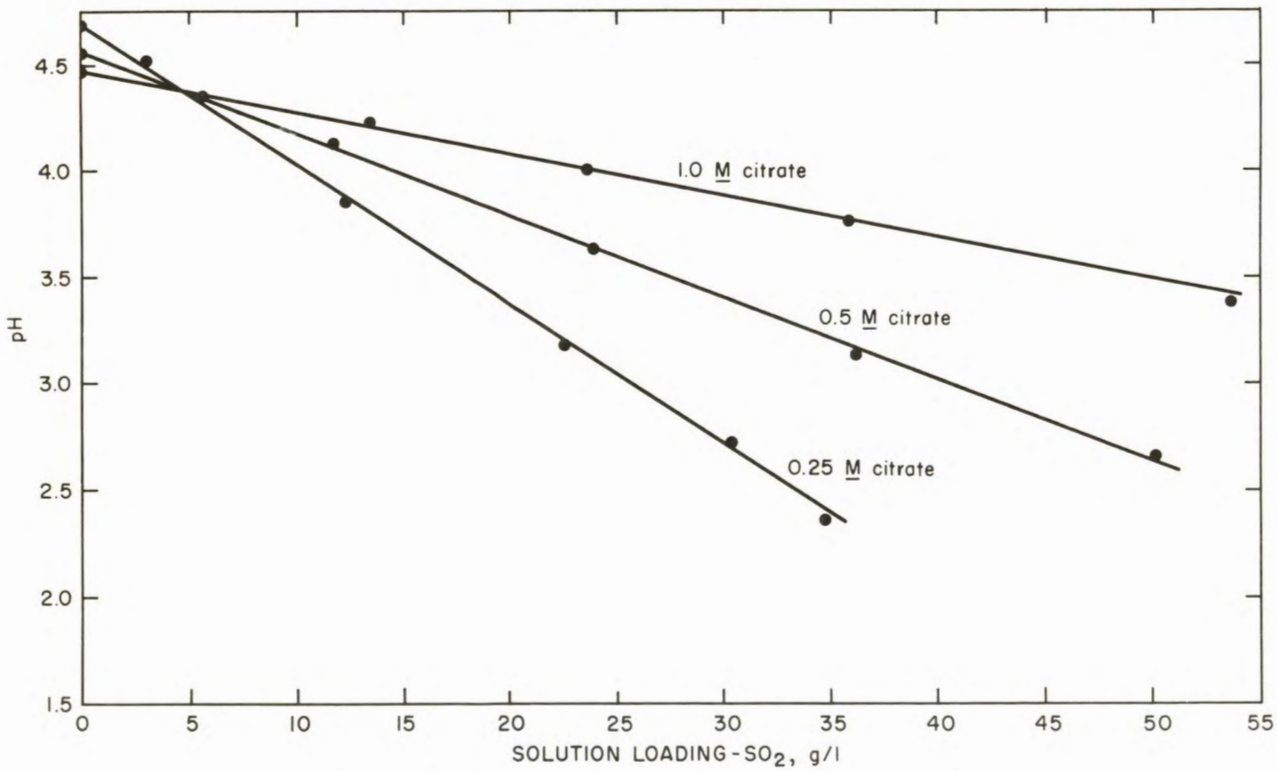

FIGURE 10. - Effect of SO_2 loading on solution pH.

An initial pH of 4.6 appears optimum. This is obtained by making up fresh absorbent solution having an NaOH to citric acid molar ratio of 2:1 or an Na_2CO_3-to-citric acid ratio of 1:1. Addition of 0.2 to 0.3 M sodium thiosulfate to the fresh citrate solution has but slight effect on the pH. After a few cycles, the pH of the solution stabilizes at about 4.2 provided no appreciable H_2SO_4 mist or entrained cooling liquor is present in the gas stream, an efficient H_2S precipitation system is maintained, and a slight excess of H_2S is used in regeneration. Operation at an SO_2-loaded solution pH of as low as 3.0 may be feasible if the SO_2 capacity of the solution is adequate for the specific system.

In the 4-inch-diameter by 12-foot-tall, packed absorption tower, 99-percent SO_2 absorption was obtained over a wide range of gas composition, temperature, solution pH, and citrate content as long as the solution SO_2 loading did not exceed about 65 percent of the equilibrium loading. Results from continuous tests of 10 to 15 shifts duration on 20 cfm of feed gas at 45° C are shown in table 1. The absorbent solution was 0.5 M citrate, and the regenerated solution pH ranged from 4.1 to 4.5.

TABLE 1. - Results of continuous tests in the 20-cfm test plant

Feed gas, pct SO_2	Absorbent SO_2 loading, g/l	Offgas, pct SO_2	SO_2 absorption, pct
0.3	5.8	0.0121	95.9
.5	10.0	.0042	99.2
1.0	7.2	.0083	99.2

In the San Manuel pilot plant, the cleaned and cooled gas was passed upward through a 14-inch-diameter (1 square foot) tower containing 1-inch plastic saddles. The tower was initially constructed of clear plastic with space for 12 feet of packing. Subsequently, addition of two 8-foot-long polyvinyl chloride sections increased the packing space to 28 feet. A mist pad at the top removed solution droplets from the exhaust gas. Regenerated and clarified solution was introduced at the top of the tower through a spray nozzle, and after percolating down through the packing, accumulated in a sump, then flowed by gravity to a 200-gallon reactor feed storage tank.

Pressure drop was 3 inches water gage with 12 feet of packing and 7.5 inches water gage with 28 feet of packing at gas flows of 200 cfm. Sulfur dioxide absorption was 93 to 99 percent from gas flows of 90 to 300 cfm of 1.1 to 1.7 percent SO_2 content, and temperatures of 42° to 52° C. Absorbent solution was 1 M in citrate and the pH was 3.1 to 3.8. The solution was loaded to between 5 and 16 grams SO_2 per liter.

For the Bunker Hill pilot plant, a 2.5-foot-diameter by 30-foot-high packed absorption column is being provided. When treating 1,000 cfm of 0.5 percent SO_2 gas with 0.5 M citrate solution, the solution flow through the column will be about 10 gallons per minute and the SO_2 loading, about 11 grams per liter.

SULFUR PRECIPITATION AND SOLUTION REGENERATION

Precipitation of sulfur and regeneration of the solution is accomplished by vigorously agitating the SO_2-laden citrate solution in a closed, stirred reactor while introducing H_2S gas below the impeller in the ratio of 2 moles of H_2S per mole of SO_2. The reaction is moderately exothermic and results in the liberation of 1,580 Btu per pound of SO_2. In batch tests, precipitation can be completed in 1 minute.

In continuous systems, reaction time of about 15 minutes, and a temperature of 60° to 70° C appears desirable for complete regeneration and agglomeration of colloidal sulfur that forms initially.

When pure H_2S is used in a continuous system, the reaction can be accomplished in a closed, single-stage vessel. The H_2S addition can be readily controlled by adding the gas at a rate sufficient to maintain a slight positive pressure of H_2S above the solution. No H_2S is lost because the reactor is not vented. It is not possible to add a significant excess of H_2S because of its low solubility after all the SO_2 has been reacted. The regenerated solution flows from the reactor through a liquid seal leg to prevent leakage of H_2S.

Reaction of the absorbed SO_2 with diluted H_2S also proceeds rapidly. However, because inert gases such as CO_2 or methane accompanying the H_2S need to be vented, the reaction should preferably be conducted in a series of reactors or in a multistage reactor with countercurrent flow of H_2S gas and SO_2-loaded citrate solution. The H_2S-CO_2 reactant gas, such as would be produced from the reaction of sulfur, methane, and steam, is introduced under the impeller of the last reactor and flows upward countercurrent to the gravity flow of SO_2-loaded liquor. A small amount of H_2S contained in the gas vented from the first reactor is incinerated to SO_2. The incinerated gas can then be injected into the absorber for SO_2 removal.

A series of three 5-liter reactors used for solution regeneration with 80 percent H_2S gas in the laboratory is shown in figure 11. The reactors are 6 inches in diameter and contain three 5/8-inch-wide baffles spaced vertically along the reactor walls. The impellers in the reactors are 2-1/2 inches in diameter and have four 5/8-inch-high flat blades. An agitator speed of 1,400 rpm is necessary for rapid sulfur precipitation and regeneration of the solution.

The most efficient utilization of H_2S was obtained by using the three-stage countercurrent flow configuration. Even so, 1 to 3 percent excess H_2S over the stoichiometric requirement was necessary to maintain the optimum pH and achieve complete regeneration of the solution. Cocurrent flow of H_2S and SO_2-loaded citrate solution was tried to facilitate gas and slurry flow, but H_2S utilization declined and at least 5 percent excess H_2S was required to precipitate all the sulfur and regenerate the solution.

At San Manuel, solution regeneration and sulfur precipitation with pure H_2S was accomplished in a tightly sealed and baffled stainless steel tank of

FIGURE 11. - Laboratory sulfur precipitation and separation assembly.

about 70-gallon capacity. The tank was fitted with a 6-inch-diameter turbine agitator rotating at 800 to 1,200 rpm through a gastight packing gland. Sulfur dioxide-bearing citrate solution was pumped from the reactor feed tank and metered to the reactor through a flowmeter. Hydrogen sulfide was introduced through an open pipe under the agitator and dispersed into fine bubbles. The liquid H_2S at 250 psig stored in the tank truck was vaporized in a heat exchanger and reduced in pressure to about 30 psi. The gas then passed through an automatic control valve that maintained a pressure of H_2S above the slurry in the reactor at 4 to 30 inches water gage pressure. Gas flow was measured with a flowmeter. Hydrogen sulfide addition could also be manually controlled using a manometer to determine reactor pressure. Retention time of the slurry in the reactor ranged from 5 to 15 minutes, depending upon the solution flow rate.

For the Bunker Hill pilot plant, three 100-gallon closed stirred tanks are being provided. At a solution flow of 10 gpm, retention time will be 30 minutes when using all three reactors.

SEPARATION OF SULFUR FROM REGENERATED SOLUTION

Alternative liquid-solid separation procedures such as filtration, thickening, hydrocloning, centrifuging, and more recently, oil flotation have been used for separation of the sulfur from the bulk of the citrate solution.

Final recovery of occluded solution is made by melting the sulfur slurry or cake at about 135° C and a pressure of 35 psi, then separately withdrawing the liquid sulfur and aqueous solution from a pressurized settler. This technique is only applicable when using a buffering reagent such as citric acid that is stable under sulfur melting conditions.

The sulfur slurry filters rapidly under vacuum, but the cake cracks and dries to only about 20 percent solids. Thickening of a sulfur slurry containing 1 to 3 percent solids results in a product containing less than 10 percent solids. Tests made on sulfur slurries, produced in the H_2S precipitation step, demonstrated that two-stage hydrocloning of a slurry containing about 1 percent solids would produce a final underflow of 12 to 15 percent solids. Batch or continuous centrifuging of thickened slurries produced cakes containing up to 60 percent solids.

A recently developed technique that appears promising, floats the sulfur from the slurry. In batch tests, 2 percent or less of kerosene or oil by weight of sulfur was added and the slurry briefly agitated, then settled. The sulfur floated rapidly to the surface in the form of a seemingly dry powder that was readily removed by suction or skimming. The powder contained 40 to 80 percent sulfur depending upon the amount of hydrocarbon added, the temperature of the slurry, and the degree and duration of agitation. Separation of sulfur from the slurry was complete leaving a clear solution for recycle. Figure 12 shows a typical sulfur slurry from the H_2S precipitation reaction before and after treatment with kerosene. During normal operation in the 20-cfm continuous citrate test plant, the sulfur float product contained about 50 percent solids with kerosene additions of 2 to 3 weight-percent of sulfur. Less volatile hydrocarbons also float the sulfur.

In the continuous laboratory assembly, the slurry was agitated with kerosene or oil, settled, and the sulfur powder skimmed in the apparatus shown in figure 13. About 80 pounds of the damp powder was accumulated in 24 hours of laboratory operation on 0.5 percent SO_2 gas. The moist cake was then melted and partitioned in 1 hour using the heat exchanger and settler shown in figure 14. Molten sulfur was withdrawn through a valve at the bottom left of the settler. Citrate solution with hydrocarbon floating on the surface was withdrawn from the top for recycle.

Very little decomposition of citrate occurs in sulfur melting. In tests made in an autoclave at 135° C, about 25 percent of the citrate in a solution at pH 4.5 was decomposed in 100 hours. On the basis of a projected retention

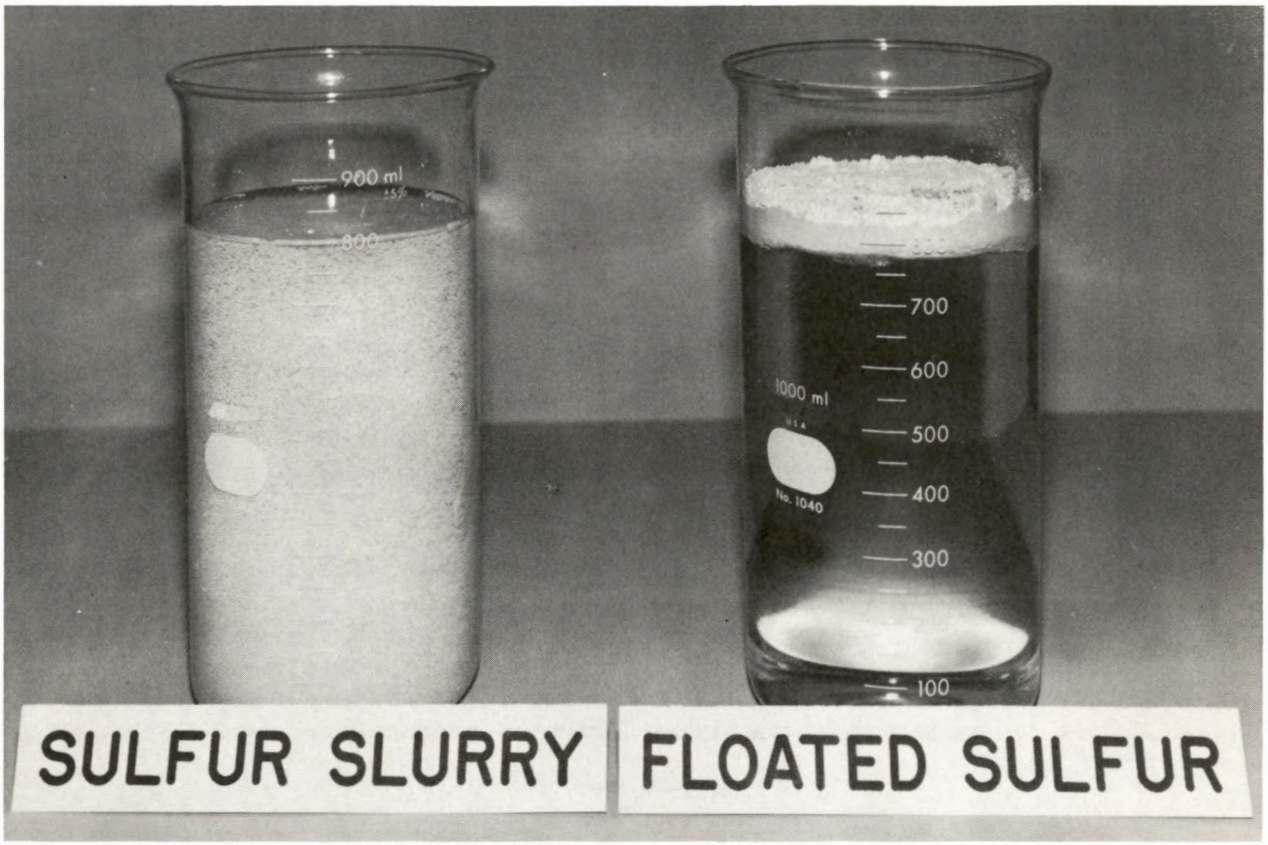

FIGURE 12. - Sulfur flotation demonstration.

time of 20 minutes in a continuous melting system, this represents the equivalent of 300 melting cycles. Assuming that 1 ton of 0.5 M citrate solution accompanies each ton of sulfur in the melter, the decomposition amounts to only 0.7 pound of citrate per ton of sulfur melted. More importantly, the autoclaved citrate solution showed no loss in capacity to absorb SO_2. Possibly the decomposition of citrate forms other organic buffering compounds.

Some decomposition of the normally present thiosulfate occurs during melting in accordance with reactions 11 and 12 shown earlier. The quantity of sulfate formed is dependent on the concentration of thiosulfate, temperature, and duration of heating. Based on laboratory tests with 0.5 M citrate and 0.3 M thiosulfate solution, the quantity of sulfate formed in a continuous melting system with a retention time of 20 to 30 minutes at 135° C would be 3 pounds per ton of sulfur melted.

Analysis of melted sulfur prepared before adopting the oil flotation technique showed the product contained about 0.05 percent carbon. Further analysis of the sulfur revealed that this carbon was not in the form of citrate but might be decomposition products of citrate. Sulfur recovered by kerosene flotation and melting contains about 0.2 percent carbon.

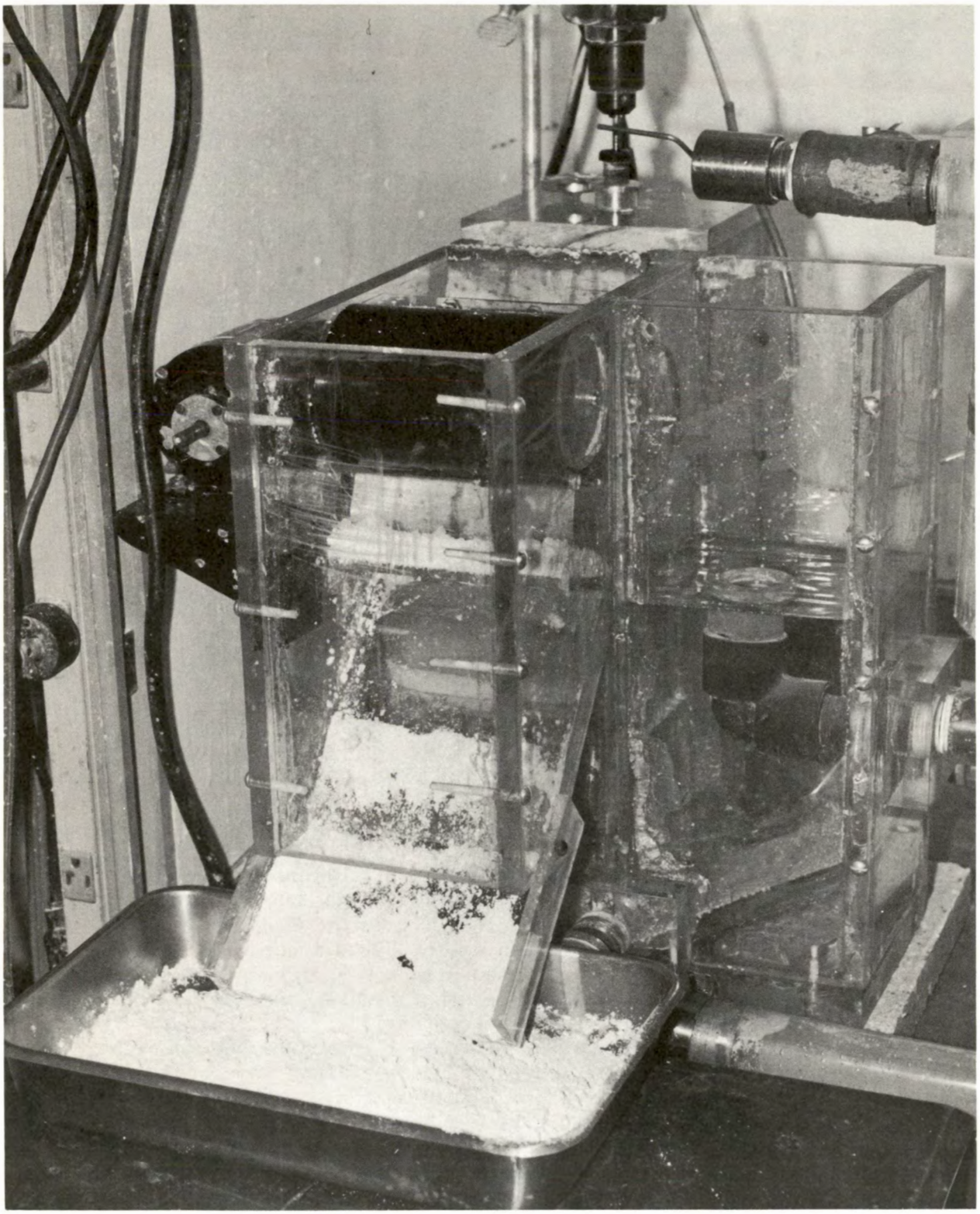

FIGURE 13. - Laboratory sulfur flotation unit.

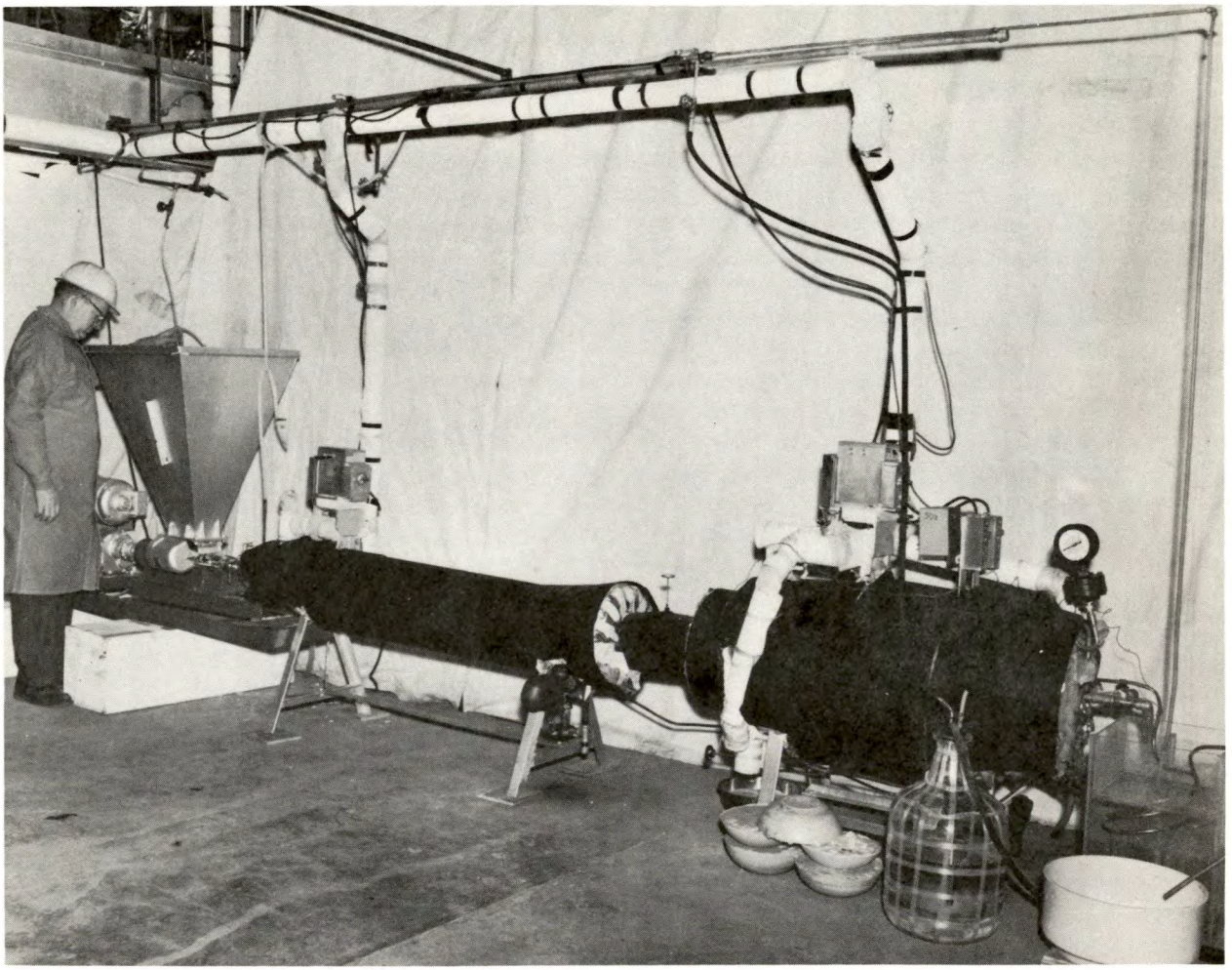

FIGURE 14. - Laboratory sulfur melter and settler.

In the San Manuel pilot plant, the slurry of sulfur and regenerated solution flowed from the reactor tank through a liquid gas trap to a 200-gallon, gently agitated holding tank where complete flocculation of the sulfur occurred. Next in line was a 54-inch-diameter by 40-inch-deep thickener where most of the sulfur settled and was pumped with a Moyno[7] pump to a 6-inch-diameter, solid bowl Sharples centrifuge, that dewatered the slurry from about 5 percent solids to between 40 and 60 percent solids. The centrifuge cake discharged to a holding tank, and the filtrate returned to the thickener. Regenerated solution overflowing the thickener contained some coarse floccules of sulfur. The solution went first to a holding tank and then was clarified by a Sparkler filter as the solution flowed to the spray nozzle at the top of the absorption tower. An in-line, water-cooled heat exchanger provided for cooling the recycled solution when required.

[7] Reference to specific company or brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

The principal problem in handling the precipitated sulfur was that some of the sulfur flocs floated in the thickener and the thickener underflow was the variable density. The floating of sulfur results from small bubbles of SO_2 attached to the flocs, and the amount of floating sulfur could generally be correlated with the concentration of residual SO_2 in the regenerated solution. When the addition of H_2S was properly controlled, only small amounts of sulfur floated. The nonuniformity of the thickener underflow was caused by intermittent operation and the relatively shallow compaction zone of the thickener.

When properly adjusted and fed with a slurry of reasonably uniform density, the continuous solid bowl centrifuge performed effectively and delivered a cake containing up to 60 percent solids and a filtrate containing only small amounts of entrained sulfur.

The thick paste of sulfur from the centrifuge was repulped with regenerated solution to a consistency of about 20 percent solids that could be moved with a Moyno pump through a steam-heated shell and tube heat exchanger where the slurry temperature was raised to about 135° C. The molten mixture of sulfur and solution then entered a steam-jacketed, glass-lined, unagitated reaction kettle of about 20-gallon capacity where the molten sulfur settled and was intermittently withdrawn through an automatic valve controlled by level probes in the kettle. Molten sulfur from the settling kettle was cooled in steel pans holding about 200 pounds. Solution free of sulfur was continuously discharged from the top of the kettle through a regulating valve that controlled the pressure at about 35 psig. The hot solution then was cooled and partly evaporated by flashing in an air-swept tank, and the cooled solution returned by gravity to the absorption tower feed tank.

The main problem encountered in melting sulfur was plugging of the heat exchanger as a result of inadequate temperature or failure to adequately flush before a shutdown. When the gas feed to SO_2 absorption was clean, the sulfur discharged from the autoclave solidified as a bright yellow product, but when the gas was dirty, the sulfur was contaminated with metal sulfide impurities.

For the Bunker Hill pilot plant a 100-gallon agitated tank for mixing oil and slurry, and a 50-gallon settler with sulfur-powder skimmer will be provided. The moist sulfur will be accumulated and melted on one shift in a heat exchanger, then partitioned in a 1-foot-diameter by 4-foot-long pressurized settler. One-third of the sulfur will be cast into 100-pound blocks, and the remainder will be recycled to prepare H_2S for solution regeneration.

GENERATION OF H_2S

Laboratory studies on preparation of H_2S for precipitating sulfur from SO_2 loaded solution included the following reactions: methane, sulfur, and steam; carbon disulfide and steam; carbon monoxide, sulfur, and steam; methane and sulfur dioxide; base metal sulfides and copper matte with acids or steam; and copper sulfide concentrate, carbon, and lime to produce calcium sulfide for conversion to H_2S.

Carbon disulfide is produced commercially by passing sulfur vapor and methane through a catalyst bed of activated alumina at a temperature of 700° C. The reaction, equation 14 shown earlier, converts half the sulfur to CS_2 and half to H_2S. In the presence of steam, CS_2 is hydrolyzed to produce CO_2 and H_2S. Figure 15 is the laboratory apparatus used in studying the hydrolysis of CS_2, and the single-stage reaction of methane, sulfur, and steam. The reactor was a 1-inch-diameter stainless steel tube packed with alumina catalyst. Figure 16 shows the effect of temperature on the hydrolysis of CS_2 in the presence of excess steam, and figure 17 shows the effect of temperature on the reaction of methane, with excess sulfur and steam. Conversion of CS_2 to H_2S at temperatures above 350° C is shown to go nearly to completion in a fraction of a second. The reaction of methane, sulfur, and steam is shown to be 98 percent complete based on methane at 700° C in 12 seconds. After condensing excess sulfur and steam, the product gas contained 20 percent CO_2, 0.1 percent COS, and over 79 percent H_2S.

Tests on the reaction of CO, sulfur, and steam over an activated alumina catalyst at 460° C showed 99 percent completion based on CO in 10 seconds. The product gas contained 50 percent each CO_2 and H_2S. Tests on reaction of SO_2 and CH_4 over the alumina catalyst showed 85 percent conversion of the SO_2 to H_2S at 850° C in 2.5 seconds.

Acidulation of chalcopyrite with sulfuric acid in the presence of metallic iron resulted in a 75-percent conversion of sulfur to H_2S. When using

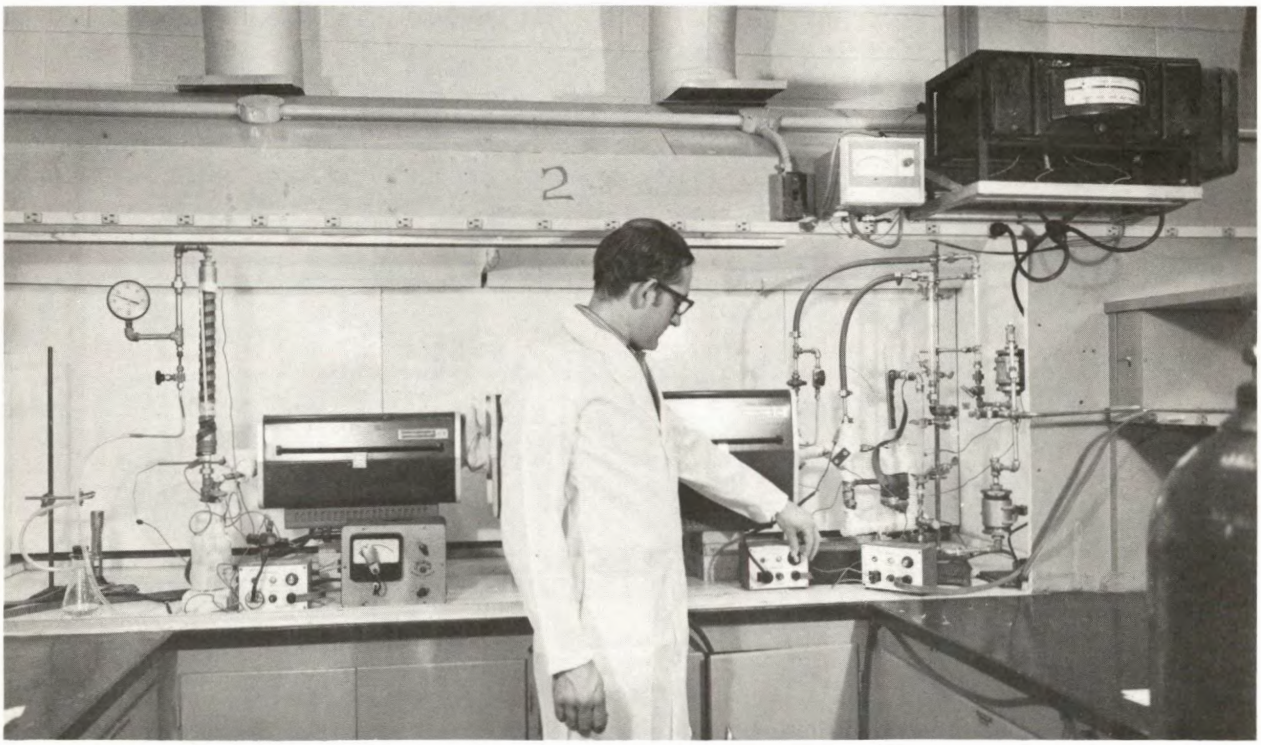

FIGURE 15. - Laboratory catalytic H_2S generator.

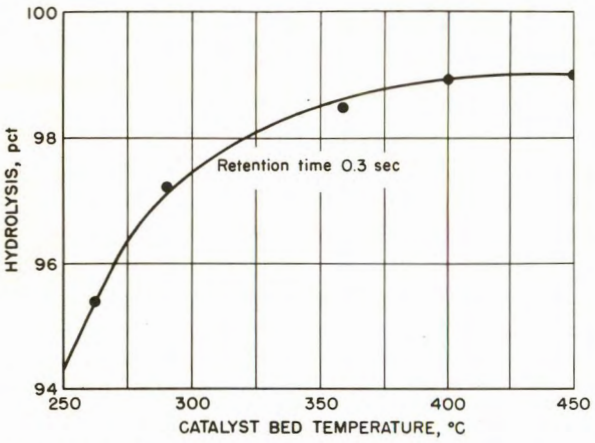

FIGURE 16. - Effect of temperature on hydrolysis of CS_2 with steam.

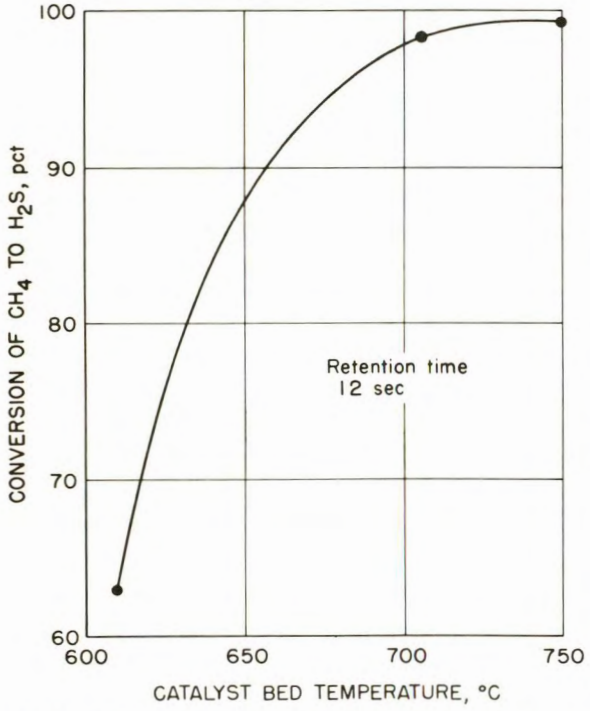

FIGURE 17. - Effect of temperature on reaction of sulfur, methane, and steam.

HCl, 95 percent of the sulfur was converted to H_2S.

Only a 25-percent conversion efficiency was obtained by the direct reaction of chalcopyrite concentrates with steam in a fluidized-bed reactor at a temperature of 950° C. A 60-percent yield of sulfur gases including H_2S, sulfur vapor, SO_2, and possibly SO_3 was obtained by the direct reaction of molten copper matte with steam. A 40-percent yield of H_2S was obtained by roasting chalcopyrite concentrates and lime at 650° C to produce CaS and then leaching with water and CO_2 to liberate H_2S.

To integrate H_2S preparation in the 20-cfm laboratory assembly, a 1/2-cfm H_2S generator was designed, assembled, and operated on recycled sulfur, methane, and steam. The generator operated satisfactorily over an H_2S production range of 0.14 to 0.71 cfm, the latter being more than sufficient when feeding 20 cfm of 0.5-percent-SO_2 gas to the laboratory assembly. Near theoretical H_2S concentration of 80 percent was produced at an overall methane conversion of 98.9 percent. About 12 percent excess sulfur was necessary to obtain low methane in the product gas. The exothermic reaction of sulfur, methane, and steam provided enough heat to maintain, and at times, exceed the optimum reaction temperation of 700° C when the reactants were preheated. The generated H_2S proved interchangeable with tank H_2S for regeneration of the SO_2-loaded citrate solutions.

For the Bunker Hill pilot plant a package unit rated nominally at 1 ton H_2S per day will be provided for converting recycled sulfur, natural gas, and steam to H_2S.

PRELIMINARY COST ESTIMATES

Preliminary cost estimates of the SO_2-H_2S system for treating different waste gases were prepared to determine whether projected process economics

justified continued testing and development. Estimates are here presented for treatment of copper smelter gas by two routes, for an electricity generating plant burning high-sulfur coal or oil, and for a refinery Claus plant tail gas. Sulfur dioxide removal efficiency of 99 percent was projected for the smelter and 95 percent for the powerplant and Claus tail gas.

A generalized flowsheet similar to that shown for the San Manuel pilot plant was used for scale-up except for gas cleaning and separation of sulfur from the regenerated solution. Three-stage hydrocloning to 10 percent solids replaces thickening and centrifuging in the flowsheet for the copper smelter and electric powerplant. Oil flotation of sulfur from the slurry is used in the Claus tail gas flowsheet. Although a detailed estimate of oil flotation for sulfur separation in lieu of hydrocloning was not prepared for the copper smelter and powerplant flowsheets, capital and operating savings of 25 to 50 percent in the sulfur separation step appears possible.

Capital costs were estimated by standard chemical engineering cost estimating procedures and from published information. The gas-cleaning equipment costs were taken from the literature and assume utilization of the same type of equipment used in cleaning smelter gas for production of H_2SO_4. The cost of H_2S-generating equipment was estimated by scaling-up equipment tested in the laboratory. Tail gas from the SO_2-H_2S process would be reheated from the absorption temperature of 45° to 50° C to 170° C for disposal through a stack. Reheating costs are included with the absorption costs.

Estimates of operating costs are based on direct labor at $4.20 per hour, electric power at $0.01 per kW-hr, natural gas at $0.45 per thousand cubic feet, steam at $0.34 per thousand pounds, and water at $0.03 per thousand gallons for cooling and $0.17 for process. Other assumptions are supervision of direct labor and maintenance labor at 15 and 20 percent, respectively; maintenance labor at 3 percent of fixed capital costs; payroll overhead at 25 percent; administration and overhead at 40 percent of direct labor, maintenance labor, maintenance supplies, and operating supplies; taxes and insurance at 2 percent; an amortization period of 12.5 years; and 330 operating days per year except for the powerplant estimate, which is based on 6-year amortization and 292-day operation per year. The operating cost for the smelter and powerplants assume a loss of $3.70 of citric acid per long ton of product sulfur. Because availability of H_2S obviates sulfur recycle in the Claus tail gas flowsheet, citrate loss is estimated at $1.25 per long ton of sulfur. Costs for Na_2SO_4 removal were estimated on the basis of conversion of 1 percent of the removed sulfur to sulfate in the system.

Copper Smelter

Estimates were made for alternative gas-emission-control systems at a 100,000-ton-per-year hypothetical copper smelter. In one system, converter and reverberatory gases are combined for treatment by the SO_2-H_2S process. In the other system, converter gas is assumed to feed an existing sulfuric acid plant, and only the reverberatory furnace gas is treated by the SO_2-H_2S process.

Combined gas flow from the reverberatory and converter flues is estimated at 260,000 scfm of 2.2 percent SO_2 gas. To accommodate smelter operating fluctuations, the SO_2 control plant is sized to handle peak flows of 333,000 scfm. Gases are assumed to have been precleaned with existing dry electrostatic precipitators. A spray chamber and electrostatic mist precipitator are used for final gas cooling and cleaning. The yield of sulfur based upon a 99-percent removal efficiency is 317 long tons per day. Table 2 is a cost estimate for this system.

TABLE 2. - Summary of costs for converter and reverberatory gases

Unit operation	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Gas cooling and cleaning..	2.1	$5,197,000	$1,518,000	$14.50
Absorption.....	2.1	936,000	758,000	7.24
Sulfur precipitation.....	4.2	387,000	210,000	2.01
Sulfur separation.....	4.3	3,719,000	1,158,000	11.06
H_2S generation.....	4.2	2,200,000	1,812,000	17.31
Na_2SO_4 removal.....	2.1	799,000	416,000	3.97
Facilities, 10 pct.....	-	1,324,000	-	-
Utilities, 12 pct.....	-	1,589,000	-	-
Fixed capital.....	-	16,149,000	-	-
Working capital.....	-	1,407,000	-	-
Total.....	19.0	17,556,000	5,872,000	56.09

A capital cost of about $17.5 million is estimated. The $56-per-long-ton-sulfur operating cost without credit for possible value of the sulfur is equivalent to 2.9 cents per pound of copper produced.

For the smelter system in which an existing H_2SO_4 plant processes the converter gas, feed gas to the SO_2-H_2S process would be about 200,000 scfm of 1 percent SO_2 reverberatory gas. Yield of sulfur based on 99-percent removal is 107 long tons per day. Table 3 is a cost estimate for this system. A capital cost of about $10 million is estimated. Cost of sulfur recovery at $88 per long ton of sulfur is equivalent to 1.6 cents per pound of copper produced.

TABLE 3. - Summary of costs for reverberatory gas

Unit operation	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Gas cooling and cleaning..	2.1	$3,841,000	$1,158,000	$32.68
Absorption.....	2.1	439,000	309,000	8.72
Sulfur precipitation.....	4.2	202,000	137,000	3.88
Sulfur separation.....	4.3	1,813,000	587,000	16.58
H_2S generation.....	4.2	957,000	722,000	20.38
Na_2SO_4 removal.....	2.1	368,000	193,000	5.44
Facilities, 10 pct.....	-	762,000	-	-
Utilities, 12 pct.....	-	915,000	-	-
Fixed capital.....	-	9,297,000	-	-
Working capital.....	-	730,000	-	-
Total.....	19.0	10,027,300	3,106,000	87.68

Powerplant

A limited amount of test data available on absorption of SO_2 from gases containing only 0.1 to 0.3 percent SO_2 indicate the SO_2-H_2S process will effectively remove 92 to 98 percent of the SO_2 from coal- or oil-burning powerplant stack gases. Because powerplant gases contain only about one-tenth the SO_2 concentration of copper smelter gas, scrubbing and cooling requirements would be 10 times larger for equivalent sulfur yield. Absorption in citrate solution likewise would involve contacting a greater volume of gas with citrate solution. The loaded citrate solution would be considerably lower in SO_2 concentration; hence, the reaction with H_2S and the separation of the citrate-sulfur slurry involves handling larger volumes per unit of sulfur produced. Requirements for sulfur melting and H_2S generation would be the same as that for a smelter producing the same amount of sulfur.

An economic evaluation based on 1970 costs was made by Katell and Morel of a citrate absorption system for removal of SO_2 from flue gas for a 1,000-megawatt powerplant utilizing 3 percent sulfur coal or 4 percent sulfur Kuwait residual oil (9). Assuming 95-percent recovery of input sulfur, the capital investment was estimated to be $26,280,000 and $25,380,000 for the coal and oil, respectively. Assuming no credit for the sulfur, the removal cost was estimated to be 1.26 and 1.215 mills per kW-hr for the coal and oil, respectively.

A new cost estimate for a 1,000-megawatt coal-burning powerplant was made by our Process Evaluation Group at the Salt Lake City Metallurgy Research Center based on 1972 costs. Based on burning 8,400 tons per day of coal containing 3 percent sulfur, the gas flow is 1,730,000 scfm (60° F) with an SO_2 content of 0.24 percent. The yield of sulfur, assuming 95-percent removal, is about 214 long tons per day. Table 4 is a cost estimate for that system. The capital investment is estimated at about $31 million. Operating costs for removing 95 percent of the SO_2 from the stack gas, assuming no credit for sulfur, is $4.10 per ton of coal and 1.4 mills per kW-hr.

TABLE 4. - Summary of costs for 1,000-megawatt powerplant

Unit operation	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Gas cooling and cleaning..	2.1	$6,294,000	$2,092,000	$33.56
Absorption.....	2.1	10,951,000	4,438,000	71.18
Sulfur precipitation.....	4.2	870,000	361,000	5.80
Sulfur separation.....	4.3	3,184,000	1,273,000	20.41
H_2S generation.....	4.2	1,665,000	1,440,000	23.10
Na_2SO_4 removal.....	2.1	664,000	466,000	7.47
Facilities, 10 pct.....	-	2,339,000	-	-
Utilities, 12 pct.....	-	2,807,000	-	-
Fixed capital.....	-	28,774,000	-	-
Working capital.....	-	2,194,000	-	-
Total.....	19.0	30,968,000	10,070,000	161.52

Claus Plant

The Claus process is used at oil and chemical refineries and natural gas processing plants to convert H_2S to sulfur. Process efficiency is typically about 92 percent. The offgas is subsequently incinerated to convert H_2S and other odorous sulfur species to SO_2, resulting in an SO_2 concentration of about 2 percent in the tail gas emission. Because the gas is already clean, only cooling is needed before treatment by the SO_2-H_2S process. Also, the availability of onsite H_2S eliminates recycling of sulfur and consumption of natural gas.

Feed gas to the emission-control plant was estimated at 20,000 scfm containing 1.9 percent SO_2. Provision is made for cooling the gas from 600° to 45° C. The yield of sulfur based on 95-percent removal is 20 tons per day. Table 5 is a cost estimate for this system.

TABLE 5. - Summary of costs for Claus tail gas

Unit operation	Number of operators	Capital cost	Annual operating cost	Unit production cost per long ton of sulfur
Gas cooling.....	2.1	$874,000	$276,000	$12.69
Absorption.....	2.1	320,000	142,000	6.54
Sulfur precipitation.....	2.1	284,000	162,000	7.45
Sulfur separation.....	2.1	320,000	122,000	5.62
Na_2SO_4 removal.....	.6	124,000	54,000	2.50
Facilities, 10 pct.....	-	190,000	-	-
Utilities, 12 pct.....	-	229,000	-	-
Fixed capital.....	-	2,341,000	-	-
Working capital.....	-	178,000	-	-
Total.....	9.0	2,519,000	756,000	34.80

The $35 per-long-ton sulfur production cost applies to the 24 percent of the total sulfur that comes from treating the tail gas. If spread over the entire sulfur production, the tail gas processing cost would be equivalent to $8.35 per ton of sulfur.

Substitution of a buffered SO_2-H_2S plant for a conventional Claus plant would yield 99-percent sulfur recovery without tail gas treatment. In such a system, one-third of the H_2S removed from refinery offgas or sour gas would be incinerated to SO_2. The incinerated gas would be cooled and the SO_2 absorbed in a buffered solution followed by precipitation of sulfur and regeneration of the absorbent with the remaining two-thirds of the H_2S, and recovery of the sulfur from the aqueous slurry. Laboratory tests made on gases containing 10 to 17.5 percent SO_2, the concentration expected by incineration of the H_2S, resulted in 99.9-percent absorption of the SO_2. Although no cost estimates have been made, the laboratory tests indicate that the SO_2-H_2S process merits study as an alternative to Claus plants. Gas volume to the absorber would be about the same as that required for treating a comparable Claus plant tail gas. However, because highly concentrated H_2S would be incinerated and much more heat generated, additional cooling capacity would be required. Also,

more sulfur separation equipment would be required because about four times as much sulfur would be produced as in a comparable SO_2-H_2S plant treating only Claus plant tail gas.

SUMMARY

Prolonged laboratory and limited pilot plant testing has shown the Bureau of Mines buffered SO_2-H_2S process is capable of substantially complete removal of SO_2 from industrial waste gases. Most of the SO_2 is converted to elemental sulfur with only about 1 percent converted to sulfate regardless of the SO_2 and oxygen content of the feed gas. Preliminary estimates indicate that emission-control plants using the process would be costly but competitive. The ability of the process to capture over 95 percent of the SO_2 with conversion to storable sulfur of potential economic value justifies continued study and development. Forthcoming pilot plant tests by Pfizer-McKee-Peabody and Bureau of Mines-Bunker Hill should provide useful data for engineering evaluation and cost estimates.

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