MASTER

CONTROL OF HYDROGEN SULFIDE EMISSION FROM GEOTHERMAL POWER PLANTS

Final Report

Volume II

Laboratory Results and Process Engineering Evaluations

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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
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Contract No. EY-76-C-02-2730.*000

Final Report on Task A.1

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Corrosion Studies on Austenitic Stainless Steel

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SUMMARY

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.

It is recommended that the scrubbing column and trim for the 100M FPH field test facility be constructed of C20Cb3 and C20 alloys insofar as possible, and that titanium, which is passive under all conditions tested, be considered as a back up material.

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. While little evidence has been 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. The order of passivity of the alloys tested under simulated process compositions is:

T1 >> EB26-1 > C20Cb3 ~ UHB904L > T330 ~ T310 > T304 ~ T316

These results were confirmed in field test work on an 8" scrubbing column system on real geothermal steams. In general, the wrought alloys appear to show superior resistance to the comparable cast version.

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.

OBJECTIVES

Preliminary autoclave testing in synthetic solutions under simulated scrubbing conditions had demonstrated that austenitic stainless steels showed promise as generally useful materials of construction, although they could be activated and corrode rapidly under some conditions. There is an obvious economic advantage to the use of stainless steel vis-a-vis titanium, which is known to be passive, particularly in trim components such as pumps and valves.

The objective of this task is to verify the suitability of austenitic stainless steel under a wide range of operating conditions and for forms which would be utilized in the construction of process equipment. This would entail testing a variety of solution compositions and alloy types and for testing alloys in the plain, stressed, and welded states as well as testing for galvanic and crevice corrosion and for wrought and castable alloys.

The limits of utility of various alloys was to be defined in terms of maximum allowable acidity or chloride or minimum allowable copper contents for manageable corrosion rates for the bare metal, stressed, welded, creviced, and galvanically coupled states. Potentiostatic and corrosion probe testing would be used to supplement the results of coupon immersion testing.

TEST PLAN

The corrosion rates of commercially available austenitic stainless steels under simulated scrubber conditions were to be determined by penetration rates calculated from weight loss measurements on test coupons.

A variety of alloys was to be tested, and mill test reports were to be obtained for each so that exact compositions would be known. The coupons would be immersed to varying degrees to test for interface corrosion, and welded and stressed (bent) coupons would be tested. Galvanic couples would be formed with dissimilar alloys and crevices would be created

between coupons by bolting them together with and without gasketing material.

While the temperature and pressure of the test would be limited to a nominal 175°C, 115 psig, test solution compositions would be varied over wide range of copper contents (0.5-5 g/l), acidities (4-42 g/l H_2SO_4), pH's (derived from varying $(NH_4)_2SO_4$ contents from 50-200 g/l), and chloride contents (0-25 ppm Cl^-). In addition to weight loss (penetration rate), the corrosion mechanism was to be determined visually and metallographic examination would be carried out as required.

Limited potentiostatic testing would be carried out at process conditions in addition to the coupon testing to determine the relative passivities of the alloys tested in the absence of the cupric ion. Also, the use of commercially available corrosion monitoring instruments would be evaluated in this system in an attempt to obtain back up or alternative data to supplement the results of coupon testing and to determine their suitability for use as a direct readout field analytical and control instrument.

EQUIPMENT, PROCEDURES, AND ANALYTICAL TECHNIQUES

Coupon testing was carried out in stirred and unstirred autoclaves and in the laboratory (4" dia) scrubber on simulated fluids and in the 8" dia field scrubbing unit during a test on geothermal steam. Potentiostatic testing was carried out in an unstirred autoclave on simulated (but copper free) fluids while tests with commercially available corrosion monitoring instruments were carried out on both the laboratory and field scrubbing units.

Coupon Testing

Coupon testing was carried out as a modified Huey test according to procedures specified in NACE Standard TM 02-70, "Laboratory Corrosion Testing of Metals on the Process Industries". Generally, however, the tests were of shorter duration than recommended in an attempt to cover

as wide a variety of samples and conditions as possible in a limited time. Occasionally, more coupon surface than recommended, (125 ml/in.²) was exposed as well.

The coupons were inserted in about one litre of test solution which was contained in a two litre glass liner fitted inside two litre Parr autoclaves, Model No. 4522. The autoclaves were equipped with pressure gauges and one was fitted with a thermowell, agitator, and sample tube. A thermocouple was inserted in the thermowell to measure and control the temperature in the autoclave by varying the heat input to an electrically heated jacket. A six bladed turbine agitator was used in the stirred autoclave, with the speed controlled, as desired, from 0-600 rpm. The temperature (pressure) in the unstirred autoclave was controlled by varying the Variac setting to control voltage input to heating tapes wrapped around the autoclave. Generally, the stirred autoclave was used for short term tests (< 72 hrs) because of the difficulty of maintaining a shaft seal under the conditions run while the unstirred autoclave was used for longer tests.

For testing in the 4" laboratory and 8" field scrubbing units, the coupons were mounted directly on test racks and inserted in the column sumps.

Test coupons of certified composition were obtained either directly from the alloy manufacturers or from Corrosion Test Supplies Co. The coupons used were generally 1/2" x 3" x 1/16" or 1/8" thick, 1" x 2" x 1/8" thick, or were disks of about 1-1/2" dia x 1/4" thick. The composition of all alloys tested is summarized in Table I. Since, in general, the test coupons were used more than once, they were inspected visually and their condition and test history noted prior to each test. The dimensions and state of the coupon (plain, welded, stressed, etc.) were noted and they were weighed on an analytical balance, along with a "blank" sample, to within ± 0.1 mg. Crevice or galvanically coupled specimens were then prepared if required

Table I

Composition of Alloys Tested

Alloy	Sample No.	C	Mn	P	S	Si	Ni	Cr	Mo	Cu	Ti	Co	Al	Sn	Others				
304	1-6	.062	1.63	.016	.007	.53	8.23	18.35	.06	.13									
304	11-17	.05	1.45	.026	.009	.70	9.10	18.50											
304	7-10	.055	1.71	.022	.025	.55	8.40	18.34	.11	.08									
304	18-20	.07	1.78	.032	.004	.55	9.05	18.10	.26	.22									
304L	1-6	.025	1.73	.020	.015	.48	10.06	18.45	.11	.06									
304L	11-17	.024	1.83	.015	.007	.56	10.10	18.38											
304L	7-10	.014	1.64	.032	.013	.53	10.30	18.00											
304L	18-20	.026	1.70	.019	.012	.40	10.08	18.63	.19	.32									
316	1-6	.018	1.34	.023	.026	.54	11.67	16.84	2.24	.13		.34							
316	11-17	.067	1.65	.030	.017	.46	13.31	16.48	2.17										
316	7-10	.059	1.38	.028	.020	.79	12.32	17.33	2.63										
316	18-20	.050	1.75	.017	.019	.71	13.11	17.63	2.76	.14		.11							
316L	1-6	.009	1.60	.029	.011	.45	13.07	17.42	2.15										
316L	11-17	.022	1.82	.014	.024	.44	13.43	17.08	2.54										
316L	7-10	.030	1.82	.030	.020	.75	13.39	17.60	2.05	.27		.17							
316L	18-20	.020	1.56	.022	.014	.54	11.60	17.71	2.67	.39		.26							
310	1-3	.042	1.86	.022	.020	.52	19.59	25.04	.31	.20	.07		.05	.003		Pb	.001		
310	4-8	.069	1.77	.028	.014	.46	20.40	25.30											
310	9-10	.054	1.64	.023	.011	.69	19.84	24.32	.20	.12		.06							
330	1-3	.04	1.46	.013	.013	1.11	35.04	19.03											
330	4-6	.04	1.68	.012	.015	1.32	35.63	18.08											
C20Cb3	(all)	.03	.20	.02	.002	.47	33.08	19.37	2.19	3.21									
D20	(all)	.043	.75	.024	.018	.93	28.20	20.38	2.18	3.23									
ISO-20	(all)	.06	.67	.011	.013		27.7	19.9	2.05	3.10									
Worthite ⁽¹⁾		.07					24	20	3										
DH8904L ⁽¹⁾	(all)	.02	1.75			.35		20	4.5	1.5									
EB26-1	(all)	.0010	.01	.012	.013	.22	.10	25.69	2.03	.01									
T1	1	.014									BeI					Fe	N	O	H
																.049	.014	.093	.008
T1	2	.012									BeI					.02	.013	.114	.0030

(1) Nominal composition.

and the samples were immersed to the desired extent (completely, half, or unimmersed) in the test solution by hanging them with wires looped over the top edge of the autoclave's liner.

Test solutions were made up by dissolving the required amount of reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, and H_2SO_4 in distilled water. The desired chloride concentration was obtained by adding in the required amount of a standard 1000 ppm Cl^- solution prepared from sodium chloride and distilled water. The copper content of the solution was checked against calibrated standards before and after the tests by spectrophotometric analysis at 825 μ . The solution pH's were also measured before and after the test with a Corning Model 109 pH meter.

After the samples had been immersed, the liner was placed inside the autoclave, the system closed, and the space above the solution swept with nitrogen to purge oxygen while the solution was brought to boiling. The flow of nitrogen was shut off when the solution temperature approached 100°C, but the vent was left open for at least five minutes after a steady stream of steam was evolved to insure all inerts had been purged. The vent was then closed and the autoclave brought to temperature as rapidly as possible. Care was taken, however, to minimize the "overshoot" of the control set point by decreasing the rate of heat input as the temperature approached 150°C.

At the conclusion of the test, the autoclave was removed from its heat source and quenched by immersion in cold water. The pressure (vacuum) in the vapor space above the cooled solution was recorded, and the autoclave was opened. The level of coupon immersion, the state of the coupons, and the appearance of the solution were recorded. The solution copper content and pH were then recorded, the coupons were cleaned, inspected under a metallograph if they showed evidence of attack, and reweighed. Corrosion rate was calculated from the observed weight loss and the known coupon density, immersed area, and test duration.

Coupon testing carried out in the 4" laboratory and 8" field scrubbing columns was conducted in a similar manner, except that the specimens were mounted on test racks inserted in the column sumps and the solution compositions and test times were dictated by H₂S scrubbing efficiency test considerations.

Potentiostatic Testing

Anodic oxidation behavior is a measure of the passivity of metals, and can be related to the metals resistance to corrosion. This method has been used to survey the properties of five alloys under conditions of temperature and solutions composition comparable to those expected in an integrated process. The samples were potentiostatted at a series of potentials anodic of the rest potential. At each of these potentials the current was monitored as a function of time. From these data, current density potential curves were derived which provide the characterization of the metals.

The test cell was a glass lined two litre autoclave similar to that used in coupon testing except that no stirrer was used. The thermocouple well and gas dispersion tube were Teflon coated to prevent corrosion since these were immersed in the solution during the experiments and the test solutions contained no copper.

Three solutions were tested:

- 2N H₂SO₄
- 100 g/l (NH₄)₂SO₄, 24 g/l H₂SO₄, 5 ppm Cl⁻
- 100 g/l (NH₄)₂SO₄, 24 g/l H₂SO₄

The solutions were purged for 30 minutes with N₂ gas prior to bringing the contents of the autoclave to test temperature and pressure.

The five alloys tested were:

- 304 stainless
- 316 stainless
- 310 stainless
- C20Cb3
- E Brite

Leads were spot welded to the samples and the sample and the leads were covered with heat shrinkable Teflon tubing. The one exposed face of the sample was then polished.

For the potentiostatic measurements, a shiny Pt counter electrode and a dynamic hydrogen reference electrode (DHE) were used. The potentials were set with a potentiostat (Wenking) and the currents were recorded with a strip chart recorder. The current was followed until it became relatively constant. Typically this required 3 to 10 minutes.

Corrosion Monitoring Instrumentation Testing

The use of on-line corrosion measuring instrumentation was evaluated in both laboratory and field testing.

A Magna series 7000 probe with either stainless steel or Carpenter 20 elements was inserted in the sump of the 4" laboratory columns for certain test series. The probe output was read directly, in mills per year, on a Magna Model 1120 Corrator. Test coupons were also inserted in the sump during these tests so that the instantaneous corrosion rate read outs could be checked against the integrated corrosion rate determined by coupon weight loss measurements.

The operating principal of this instrument, which measures the current (voltage) flow between electrodes for a small potential difference (current) is essentially the same as for Petrolite's Model M-212/AA-509 SS-E except that a third element is not used.

A Magna Model 2053 Corrosimeter probe with a 40 mill Carpenter 20 wire element was inserted in the sump of the 8" field test column. The probe output (resistance readings) were read on a Magna Model CK-3 Corrosometer. Test coupons were also inserted in the sump during these tests so that the corrosion rate derived from probe readings could be checked against the integrated corrosion rate determined by coupon weight loss measurements.

TEST RESULTS

Coupon Testing

Thirty three coupon test experiments were carried out in seven test series in which the coupons were exposed to:

- Solutions containing varying H_2SO_4 contents at a fixed Cu, $(NH_4)_2SO_4$, Cl^- content.
- Solutions containing varying $(NH_4)_2SO_4$ contents at a fixed Cu, H_2SO_4 , Cl^- content.
- Solutions containing varying Cu contents at a fixed H_2SO_4 , $(NH_4)_2SO_4$, Cl^- content.
- Solutions containing varying Cl^- contents at a fixed Cu, H_2SO_4 , $(NH_4)_2SO_4$ content.
- Solutions as above but in which the coupons were welded or stressed.
- Solutions as above but in which the coupons of dissimilar metals were galvanically coupled.
- Solutions as above but in which the coupons were fastened together to form crevices between the flat surfaces.

The test conditions and results are summarized in Table II. In about a third of the tests, conditions were such that significant

Table II

Corrosion Test Log
Coupon Testing, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Comp., Test Duration		Corrosion Rate	Comments
		C	NI	Gr	Mo	Others						
1	304-4	0.062	8.23	18.35	0.06	-	P, 1/2	New	2 g/l Cu + 0.4	4.5	No effect	
	304L-2	0.025	10.06	18.45	0.11	-	P, 1/2	"	pH 2 + 1.7	1.1	No effect	
	316-2	0.018	11.67	16.84	2.14	-	W, 1/2	"	100 g/l (NH ₄) ₂ SO ₄	2200	General metal loss, sulfide film	
	316L-4	0.009	13.07	17.42	2.15	-	P, 1/2	"	5 ppm Cl ⁻ , 24 hr	10.6	No effect	
2	304L-7	0.014	10.3	18.0	-	-	W, 1/2	New	2 g/l Cu + 0.4	2000	General metal loss, sulfide film	
	316-12	0.067	13.31	16.48	2.17	-	S, 1/2	"	pH 2 + 1.7	0.9	No effect	
	316-18	0.05	13.11	17.63	2.76	-	W, 1/2	"	100 g/l (NH ₄) ₂ SO ₄	1200	General metal loss, sulfide film	
	316L-18	0.02	13.6	17.71	2.67	-	W, 1/2	"	5 ppm Cl ⁻ , 24 hr	900	General metal loss, sulfide film	
3	304L-8	0.014	10.3	18.0	-	-	W, 1/2	New	2 g/l Cu	6.3	Light staining, spotting	
	316-4	0.018	11.67	16.84	2.14	-	P, 1/2	"	pH 2.30	38.2	Metal loss above interface	
	316-19	0.05	13.11	17.63	2.76	-	W, 1/2	"	100 g/l (NH ₄) ₂ SO ₄	0.8	Light staining, spotting	
	316L-19	0.02	13.6	17.71	2.67	-	W, 1/2	"	5 ppm Cl ⁻ , 63 hr	19.0	Metal loss under dried solids	
4	304-4	0.062	8.23	18.35	0.06	-	P, 1/2 From 1		2 g/l Cu	0.4	Light staining, spotting	
	304L-4	0.025	10.06	18.45	0.11	-	P, 1/2		pH 2.08	0.4	Light staining, spotting	
	316-19	0.05	13.11	17.63	2.76	-	W, 1/2 From 3		100 g/l (NH ₄) ₂ SO ₄	0.9	Light staining, spotting	
	316L-4	0.009	13.07	17.42	2.15	-	P, 1/2 From 1		0 ppm Cl ⁻ , 64 hr	0.5	Light staining, spotting	
5	304-4	0.062	8.23	18.35	0.06	-	S, 1/2 From 1,4		2 g/l Cu	1.0	Light staining, spotting	
	304L-4	0.025	10.06	18.45	0.11	-	P, 1 From 4		pH 2.42	0.4	Light staining, spotting	
	316-19	0.05	13.11	17.63	2.76	-	W, 1/2 From 3,4		100 g/l (NH ₄) ₂ SO ₄	2.2	Light staining, spotting	
	316L-4	0.009	13.07	17.42	2.15	-	P, 0 From 1,4		2 ppm Cl ⁻ , 62 hr	0	No change	
6	304-4	0.062	8.23	18.35	0.06	-	S, 1/2 From 1,4,5		2 g/l Cu	1.2	Light staining, spotting	
	316-19	0.05	13.11	17.63	2.76	-	W, 1/2 From 3,4,5		pH 1.95	1.0	Light staining, spotting	
	310-1	0.042	19.59	25.04	0.31	-	P, 1/2 New		100 g/l (NH ₄) ₂ SO ₄	0.2	Light spotting above interface	
	330-1	0.04	35.44	19.03	-	-	P, 1/2 New		5 ppm Cl ⁻ , 63 hr	0.5	Light spotting above interface	
	Ti-1	0.012	-	-	-	>99.8 Ti	P, 1/2 New		--	-	Light staining, spotting	
	EN 76-1-1	0.01	0.3	26.0	1.0	-	P, 1/2 New		--	0.1	Light spotting above interface	
		max	max	nom	nom							

Notes: 1 = Completely immersed, 1/2 = half immersed, 0 = unimmersed
P = Plain (straight), W = Welded, S = Stressed
All tests at (nom) 175°C, 115 psig.

Table II (continued)

Corrosion Test Log
Coupon Testing, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %					Sample Shape	Sample History	Solution Comp., Corrosion		Comments
		C	Ni	Cr	Mo	Others			Test Duration	Rate, MPY	
7	310-1	0.042	19.59	25.04	0.31		P, 1/2	From Test 6	2 g/l Cu + 0.05 pH 1.00 + 1.26	700	General loss of metal
	330-1	0.04	35.04	19.03	-		P, 1/2	"		>3000	General loss of metal
	Ti-1	0.012	-	-	-	>99.8 Ti	P, 1/2	"	100 g/l (NH ₄) ₂ SO ₄	-	Light staining, spotting
	EN26-1-1	.01mx	.3mx	26 nom	1 nom		P, 1/2	"	5 ppm Cl ⁻ , 93 hr	21.7	Light staining
8	C20Cb-1	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2	New	2 g/l Cu + 0.1 pH 1.00 + 1.20	220	Dark staining
	C20Cb-2/3	.03	33.08	19.37	2.19	Cb+Ta.8	C, 1	"		260	Dark stain, crevice corrosion
	EN26-1-1	.01mx	.3mx	26 nom	1 nom		P, 1/2	From 6,7	100 g/l (NH ₄) ₂ SO ₄	39.6	Intergranular corrosion
	EN26-1-2/3	"	"	"	"		S, C, 1	New	5 ppm Cl ⁻ , 40 hr	4.9	No effect
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6,7		-	Light staining
9	304L-8	.014	10.3	18.	-		W, 1/2	From 3	2 g/l Cu	4.1	Light staining
	316L-4	.009	13.07	17.42	2.15		P, 1/2	From 1,4,5	pH 1.60 + 1.67	1.5	Light staining
	310-2	.042	19.59	25.04	0.31		P, 1/2	New	100 g/l (NH ₄) ₂ SO ₄	0.6	Light staining, spotting
	C20Cb-1	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2	From 0	5 ppm Cl ⁻ , 66 hr	3.4	Light staining
	EN26-1-1	.01mx	.3mx	26 nom	1 nom		P, 1/2	From 6,7,8		0.4	No effect
	Ti-1	.012	-	0	-	>99.8 Ti	P, 1/2	From 6,7,8		-	Light staining
10	304L-8	.014	10.3	18.	-		W, 1/2	From 3,9	2 g/l Cu + 1.9	4.4	Stain removed
	316L-4	.009	13.07	17.42	2.15		P, 1/2	From 1,4,5,9	pH 1.26 + 1.31	3.2	Stain removed
	310-2	.042	19.59	25.04	0.31		P, 1/2	From 9	100 g/l (NH ₄) ₂ SO ₄	1.7	Stain removed
	C20Cb-1	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2	From 8,9	5 ppm Cl ⁻ , 65 hr	5.7	Stain removed
	EN26-1-1	.01mx	.3mx	26 nom	1 nom		P, 1/2	From 6,7,8,9		1.9	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6,7,8,9		0.7	Light staining
11	C70-1/316-12	.03/	33.08/	19.37/	2.19/		C, 1	From 8,9,10/New	2 g/l Cu + 1.82	5.1/9.6	Light crevice corrosion, 316-12
		.067	13.31	16.48	2.17						
	C20Cb-2/3	.03	33.08	19.37	2.19	Cb+Ta.8	C, 1	From 8	pH 1.26 + 1.21	7.2	Stain removed
	C20Cb-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	New	100 g/l (NH ₄) ₂ SO ₄	2.4	Light staining, spotting
	C20Cb-5	.03	33.08	19.37	2.19	Cb+Ta.8	S, 1/2	New	5 ppm Cl ⁻ , 70 hr	1.6	Light staining, spotting
	EN26-1-4	.01mx	.3mx	26 nom	1 nom		P, 1/2	New		0.5	Light staining, spotting
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-10		0.3	Light staining, spotting

Notes: 1 = Completely immersed, 1/2 = half immersed, 0 = unimmersed.
P = Plain (straight), W = welded, S = stressed, C = with crevice.

Table 11 (continued)

Corrosion Test Log
Coupon Testing, Closed Autoclave

Test No.	Sample Designation	C	Sample Composition, %				Sample State	Sample History	Solution Comp., Test Duration	Corrosion Rate, MPY	Comments
			Al	Cr	Mo	Others					
12	304L-8	.014	10.3	18.	-		W, 1/2	From 3,9,10	2 g/l Cu + 2.07	14.1	Light staining
	316-12	.067	13.31	16.48	2.17		P, 1/2	From 11	pH 1.03 + 1.0	12.6	Light staining
	C20Cb3-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	From 11	100 g/l (NH ₄) ₂ SO ₄	2.4	Light staining
	C20Cb3-5	.03	33.08	19.37	2.19	Cb+Ta.8	S, 1/2	From 11	5 ppm Cl ⁻ , 40 hr	3.2	Light staining
	EN26-1-4	.01 max	.3max	26 nom	1 nom		P, 1/2	From 11		5.8	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-11		2.6	Light staining
13	304L-8	.024	10.3	18.	-		W, 1/2	From 3,9,10 12	2 g/l Cu + .09	780	General loss of metal
	316-12	.067	13.31	16.48	2.17		P, 1/2	From 11,12	pH 1.25 + 1.20	10.6	Light staining, spotting
	C20Cb3-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	From 11,12	200 g/l (NH ₄) ₂ SO ₄	15.9	Light staining
	C20Cb3-5	.03	33.08	19.37	2.19	Cb+Ta.8	S, 1/2	From 11,12	5 ppm Cl ⁻ , 62 hr	-	Light staining
	EN26-1-4	.01 max	.3max	26 nom	1 nom		P, 1/2	From 11,12		0.1	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-12		-	Light staining
14	310-2	.042	19.59	25.04	0.31		P, 1/2	From 9,10	2 g/l Cu	1.5	No effect
	C20Cb3-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	From 11,12 13	pH 1.17 + 1.11	3.5	Stain lightened
	C20Cb3-2/5	.03	33.08	19.37	2.19	Cb+Ta.8	P/S, C, 1/2	From 9-11, 11-13	200 g/l (NH ₄) ₂ SO ₄	5.6	Stain lightened
	EN26-1-4	.01 max	.3max	26 nom	1 nom		P, 1/2	From 11,12, 13	5 ppm Cl ⁻ , 62 hr	2.0	Dark staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-13		3.1	Light staining
15	304L-9	.014	10.3	10.	-		W, 1/2	New	2 g/l Cu + .12	26.2	Interface pitting, oxide film
	316-12	.067	13.31	16.48	2.17		P, 1/2	From 11,12 13	pH 1.17 + 1.06	5.1	Light pitting
	C20Cb3-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	From 11-14	200 g/l (NH ₄) ₂ SO ₄	1.7	Light staining
	C20Cb3-5	.03	33.08	19.37	2.19	Cb+Ta.8	S, 1/2	From 11-14	0 ppm Cl ⁻ , 86 hr	2.2	Light staining
	EN26-1-4	.01 max	.3max	26 nom	1 nom		P, 1/2	From 11-14		1.8	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-14		-	Light staining
16	150-20	.06	27.7	19.9	2.05		P, 1	New	2 g/l Cu + .03	500	Pitting, general loss of metal
	C20Cb3-4	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1/2	From 11-15	pH .8 + .98	260	Dark staining
	C20Cb3-2/5	.03	33.08	19.37	2.19	Cb+Ta.8	P/S, C, 1/2	From 9-12, 11-15	100 g/l (NH ₄) ₂ SO ₄	230	Light crevice corrosion
	EN26-1-4	.01 max	.3max	26 nom	1 nom		P, 1/2	From 11-15	0 ppm Cl ⁻ , 40 hr	65.6	Intergranular corrosion
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-15		-	Dark staining

Notes: 1 = Completely immersed, 1/2 = half immersed, 0 = union
P = Plain (straight), W = welded, S = stressed, C = with device.

Table II (continued)

Corrosion Test Log
Coupon Testing, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Comp., Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
17	316-12	.067	13.31	16.48	2.17		P, 1/2	From 11-13, 15	1 g/l Cu + .92	2.2	Light staining
	Durimet 20	.039	27.83	19.2	2.05		P, 1	From Scap- ing Tests	pH 1.6 + 1.63	1.3	No affect
	ISO-20-2	.06	27.7	19.9	2.05		P, 1	New	100 g/l (NH ₄) ₂ SO ₄	16.9	Severe pitting
	C20Cb3-3	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2	From 8,11	5 ppm Cl ⁻ , 48 hr	1.7	Stain lightened
	EB26-1-5	.01 max	.3 max	26 nom	1 nom		P, 1/2	New		0.3	Spotting above interface
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-16		-	Light staining
18	316-22	.067	13.31	16.48	2.17		P, 1/2	From 11-13, 13,17	5 g/l Cu	3.1	Dark staining
	Durimet 20	.039	27.83	19.2	2.05		P, 1	From 17	pH 1.69	1.4	No affect
	ISO-20-3	.06	27.7	19.9	2.05		P, 1	New	100 g/l (NH ₄) ₂ SO ₄	3.4	Light pitting
	C20Cb3-3	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2	From 8,11, 17	5 ppm Cl ⁻ , 64 hr	1.5	Dark staining
	EB26-1-5	.01 max	.3 max	26 nom	1 nom		P, 1/2	From 27		0.3	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-27		-	Light staining
19	Durimet 20	.039	27.83	19.2	2.05		P, 1	From 17,18	2 g/l Cu + .09	240	Severe pitting
	C20Cb3-1	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1	From 8-10, refinished	pH 1.02 + 1.15	80.3	Dark staining
	C20Cb3-3	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1	From 8,11, 17,18	50 g/l (NH ₄) ₂ SO ₄	82.1	Dark staining
	C20Cb3-2/4	.03	33.08	19.37	2.19	Cb+Ta.8	P/W,C, 1/2	From 9-12 & 16,21-16	5 ppm Cl ⁻ , 64 hr	160	Crevice corrosion
	EB26-1-5	.01 max	.3 max	26 nom	1 nom		P, 1/2	From 17,18		27.6	Intergranular corrosion
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-10		-	Light staining
20	Durimet 20	.039	27.83	19.2	2.05		P, 1	From 17-19	2 g/l Cu + .02	110	Pitting
	Worthite	.07 max	24 nom	20 nom	3 nom		P, 1	New	pH 1.1 + 1.22	79.1	Pitting
	C20Cb3-2/3	.03	33.08	19.37	2.19	Cb+Ta.8	P, C, 1	See 19	50 g/l (NH ₄) ₂ SO ₄	85.7	Crevice corrosion
	EB26-1-8	.01 max	.3 max	26 nom	1 nom		P, 1/2	New	5 ppm Cl ⁻ , 65 hr	9.4	Light staining
	EB26-1-6/7	.01 max	.3 max	26 nom	1 nom		S/P, C, 1/2	New		-	Light staining
	EB26-1-12	.01 max	.3 max	26 nom	1 nom		W, 1	New		10.5	Dark stain on heat zone
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-29		-	Dark staining

Notes: 1 = Completely immersed, 1/2 = half immersed, 0 = unimmersed.
P = Plain (straight), W = welded, S = stressed, C = with crevice.

Table II (continued)

Corrosion Test Log
Coupon Testing, Unstirred, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %				Other	Sample State	Sample History	Exposition Comp. Test Duration	Corrosion Rate, MPY	Comments
		C	W	Cr	Mo						
21	304L-8	.014	10.3	18.			W, 1/2	From 15	2 g/l Cu	9.4	Light staining
	316L-4	.009	13.07	17.42	2.15		P, 1/2	From 1,4,5, 9,10	pH 1.59 + 1.46	5.5	Light staining
	316-2	.042	19.59	25.04	.31		P, 1/2	From 9,10,14	100 g/l (NH ₄) ₂ SO ₄	2.2	Light staining
	C20Cb3-1	.03	33.08	19.37	2.19	Ch+Ta.8	P, 1	From 8-10,19	5 ppm Cl ⁻ , 89 hr	9.3	Light staining
	ES26-1-7	.01 mm	.3 mm	26 nom	1 nom		P, 1/2	From 20		3.2	Dark staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 4-20		0.2	Light staining
22	316-2	.042	19.59	25.04	.31		P, 1/2	From 9,10,14 21	2 g/l Cu	1.9	Light staining
	C20Cb3-1	.03	33.08	19.37	2.19	Ch+Ta.8	P, 1	From 8-10,19, 21	pH 1.5	5.8	Stain lightened
	C20Cb3-2/5	.03	33.08	19.37	2.19	Ch+Ta.8	P/3,C,1/2	See 20/16		13.1	Stain lightened
	ES26-1-7	.01 mm	.3 mm	26 nom	1 nom		P, 1/2	From 20,21	5 ppm Cl ⁻ , 48 hr	2.9	Dark staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 4-21		1.1	Light staining
	316-2	.042	19.59	25.04	.31		P, 1/2	From 9,10,14 21,22	2 g/l Cu	1.1	Light staining
23	C20Cb3-1	.03	33.08	19.37	2.19	Ch+Ta.8	P, 1	From 8-10,19 21,22	pH 1.42 + 1.41	9.1	Light staining
	C20Cb3-2/5	.03	33.08	19.37	2.19	Ch+Ta.8	P/3,C,1/2	See 22	100 g/l (NH ₄) ₂ SO ₄	3.3	Light staining
	ES26-1-7	.01 mm	.3 mm	26 nom	1 nom		P, 1/2	From 20-22	5 ppm Cl ⁻ , 181 hr	0.8	Light staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-22		0.1	Light staining
24	Durimet 20	.039	27.83	19.2	2.05		P, 1	New	2 g/l Cu	2.8	No effect
	316-13	.067	13.11	16.48	2.17		P, 1/2	New	pH 1.6	5.9	Dark staining
	C20Cb3-2/316-14	.03/.067	33.08/13.31	19.37/16.48	2.19/2.17	Ch+Ta.8	P, 1/2,1/2,C	See 22/ new	200 g/l (NH ₄) ₂ SO ₄	1.9/5.7	No effect/dark staining
	ES26-1-7/316-15	.01/.067	.3/13.31	26/16.48	1/2.17		P, 1/2, C	From 20-23/ new	5 ppm Cl ⁻ , 185 hr	0.8/5.5	Light staining/dark staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-23		0.1	Light staining
25	Durimet 20	.039	27.83	19.2	2.05		P, 1/2	From 24	2 g/l Cu	4.5	No effect
	316-13	.067	13.11	16.48	2.17		P, 1/2	From 24	pH 1.48	7.8	Dark staining
	C20Cb3-2/316-14	.03/.067	33.08/13.31	19.37/16.48	2.19/2.17	Ch+Ta.8	P, 1/2,1/2,C	See 23/ From 24	100 g/l (NH ₄) ₂ SO ₄	2.4/7.6	No effect/light staining
	ES26-1-7/316-15	.01/.067	.3/13.31	26/16.48	1/2.17		P, 1/2, C	From 20-24	5 ppm Cl ⁻ , 96 hr	2.3/9.7	Light staining/dark staining
	Ti-1	.012	-	-	-	>99.8 Ti	P, 1/2	From 6-24		0.2	Light staining

Notes: 1 = completely immersed, 1/2 = half immersed, Ø = waterlogged
P = Plain (straight), W = welded, S = stressed, C = with crevice.

Table II (continued)

Corrosion Test Log
Coupon Testing, Unstirred, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %				Z Others	Sample State	Sample History	Solution Comp. Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mn						
26	J16-13	.067	13.31	16.48	2.17		P, 1/2	From 24, 25	2 g/l Cu + 1.8 pH 1.22	5.2	Light staining
	D20-2	.039	27.83	19.2	2.05		P, 1	From 24, 25		2.4	No effect
	C20Cb3-2/316-14	.03/.067	13.08/	19.37/	2.19/2.17	Cb+Ta.8	P, 1/P, 1/2, C	See 25	100 g/l (NH ₄) ₂ SO ₄	2.0/4.4	No effect/light staining
	E826-1-7/316-15	.01/.067	13.31	16.48			P, 1/2, C	See 25	25 ppm Cl ⁻ , 153 hr	0.2/3100	No effect/local galvanic corrosion
	Ti-1	.012	13.31	16.48		> 99.8 Ti	P, 1/2	From 6-25		-	No effect
27	D20-2	.039	27.83	19.2	2.05		P, 1	From 24-26	2 g/l Cu + .05 pH .98 + 1.13	13.3	Dark staining, pitting
	C20Cb3-2/316-14	.03/.067	33.08/	19.37/	2.19/2.17	Cb+Ta.8	P, 1/P, 1/2, C	See 26		6.0/156	Dark stain/general loss of metal
	E826-1-7/316-15	.01/.067	13.31	16.48	1/2.17		P, 1/2, C	See 26	75 g/l (NH ₄) ₂ SO ₄	-/110	Intergranular attack/general loss of
	Ti-1/316-16	.012/.067	13.31	16.48	-/2.17	> 99.8 Ti	P, 1/2, C	From 6-26/New	3 ppm Cl ⁻ , 255 hr	-/2600	Light stain/local galvanic corrosion
			13.31	16.48							
28	J16L-11/12	.022	13.43	17.08	2.54		P, 1/2, C	New/New	2 g/l Cu pH 1.22	20.7/17.4	Crevices corrosion above interface
	J16L-13/Eb-10	.022/.01	13.43/	17.08/	2.54/2		P, 1/2, C	New/See B.1-3		58.8/1.2	Galvanic corrosion above interface
	J16L-14/Ti-2	.022/.012	13.43/	17.08/	2.54/-	> 99.8 Ti	P, 1/2, C	New/See B.1-3	100 g/l (NH ₄) ₂ SO ₄	180/-	Crevices corrosion under clamp
	E826-1-4/Ti-1	.01/.012	13.31	16.48	1/	> 99.8 Ti	P, 1/2, C	See 16/From 6-27	5 ppm Cl ⁻ , 237 hr	1.8/0.7	Dark staining above interface
29	J04-14/C20Cb3-3	.05/.03	9.1/	18.5/	-/	Cb+Ta.8	P, 1/2, C	See B.1-4/20	2 g/l Cu + .7	2.4/13.7	Light staining
	J16-16/C20Cb3-2	.067/.03	13.31/	16.48/	2.17/	Cb+Ta.8	P, 1/2, C	See B.1-4/27	pH 1.22	1700/7.4	Interface corrosion/light pitting
	J04-13/E826-1-13	.05/.01	9.1/	18.5/	-/		P, 1/2, C	See B.1-4	100 g/l (NH ₄) ₂ SO ₄	2.8/	Light staining
	J04-12/Ti-2	.05/.012	9.1/	18.5/	-/	> 99.8 Ti	P, 1/2, C	See B.1-4/28	5 ppm Cl ⁻ , 162 hr	2.7/-	Light staining

1 = Completely immersed, 1/2 = half immersed, 0 = unimmersed.
 P = Plain (straight), W = welded, S = stressand, C = with crevices.

Table II (continued)

Corrosion Test Log

Coupon Testing, Unstirred, Closed Autoclave

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Comp. Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
30	C20Cb3-6	.03	33.08	17.37	2.19	Cb+Ta.8	P, 1/2	New	2 g/l Cu	2.5	Light staining
	904L-2	.02 max	25	20	4.5		P, 1/2	New	pH 1.12	1.8	No effect
	EB26-1-15	.01 max	.3 max	26 nom	1 nom		P, 1/2	New	75 g/l (NH ₄) ₂ SO ₄	1.8	Dark staining
	Ti-2	.012	-	-	-	>99.8 Ti	P, 1/2	See 29	5 ppm Cl ⁻ , 160 hr	1.0	Light staining
31	C20Cb3-6 / 7	.03	33.08	19.37	2.19	Cb+Ta.8	P, 1/2, C	See 30/8.1-5	2 g/l Cu + .1	25.5/23.6	Crevice corrosion
	904L-1/5	.02 max	25	20	4.5		P, 1/2, C	New/New	pH 1.12 + 1.42	60.5/60.8	Crevice Corrosion
	EB26-1-15/15	.01 max	.3 max	26 nom	1 nom		P, 1/2, C	See 29/30	75 g/l (NH ₄) ₂ SO ₄	2.64/.56	Light staining
	Ti-1/Ti-2	.012	-	-	-	>99.8 Ti	P, 1/2, C	See 28/30	5 ppm Cl ⁻ , 63 hr	.67/-	Light staining
32	304-8/9	.05	8.4	18.34	.11		W/P, 1/2, C	See 3.1-5	2 g/l Cu + .01	85.4/87.5	Light crevice corrosion
	904L-2/6	.02 max	25	20	4.5		P/W, 1/2, C	See 30/New	pH 1.22 + 1.38	46.6/34.3	Crevice corrosion
	C20Cb3-4/7	.03	33.08	19.37	2.19		W/P, 1/2, C	See 3.1-3/31	100 g/l (NH ₄) ₂ SO ₄ 5 ppm Cl ⁻ , 135 hr	38.1/24.2	Crevice corrosion
33	304L-19/20	.026	10.08	18.63	.19		W/N, 1/2, C	New/New	2 g/l Cu, reformed	575/895	Crevice corrosion
	D20-3	.039	27.83	19.2	2.05		P, 1	See 3.1-3	pH 1.18	42.8	Pitting
	C20Cb3-1	.03	33.08	19.37	2.19		P, 1/2	See 3.1-4	100 g/l (NH ₄) ₂ SO ₄	14.9	Light staining
	EB26-1-18	.01 max	.3 max	26 nom	1 nom		P, 1/2	New	5 ppm Cl ⁻ , 48 hr	0.5	No effect.
34	304-19	.07	9.05	18.1	.26		W, 1	New	3 g/l Cu	4.8	Light staining
	304L-11	.024	10.1	18.38			P, 1	New	pH 1.4	1.8	Light staining
	316-7	.059	12.32	17.33	2.63		W, 1	See 3.1-3	60 g/l (NH ₄) ₂ SO ₄	0.1	No effect
	316L-16	.022	13.43	17.08	2.54		P, 1	New	30 hr	2.3	Light staining
	UNB904L-4	.02 max	25	20	4.5		P, 1	New	(field test	0.6	No effect
	EB26-1-17	.01 max	.3 max	26 nom	1 nom		P, 1	New	in 8" column)	0.2	No effect
	C20Cb3-12/13	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1, C	New		95/95	Crevice corrosion
	C20Cb3-10	.03	33.08	19.37	2.19	Cb+Ta.8	W, 1	New		3.2	Light staining
	Ti-2	.012	-	-	-	>99.8 Ti	P, 1	See 3.		-	No effect

I = Completely immersed, 1/2 = half immersed, 0 = unimmersed.

P = Plain (straight), W = welded, S = stressed, C = with crevice.

corrosion occurred on at least one coupon. This resulted in the depletion of the copper content of the solutions which tended to make them still more corrosive since the cupric ion passivated the metal surfaces. In the following figures, a downward directed arrow indicates a corrosion rate which is likely higher than anticipated because of a loss of copper passivating ability.

As has been noted, difficulties in maintaining an adequate shaft seal restricted the use of the stirred autoclave to short term tests. When tests were run in the stirred and unstirred autoclaves under otherwise identical conditions, however, the measured corrosion rates in the latter were always higher, as shown in Table III. Since fluid motion in the unstirred autoclave was undoubtedly slow, due only to natural convection, the higher rates are likely due to a mass transfer limitation in the transport of cupric ions to the metal surface. In the following figures, the corrosion rates observed in the unstirred autoclave have been "corrected" to rates which would be expected under stirred conditions by dividing them by a factor of 1.7. The hydraulics in the stirred case are more likely to represent conditions in a scrubbing column and its piping, where fluid motion will be turbulent in areas which are not actually creviced.

The effect of varying acidities at fixed copper, ammonium sulfate, and chloride concentrations is shown graphically in Fig. 1. As expected, there is a general trend of increasing corrosion rate with increasing acidity although there is considerable scatter in the data, particularly at low acidities. Most of these data, however, came from early scoping tests in which high corrosion rates on at least one sample - and depletion of the solution's copper content - were common. The indicated corrosion rates of 0.1 MPY for titanium represent, in most cases, a measured value of zero. Even on the highest measured values, 0.7 and 2.6 MPY, no visible evidence of corrosion was apparent, and in many of the tests the titanium samples gained a small amount of weight. Essentially, the titanium used - a commercial grade - may be considered passive under all conditions tested.

Table III
Corrosion Rates in Stirred and Unstirred Autoclaves
for Identical Solution Compositions

<u>Alloy</u>	<u>Stirred Test</u>		<u>Unstirred Test</u>		<u>Ratio C.R., Unstirred/ C.R. Stirred</u>
	<u>Test No.</u>	<u>Corrosion Rate, MPY</u>	<u>Test No.</u>	<u>Corrosion Rate, MPY</u>	
304L-8 ⁽⁴⁾ 304L-9 ⁽⁴⁾	10 ⁽¹⁾	4.4	21 ⁽¹⁾	9.4	2.1
316L-4	10	3.2	21	5.5	1.7
310-2	10	1.7	21	2.2	1.3
C20Cb3-1	10	5.7	21	9.3	1.6
EB26-1-1 ⁽⁴⁾ EB26-1-7 ⁽⁴⁾	10	1.9	21	3.2	1.7
310-2	14 ⁽²⁾	1.5	22 ⁽²⁾	1.9	1.3
C20Cb3-4 ⁽⁴⁾ C20Cb3-1 ⁽⁴⁾	14	3.5	22	5.8	1.6
C20Cb3-2/5 ⁽³⁾	14	5.6	22	13.1	2.3
EB26-1-4 ⁽⁴⁾ EB26-1-7 ⁽⁴⁾	14	2.0	22	2.9	1.5

(1) Solution composition Tests No. 10, 21: 2 g/l Cu, 24 g/l H₂SO₄, 100 g/l (NH₄)₂SO₄, 5 ppm Cl⁻.

(2) Solution composition Tests No. 14, 22: 2 g/l Cu, 36 g/l H₂SO₄, 200 g/l (NH₄)₂SO₄, 5 ppm Cl⁻.

(3) Creviced samples.

(4) These alloys pairs have the same composition.

The corrosion rates of types 304 and 316 stainless steels increase from the order of 0.5 MPY at 5 g/l H_2SO_4 to about 10 MPY at 30 g/l acid. At 40 g/l acid, they are easily activated and corrode rapidly. Within the scatter of the data, there appears to be no difference between type 304 and 316 or between the normal and low carbon versions of the alloys. The behavior of types 310 and 330 stainlesses are similar except that corrosion rates are about one third those of type 304 and 316 below 30 g/l acidity. However, once activated they corrode at very high rates as well.

While there are more scatter in the data, the trend of increasing corrosion rate with increasing acidity may be seen for E Brite 26-1 as well, although rates are of the order of one fifth those of types 304 and 316 below 30 g/l acidity. However, in contrast to the austenitic stainlesses, the E Brite did not show a dissolution and general loss of metal when corroding at high acidities. Instead, severe intergranular corrosion and grain dropping were observed although calculated penetration rates were always less than 50 MPY.

The data on Carpenter 20 (Alloy C20Cb3) are also scattered, but do not show general loss of metal and dissolution at higher acidities. On the other hand, neither do they show very low corrosion rates (< 1 MPY) at low acidities. The data scatter over a range of 2-5 MPY corrosion rate at acidities between about 5 and 40 g/l acidity with no strong correlation between rate and acidity.

Thus, it appears that the resistance of C20Cb3 is superior to that of T304/316 at acidities greater than about 20 g/l, and is superior to that of T310/330 above about 30 g/l. And while it is not as passive as E Brite below 30 g/l H_2SO_4 , neither has any tendency for intergranular corrosion been observed. Very little evidence of pitting was observed in any of the wrought samples tested, nor was any accelerated attack of welds or heat effected zones adjacent to the welds noted. No evidence of stress corrosion was seen, and new, previously tested, and previously tested specimens which had been refinished all showed the same behavior

when tested in pairs under identical conditions. It was observed that higher corrosion rates, > 10 MPY say, tended to be associated with the occurrence of a grey to black stain on the surface of the samples below the liquid interface. At lower rates, no stain at all or very light staining might be observed, and the stains were sometimes removed in subsequent tests. Occasionally, a "horse collar" of metallic copper would cling to a sample at the vapor liquid interface, and evidence of accelerated corrosion would be found beneath it.

The effect of ammonium sulfate concentration at fixed copper content and acidities is shown in Fig. 2. Again, there is considerable scatter in the data, but the trend is towards decreasing corrosion rate with increasing ammonium sulfate concentration. This is consistent with the fact that, under these conditions of temperature and acidity, the sulfate-bisulfate equilibrium tends to buffer the system and at a given acidity the pH increases as the concentration of ammonium ion increases.

The ability of copper to passivate stainless steels at low concentrations is demonstrated by the results summarized in Table IV. Within the scatter of the data, copper concentrations down to 1 g/l are as effective as higher concentrations in passivating wrought stainless steels. It is likely, however, that if higher solution acidities were tested, the lower copper content solutions would lose their ability to passivate before the higher ones would. Such tests were not carried out since mass transfer considerations in the removal of H_2S dictate that copper contents of at least 2 g/l be maintained within the scrubber.

The difference in performance between cast and wrought versions of the higher stainless alloys tested is summarized in Table V. While the ISO 20 alloy shows only light pitting under conditions of relatively low acidity and high copper content, it is subject to severe pitting at lower copper contents and shows very severe pitting and intergranular attack at high acidities. Alloy D20 showed some tendency towards pitting corrosion at moderate acidities and low copper contents, and failed at higher

Corrosion Rate, MPY

Table IV

The Influence of Copper Concentration on
Corrosion Rates at Moderate Acidities⁽¹⁾

Copper Concentration, g/l	<u>1</u>	<u>2</u>	<u>5</u>
Corrosion Rate, MPY			
304L		4.1	
316	2.2		3.1
316L		1.5	
310		0.6	
D20 ⁽²⁾	1.3		1.4
ISO 20 ⁽²⁾	16.9 ⁽³⁾		3.4 ⁽³⁾
C20Cb3	1.7	3.4	1.5
EB26-1	0.3	0.4	0.3
Ti	-	-	-

⁽¹⁾ 12 g/l H₂SO₄, 100 g/l (NH₄)₂SO₄, 5 ppm Cl⁻, 175°C.

⁽²⁾ Cast alloys.

⁽³⁾ Pitting.

Table V
Performance of Cast and Wrought Alloys
under Scrubber Conditions

Test No.	16	17	18	19	20
Solution Composition					
g/l Cu	2 + .3	1	5	2 + .09	2 + .02
H ₂ SO ₄	42	12	12	34	24
(NH ₄) ₂ SO ₄	100	100	100	50	50
ppm Cl ⁻	0	5	5	5	5
Corrosion Rate, MPY					
316		2.2	3.1		
C20Cb3	260	1.7	1.5	80.3	85.7 ⁽³⁾
ISO 20	500 ⁽¹⁾	16.9 ⁽¹⁾	3.4 ⁽²⁾		
D20		1.3	1.4	240 ⁽¹⁾	110 ⁽²⁾
Worthite					79.1 ⁽²⁾

(1) Severe pitting.

(2) Light pitting.

(3) Crevice corrosion.

acidities, and Worthite seemed to show the same behavior. While all cast alloys were much more susceptible to pitting than the corresponding wrought versions, the D20 cast version of Carpenter 20 should prove serviceable at moderate acidities if copper concentrations are maintained above 2 g/t.

Test results for experiments in which coupons were subjected to galvanic coupling and for which crevices were formed are summarized in Table VI along with results for exposure of the "bare" metals under the same test conditions. Additional data for the bare metals may be derived from Figs. 1 and 2. In most cases, the corrosion rates for the creviced samples are higher than for the bare metals under the same test conditions and usually by a significant amount. In tests in which both creviced and bare metal coupons were exposed and corrosion was severe, metallic copper was inevitably found on the creviced samples. Although the resistance of bare metal samples of types 304 and 316 is superior to that of C20Cb3 at acidities below about 20 g/l, this is not the case when they are galvanically coupled to C20, EB26-1, or Ti. As expected, the corrosion rate of the lower alloys is accelerated and those of the higher alloys are reduced when they are coupled. Thus, care must be taken when specifying the composition of trim components such as thermowells, fittings, etc. for use in the scrubber system to prevent accelerated corrosion, particularly such as would be likely to occur at screwed joints where crevices would also be likely to form.

Potentiostatic Testing

A series of seven potential scans of T304 S/S were obtained at conditions comparable to those used by Osogawa and Engells. The electrolyte was 2N H_2SO_4 and scans were made at 25°C and 90°C. The results of these are shown in Figs. 3 and 4 along with Osogawa and Engells data. These data are typical of the expected current density-potential curves. With increasing anodic potential in the active region, the current density initially increases then suddenly drops. Beyond

Table VI

Crevice and Galvanic Corrosion under Simulated Scrubber Conditions

Crevice Corrosion (1)	304	304L	316	316L	C20Cb3	904L	EB26-1	Ti
<u>Solution Composition</u>								
50 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4					85.7			
50 g/l $(\text{NH}_4)_2\text{SO}_4$, 34 g/l H_2SO_4					81 160			
75 g/l $(\text{NH}_4)_2\text{SO}_4$, 34 g/l H_2SO_4					1.5 (2) 14.4	1.1 (2) 35.7	1.1 (2) 0.6	0.6 (2) 0.2
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4	50.8	5 433	4.6	3.2 11.2	5 18.3	23.8	1.7	0.1
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 42 g/l H_2SO_4					220 260		38.6 4.9	
200 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4					1.9 1.9			
200 g/l $(\text{NH}_4)_2\text{SO}_4$, 36 g/l H_2SO_4					3.4 6.6			
<u>Galvanic Corrosion (3)</u>								
<u>Solution Composition</u>								
75 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			91.8		3.5			
75 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			64.7				—	
75 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			1650					—
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			9.6		5.1			
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			4.5		1.4			
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			5.7				1.4	
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4				34.6			0.7	
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4				106				—
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4							1.1	0.4
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4	1.4				8.1			
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4				1000	4.4			
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4	1.6						—	
100 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4	1.6							—
200 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			3.4		1.1			
200 g/l $(\text{NH}_4)_2\text{SO}_4$, 24 g/l H_2SO_4			3.2				0.5	

(1) The upper number is for the "bare" metal, the lower for the creviced samples. Corrosion rates in MPY.

(2) At 24 g/l H_2SO_4 .

(3) The two metals listed at each solution composition constitute the galvanic couple tested. Corrosion rates in MPY.

Fig. 3. Potential scan comparison with Engell's data T304 S/S, 2N H₂SO₄, 25°C

—○— Engell
--△-- This work.

Volts vs. DHE

this potential, in the passive region, the current density remains low with increasing potential. The potential which signals the transition from active to passive regions is called the Flade potential. Finally at higher anodic potentials the current increases again. There is reasonable agreement between the literature values and those obtained in these experiments. There are two significant differences between the sets of data, however. The magnitudes of the current density, particularly in the passive region differ, those of Osogawa and Engells being significantly lower. This is most probably due to the experimental method. In this region many hours may be necessary to achieve equilibrium. Since the individual measurements in these tests were limited to 20 minutes, these values will tend to be higher. The second difference is a displacement of approximately 200 mV in the potential curves. Since the same displacement exist in all experiments, it is likely that it is a systematic difference in the reference electrodes.

The data for the five alloys at 175°C are presented in Figs. 5 through 7. The data for the 304, 310 and 316 stainless steels and the alloy 20 show typical current density-potential curves. However, there is also, superimposed, considerable fine structure e.g., plateaus, maxima and minima. The significance of the fine structure is indeterminate at this time since these experiments were considered to be surveying in nature. The data for the E-Brite alloy suggest that the Flade potential is cathodic of the open circuit potential. Here again the significance of the fine structure is indeterminate. The key experimental results are summarized in Table VII. The data suggest that these alloys will be in the passive region at potentials anodic of + 200 mV for these experimental conditions, which is consistent with the observed ability of the cupric ion to passivate the metals. It is difficult however to estimate the absolute corrosion rates of the various alloys from these measurements. Estimation of these would require additional experiments with much longer times allowed to achieve equilibrium.

Fig. 6. Resistance of alloy 20; 24 g/l H₂SO₄, 100 g/l (NH₄)₂SO₄, 175°C

—▽— 0 Cl⁻
—□— 5 ppm Cl⁻

Volts vs. DHE

Fig. 7. Resistance of E Brite; 24 g/l H_2SO_4 , 100 g/l $(NH_4)_2SO_4$

—□— 0 Cl⁻
—△— 5 ppm Cl⁻

Voltage vs. DNE

Table VII
Open Circuit and Flade Potentials

<u>Sample</u>	<u>Solution</u>	<u>Temp. (°C)</u>	<u>OCF vs. DHE (mV)</u>	<u>Flade Potential (mV)</u>
304	2N H ₂ SO ₄	25	-	+ 200
304	2N H ₂ SO ₄	25	(+ 400) ^a	+ 200
304	2N H ₂ SO ₄	25	+ 36	+ 200
304	2N H ₂ SO ₄	90	+ 90	+ 250
C20Cb3	S1	175	- 480	< - 200
C20Cb3	S1	175	- 480	< - 200
C20Cb3	S1	175	- 150	0
C20Cb3	S2	175	+ 75	+ 250
E Brite	S1	175	+ 95	< + 100
E Brite	S1	175	+ 95	< + 100
E Brite	S2	175	+ 500	< + 500
304	S1	175	- 75	+ 200
310	S1	175	+ 5	+ 200
316	S1	175	- 60	+ 200

S1 - 100 g/l (NH₄)₂SO₄, 24 g/l H₂SO₄.

S2 - 100 g/l (NH₄)₂SO₄, 24 g/l H₂SO₄, 5 ppm Cl⁻.

a - When current was first applied it rapidly shifted cathodic.
A new OCF of +20 mV was established.

Corrosion Monitoring Instrumentation Testing

A Magna Corporation series 7000 probe was inserted in the sump of the laboratory column during several series of short scrubbing tests. The results for two such runs are summarized in Table VIII. The corrosion rates measured on the test coupons in the sump are of the order expected for the test conditions being run. The Corrator's readings when immersed in hot (175°C), clean steam condensate during the heat up period prior to copper introduction are not unreasonable. While slightly higher than might be expected, the probe elements were new and may not as yet have been conditioned.

As soon as copper sulfate solution was admitted to the column, however, the Corrator reading rose dramatically and remained high throughout the course of the run. Inspection of the probes elements following the run showed some evidence of pitting, and small weight losses for three of the four elements. Corrosion rates calculated from these weight losses are also lower than the rates indicated by the Corrator instrument. Since repeated calibration checks during the tests indicated that the instrument was functioning properly, it must be concluded that the false high readings are characteristic of this system. It is likely that, even at the small potential difference used between the elements, a significant current is generated by the cupric/cuprous reduction/oxidation reactions occurring at the elements which are cathodic/anodic with respect to the system potential. This current would pass in parallel to the corrosion current generated by corrosion (oxidation) of the element and would be interpreted by the instrument's measuring circuit as an abnormally high corrosion rate. This problem would preclude the use of instruments employing the current measuring principal from giving accurate results in this system.

Magna Corporation's Corrosimeter was evaluated during the field test work on the 8" scrubbing column (Task C.2). With this instrument, corrosion rate is derived by measuring the rate of increase in the resis-

Table VIII

Corrater[®] Probe Response under Scrubbing Conditions

Test No.	<u>722</u>	<u>824</u>
Test Duration, hrs	3-1/2	3
Coupon Corrosion Rate, MPY ⁽¹⁾	6.7	9.5
Corrater Probe Element Material	T316	C20Cb3
Corrater Reading, MPY		
In Steam Condensate Only	1.2	1.8
In CuSO ₄ Only	75	50
In Scrubbing Solution ⁽²⁾	190	75
Corrater Elements Weight Loss, mg	+ 0.6, ⁽³⁾ 1.2	0.2, 0.4
Element Corrosion Rate, MPY ⁽⁴⁾	- , 30	5.8, 11.7

(1) Fully immersed T304L welded coupon, calculated from weight loss and test time.

(2) Acid copper sulfate, ammonium sulfate solution, pH ~ 1.

(3) Weight gain.

(4) Calculated from weight loss and test time.

tance of a wire or strip element as it loses metal while corroding. The probe used had a standard 40 mill C20Cb3 wire element. During the course of about 50 hours of exposure during four test series, the probe readings were erratic, varying by only small amounts and actually decreased slightly (by 10 units out of 1000 full scale) over the test period. Post run inspection by the manufacturer showed no corrosion of the wire element with no change in either its resistance or dimensions. The observed fluctuating resistance values were thought to be due to changes in ambient temperature. It was concluded that, if a more sensitive (thinner, less passive) element had been used, a higher corrosion rate would have been indicated giving readings of a magnitude which would have been outside the uncertainty imposed by fluctuating ambient temperatures. Thus, proper probe selection could permit this type of instrument to be used for on-line monitoring of corrosion rate.

FIELD TEST RESULTS

In addition to testing the suitability of the Corrosimeter[®] in this system, a test rack containing coupons was inserted in the sump of the 8" scrubbing column. The test results, summarized in Table IX, are consistent with the lab results presented in Figs. 1 and 2 and Tables IV and VI within the scatter of the data. The crevice test on the C20Cb3 coupons again demonstrates the susceptibility of the austenitic stainless steels to attack in this mode.

The column and its components were partially disassembled following the test and carefully inspected for evidence of corrosion, particularly crevice corrosion. The areas around the edges of the Teflon envelope gaskets at column and piping flanges were of special concern. No evidence of any corrosion, or even light etching or light staining, was found, however. Neither was any evidence of any type of corrosion or staining found on the bottom surfaces of nozzle and sight glass necks where loose solids had accumulated during the run. None was found under those few areas on the walls of the column above the normal froth area

Table IX

Field Test Results, Coupon Testing⁽¹⁾ Test No. 34

<u>Sample Material</u>	<u>Corrosion Rate, MPY</u>	<u>Effect on Sample</u>
304	4.8	Light Staining
304L	1.8	Light Staining
316	0.1	No Effect
316L	2.3	Light Staining
UHB 904L	0.6	No Effect
EB26-1	0.2	No Effect
C20Cb3	3.2	Light Staining
C20Cb3 ⁽²⁾	95	Crevice Corrosion
Ti	-	No Effect

⁽¹⁾ Average solution composition 3 g/l Cu, 60 g/l $(\text{NH}_4)_2\text{SO}_4$, 12 g/l H_2SO_4 . Test duration 50 hr.

⁽²⁾ Two coupons with crevice formed by gasket clamped between.

where a few patches of solids were found to have adhered, nor on any other column parts, including the column sieve tray. No evidence of pitting corrosion could be seen on the circulating pump casing, which was a cast version of alloy 20, although lab tests had indicated it might be susceptible (Table V). The pump's flanges, impeller, and shaft were also bright as new, and free from evidence of attack. The spool pieces connecting the pump to the column sump flange and circulating piping, which were field fabricated out of an unknown type of stainless steel - probably 304 or 316, did show a slight staining although no other evidence of corrosion was seen.

Two instances of crevice corrosion were observed on trim components however. A type 316 stainless concentric reducer had been fitted over the sieve tray downcomer seal cup to restrict liquid flow, and solids tended to pack up in the reducer. Clear evidence of corrosion was found on the inside of the reducer, where, presumably, solids had accumulated. With correct downcomer design, the need for this fitting would be eliminated.

In addition, evidence of crevice corrosion was found on the surface of the alloy plug on the recycle flow control valve on the pump discharge line. In retrospect, the surface between the valve's Teflon sleeve and plug is an almost ideal spot for crevice corrosion to occur and this valve style will be avoided in future work.

DESIGN IMPACT OF CORROSION STUDIES

The nominal scrubbing solution composition for the scrubber in closed circuit operation are 24 g/l H_2SO_4 , and 100 g/l $(NH_4)_2SO_4$ at 175°C. Under these conditions (Fig. 1) a corrosion rate of about 5 MPY would be expected for either T304/316 or C20Cb3, 2 MPY for T310/330, 1 MPY for EB26-1, and less than 0.1 MPY for titanium. Scoping testing indicated that UHB 904-L would behave essentially the same way as a C20Cb3. Under these conditions, the cast versions of the stainless alloys may be susceptible to pitting attack, and the wrought versions are subject to

crevice corrosion. The C20Cb3 will remain somewhat more passive at higher acidities than will T304/316 or T310/330, and does not show extremely high rates of corrosion (> 1000 MPY) even when severely attacked.

On these bases, C20Cb3, UHB904-L, and EB26-1 are clearly superior to T304/316 and alloy 20 and E-Brite are more readily available than T310/330, particularly for trim components. Since UHB904-L has not been approved for code construction, and is not available for use in trim components, it can not be considered a first choice as a material of construction at this time. While the E-Brite shows a higher resistance than alloy 20 at all acidities tested, it is subject to severe intergranular attack. Furthermore, it is not as readily available in trim components (pumps and valves, thermowells, etc.) and in certain forms, as is alloy 20 which is widely used in the chemical process industries.

Titanium is passive under all conditions tested and, economics aside, would be the obvious safe choice if a selection had to be made at this time for a commercial material. Obviously, too, it would be possible to mix materials, with the scrubber fabricated of one alloy and the piping and trim of others, provided that galvanic corrosion problems could be overcome.

The 100,000 lb/hr field test facility, however, is being designed with a limited life requirement in mind, so that even relatively high corrosion rates may be accepted for a few years and field repair may be made without major disruption to other production operations.

On this basis, it is recommended that the scrubber and its trim be fabricated out of alloy 20 insofar as possible and that titanium be considered a back up material.

Quotations will be solicited from vendors for both materials of construction, however, and the probable costs of equipment for a full scale (1,000,000 lb/hr) system will be estimated. It is likely that the scrubber for the large system will be of clad construction, where the relative difference in costs between alloy 20 and titanium will decrease,

particularly if a large corrosion allowance is required on the former. When the results of these evaluations have been completed, the materials selection will be reviewed again to determine if alloy 20 is the most cost effective choice.

Meanwhile, lab testing will continue to extend the range of data available on the performance of C20Cb3 and Ti, particularly, in this system.

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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task A.2

✓ Leach Regeneration Tests

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SUMMARY

Pressure leach experiments were carried out under Task A.2 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 planned, large field-test system.

Precipitates produced by scrubbing H_2S from synthetic geothermal steam were typically more reactive toward oxygen pressure leaching in acid medium than are synthetic or mineral CuS powders. In the case of scrubber solids, the preponderant reaction product of sulfide oxidation under the conditions investigated was sulfate rather than elemental sulfur. Rates of copper solubilization, corrected for diminishing interfacial area, were approximately first-order in time, 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.

The range of temperatures investigated was not sufficiently broad to establish an activation energy with certainty, but its probable value is in a range consistent with mass transport rather than chemical reaction control. At a temperature of $115^\circ C$, essentially complete reaction could be achieved in about 2 hrs when the oxygen partial pressure was maintained at ≥ 75 psi. These are relatively mild process conditions and confirm the suitability of pressure leach regeneration for small H_2S removal plants.

INTRODUCTION

In order for a H_2S removal process to be economic, it is essential that a) the H_2S removed be converted to an ultimate chemical form that may be sold, reinjected or otherwise suitably disposed of and b) any expensive chemicals used in the process be regenerable at reasonable cost. Conversion of copper sulfide to copper sulfate solution by a roast/leach process

and by acid pressure leaching are known technologies. However, they have not hitherto been applied to copper sulfide solids obtained by precipitating H_2S from geothermal steam.

In the first year of the program, it was demonstrated that the laboratory scrubber solids are amenable to oxidation by either of these likely regeneration routes. Considerations of equipment and other overall process requirements had indicated that the roast/leach route might be economically favored for large H_2S abatement plants, while pressure leaching would be favored for small systems. Consequently, further effort has been confined to the pressure-leach operation. By this route, H_2S that has been scrubbed from the geothermal steam may ultimately be converted to elemental sulfur, ammonium sulfate (relatively soluble) or gypsum ($CaSO_4 \cdot 2H_2O$, relatively insoluble). The form of the sulfate exiting the system depends upon whether net acid production is countered by addition of ammonia or lime, respectively.

A potentially very favorable circumstance arises when the NH_3 content of the geothermal steam is sufficient for internal neutralization whereby, ideally, the process would require only oxygen and make-up quantities of $CuSO_4$. Obvious factors determining neutralization requirements are the proportion of NH_3 scrubbed from the steam, the composition of the sulfide precipitate (i.e., the value of x in $Cu_{1+x}S$), and the combined stoichiometry of the sulfide precipitation and leaching reactions. For example, if elemental sulfur is a coproduct of the H_2S precipitation reaction and if the precipitate is subsequently oxidized entirely to sulfate, the overall stoichiometry would be:

The interesting result is that a larger value of x , i.e., a precipitate composition closer to Cu_2S , would reduce the requirements for acid neutralization. Specifically, under the assumptions given, the molar ratio

of NH_3 to H_2S for internal neutralization would be $1/(1+x)$ if NH_4NSO_4 is to be reinjected. For $x = 0.5$, this would mean scrubbing NH_3 and H_2S in the ratio 0.333 ppm NH_3 /ppm H_2S . This topic is treated more fully in the first annual report.

A less obvious aspect of neutralizing agent requirements in the overall H_2S removal process concerns the maximum H_2SO_4 concentration that may be maintained in the recirculating slurry, from the point of view of corrosion and H_2S scrubbing efficiency, and the minimum H_2SO_4 concentration that must be maintained during pressure leaching in order to retain the leached copper in solution. The former requirements are considered in separate reports on scrubber operation and on corrosion of materials. A comparison of solubility in $\text{CuSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{SO}_4$ solutions is included in the present report.

EXPERIMENTAL

Apparatus and Techniques

The major item of equipment employed in this work was a Parr Instrument Company 2-liter autoclave of type 316 stainless steel construction. Immersible parts included a thermowell, for the control thermocouple, and stirrer bracket fitted with a Teflon steady-bearing; thermowell and bracket were made from Carpenter 20 Cb3 alloy. Ancillary equipment included gas supply and flow regulators, temperature-controlled external heater, and motor-driven stirrer assembly.

It was recognized that for this three-phase heterogeneous reaction, adequate solids suspension and gas dispersion in the leach solution would be essential to achievement of optimum kinetics. Accordingly, the stirrer employed was the gas-dispersing turbine type, with hollow shaft having openings above the solution line and at the level of the turbine. Tests conducted in the glass liner, outside of the autoclave, revealed that vertical wall baffles, or "spoilers", such as normally employed to increase turbulence and thereby improve solids suspension, interfered with gas

dispersion. This is presumably because an appreciable tangential velocity of liquid past the lower shaft opening must be achieved in order to aspirate gas through the shaft from the atmosphere above the liquid. Visual observation indicated that the degree of gas dispersion apparently "plateaued" at above 70% of full stirrer speed (nominally 500 rpm). Subsequent pressure-leach experiments were conducted at 80%, or about 400 rpm.

A suspected discrepancy between control-thermocouple temperature indication and true reactor temperature was confirmed and quantified by comparison with a calibrated dial thermometer and with water vapor pressures as measured with a precision pressure gauge. A temperature calibration curve was constructed which enabled the reactor temperature to be read with a confidence of about $\pm 1^\circ\text{C}$.

In the pressure-leach tests, an atmosphere of nitrogen was maintained in the autoclave during heatup. Once at temperature and prior to admitting oxygen, the nitrogen was vented, and purging with autogenous steam was carried out intermittently until the system pressure had declined to a steady value, which was taken as the autogenous steam pressure. This procedure permitted a check on the reliability of initial temperature control.

Essentially the same autoclave arrangement was employed for the CuSO_4 solubility measurements as for the pressure-leach experiments.

The practice adopted was to discontinue stirring for approximately one minute prior to taking a liquid sample. This was to allow time for settling and thereby to minimize withdrawal of suspended solids, which otherwise could easily plug the sampling valve. Liquid in the sampling line was then displaced back into the reactor by means of gas overpressure. In this manner, the cumulative solids removed during sampling was minor; however, all liquid samples were routinely filtered prior to analysis.

Chemical Analysis and Computations

Chemical analytical methods were essentially as described in the First Annual Report. Briefly, liquid samples were analyzed for copper, free acid, total sulfate, and ammonium as appropriate: copper by direct photometry of the filtered solution, free acid by titration with NaOH to a pH end point, total sulfate by titration of the copper-stripped solution with $\text{Pb}(\text{ClO}_4)_2$ to a lead ion-specific electrode end point, and ammonium by use of an ammonia-specific gas-membrane electrode. Solids compositions were determined by applying the same general analytical methods to their aqueous solutions. For this purpose, copper sulfide precipitates were decomposed in concentrated HNO_3 saturated with NaClO_3 , and basic copper sulfates were dissolved in a known volume of standard perchloric acid.

In this and related project work, precise and reliable compositions of copper sulfide scrubber solids proved difficult to attain. This is because of their inherent reactivity, a consequence of deviation from simple stoichiometry (i.e., Cu_{1+x}S , rather than CuS or Cu_2S) and fine ultimate particle size. Thus, washed sulfide solids oxidized appreciably on standing wet, e.g., as moist filter cake, or during oven drying, thereby leading to low apparent copper contents. Fortunately, in the majority of leach experiments, the copper sulfide feed was reacted virtually to completion, so that some uncertainty in initial solids composition or amount did not preclude obtaining satisfactory kinetics information.

Considerable improvement in the reliability of composition determination was effected by decreasing the extent of air oxidation during the filtering and drying operations and by analysis for total sulfur. By the revised sample preparation procedure, the wet solids or filter cake was treated with dilute H_2SO_4 (about 1M) in the filter holder to remove oxidation products and then rapidly and successively washed with distilled water, ethanol and acetone. Drying was carried out for a

short period in an oven at a low temperature (ca. 80°C), the dried sample then being placed in a desiccator to cool. A further improvement consisted of maintaining a nitrogen atmosphere in the oven during drying. Sulfur determinations were performed on portions of the prepared samples by an outside analytical laboratory employing a combustion procedure. The repeatability of the sulfur determinations, as evidenced by analysis of duplicate samples, was within 1 percentage point.

The incorporation of analytical data into leach kinetics computations is illustrated here in a generalized way. If V_f is the measured final solution volume and its copper concentration is determined to be c_f , the total copper in the system is taken to be $V_f c_f + \sum_{i=1}^n v_i c_i + w_r$. The summation includes dissolved copper cumulatively removed with the total of n liquid samples (volume v_i). The amount of copper in the unreacted leach residue, including the cumulative filter residue (if significant) derived from filtering the liquid samples, is w_r in the foregoing expression. For computational purposes, the amount of copper solubilized at the time of taking the j th sample is considered to be

$$(V_f + \sum_{i=j}^n v_i) c_j + \sum_{i=1}^{j-1} v_i c_i$$

The fraction reacted, F , is then the ratio of the two quantities. For experiments where copper was present in the solution initially, its quantity (i.e., $V_{\text{initial}} c_{\text{initial}}$) was subtracted from the above sums to give total copper derivable from the solid sulfide and copper solubilized at time of sampling, respectively.

In those instances where a basic copper compound precipitated out of the solution, toward the end of the leach, its copper content was included in the amount of copper reacted. The basic copper compound in question is a product of hydrolysis and readily acid-soluble, so that its copper content is easily ascertainable. However, its occurrence, previously noted during operation of the laboratory steam scrubber,

was considered of sufficient import to warrant a short study of CuSO_4 solubility under pressure leach conditions, as described in the following section.

RESULTS

Solubility Studies

As noted above, precipitation of basic cupric sulfate occurred in several scrubber runs and pressure leach experiments. Chemical analyses of the washed and dried solids gave compositions approximating 5 Cu: 7 OH: 2 SO_4 . X-ray diffraction analysis of two samples from each type of occurrence revealed the principal crystalline phase to be antlerite, $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ (53.74% Cu). At sufficiently low concentration of free acid and high concentration of total sulfate, precipitation of this or a similar compound could limit the solubility of copper in CuSO_4 pregnant leach solution or CuSO_4 make-up solution. Solubility measurements were made in a gently stirred autoclave to determine maximum copper tenor of simulated process liquors as a function of temperature and solution composition.

With solutions of nominal copper concentration 40 g/t, no hydrolysis/precipitation occurred at temperatures of 105°C and below. Basic cupric sulfate that formed at higher temperature redissolved upon slow cooling, with stirring, to room temperature. That is, the reaction is reversible, the acid-soluble hydrolysis product being dissolved by the autogenously generated H_2SO_4 . For example, the composition of solution initially 41 g/t Cu^{2+} , 100 g/t $(\text{NH}_4)_2\text{SO}_4$ and 8.0 g/t H_2SO_4 became 34.3 g/t Cu^{2+} and 17.0 g/t H_2SO_4 at 175°C. Additional solubilities are given in Table I.

It is evident from the tabulated results that the critical parameters for establishing copper solubilities are temperature (inverse solubility relationship for the hydrolysis product) and free H_2SO_4 concentration. Increasing total sulfate in the solution decreases copper solubility; but in the anticipated normal operating range of 50-100 g/t

Table 1

Solubility in $\text{CuSO}_4/(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ Solutions

<u>Run No.</u>	<u>Initial Composition</u>			<u>$[\text{Cu}^{2+}]$, g/l, at temp.</u>		
	<u>H_2SO_4</u> <u>g/l</u>	<u>pH</u>	<u>$(\text{NH}_4)_2\text{SO}_4$</u> <u>g/l</u>	<u>140°C</u>	<u>160°C</u>	<u>175°C</u>
2	10	1.45	100	>43.4	-	40.6
6	8	1.60	100	>41.1	>41.7	34.3
5	5	1.74	75	~39	34.0	29.5
3	0	3.02	100	37.7	-	26.9
4	0	3.04	50	36.6	-	25.6
1	0	3.14	0	-	-	31.9

$(\text{NH}_4)_2\text{SO}_4$, the change is not great. In order to maintain a dissolved copper concentration of 40 g/l at scrubber temperature, the initial free acid concentration must be 10 g/l or greater. At usual pressure leach temperatures ($\leq 140^\circ\text{C}$), a minimum of 5 g/l H_2SO_4 in excess of the stoichiometric requirements of the leach reaction would need to be provided if the objective is to achieve a copper loading of 40 g/l in the make-up CuSO_4 solution. The circulating quantity of H_2SO_4 can be decreased if a lower copper loading is accepted. Whatever the pressure leach conditions, however, attention needs to be paid to the heat-exchange step wherein make-up CuSO_4 solution from the reactor is brought to scrubber temperature ($\sim 175^\circ\text{C}$).

Natural Covellite and Chalcocite

Prior investigations by others of the $\text{O}_2/\text{H}_2\text{SO}_4$ pressure leaching of natural copper sulfides had indicated appreciably slower kinetics for covellite (CuS) as compared with chalcocite (Cu_2S). An observed decrease in the specific rate (i.e., amount reacted in unit time per unit surface area) of covellite leaching with extent of reaction has been interpreted by some workers as retardation by a sulfur product layer. Chalcocite, which is typically much more rapidly leached than covellite, is generally thought to be oxidized in two stages, the products of the faster first-stage reaction being covellite and copper sulfate ($\text{Cu}_2\text{S} + 1/2 \text{O}_2 + \text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + \text{H}_2\text{O}$). In chalcocite and derivative structures, solid-state diffusion can be a factor in the mechanism of leaching, leading to changes in the composition of the sulfide phase as the reaction progresses. Examples are given in Figs. 1 and 2 of the pressure leaching behavior of natural CuS and Cu_2S (minus 100 mesh), from the work of I.H. Warren. The rates of copper dissolution increase with oxygen partial pressure and with temperature, as expected.

Fig. 1. Covellite, variation of rate of leaching of copper with temperature at "high" acidity.

Fig. 2. Chalcocite, variation of rate of leaching of copper with oxygen partial pressure.

Synthetic CuS

A pressure leach experiment was run with synthetic covellite (Fisher Reagent CuS) in order to test equipment, establish experimental procedures and provide a comparison case for the leaching of a scrubber solids. The reagent CuS was ground for 1.5 hr in a ball mill but not sieve-fractionated before adding to 1 l of 10 g/l Cu^{2+} , 62 g/l H_2SO_4 . Slurry density at the start was 6%, wt/vol. Following attainment of the operating temperature of 110°C, the nitrogen atmosphere was displaced by autogenous steam; oxygen was then admitted to a regulated partial pressure of 100 psi. At this oxygen pressure, total system pressure was 105 psig.

The synthetic covellite was attacked only slowly, in agreement with results of other workers, the rate of increase of copper concentration becoming exceedingly slow after about 2 hours (Fig. 3b). Several factors can contribute to a decline in the overall leach rate with extent of reaction. One of these factors, applicable especially when leaching powders, is the decrease in the solid/liquid interfacial area as the incompletely reacted particles become progressively diminished in size. In many instances of slurry leaching, the area effect can be taken into account by employing the fraction reacted, F , as the variable rather than, for example, amount of copper dissolved (cf. Figs. 1 and 2, where this is not done).

In particular, the function $1-(1-F)^{1/3}$ will correct for the shrinkage of the unreacted core. This expression is easily derived for a collection of uniform, isotropic particles of geometry such that their surface area varies as the 2/3 power of volume (e.g., spheres, cubes, tetrahedra, etc.) In practice, the use of $1-(1-F)^{1/3}$ appears also to serve the purpose for irregular, ground and sieved particles exhibiting a range of sizes as, for example, -325 +400 mesh. Moreover, the construction of a log-log plot of $1-(1-F)^{1/3}$ as a function of time into the reaction, as in Fig. 3, permits one to obtain the reaction order with respect to time

Fig. 3. Oxygen pressure leach kinetics of synthetic CuS (100 psi O_2 , 110°C). a) Expt. 1, b) Expt. 2.

without the necessity of presupposing a kinetic model and establishing whether the data best fit a t or $t^{1/2}$ dependence, etc. Our prior experience with oxidative leaching of sulfide concentrates was that such plots were usually linear, perhaps after an initial period of lesser slope, to high values of F . Also, the time exponent was seldom precisely 1.00 or 0.50, or whatever value is appropriate to a particular kinetic model.

The leach data of Fig. 3(a) conforms to the above behavior for the first approximately 1-1/2 hr, giving a time dependence of $t^{0.57}$. This fractional exponent is indicative of a reaction inhibition as postulated by others. Moreover, the curve deviates strongly from the initial slope, as shown, so that it is not feasible even to extrapolate to $F = 1 - (1-F)^{1/3} = 1$ in order to obtain an estimate of the time required for complete reaction. From a process design standpoint, the time required for a specified percent reaction, e.g., 95%, is a more significant quantity than initial rate constant.

For a second preliminary experiment, it was of interest to compare synthetic covellite that had been chemically altered (i.e., moved in composition toward chalcocite), thereby becoming closer in nature to the scrubber solids. For the purpose, some covellite powder that had been subjected to the prolonged action of hot CuSO_4 solution during preliminary corrosion tests (First Annual Report and December 1975 Interim Report) was employed. This partially altered copper sulfide did indeed react more rapidly initially (Fig. 3(b)), but the specific rate again fell off drastically. However, the decline in specific rate commenced at a much higher value of $1 - (1-F)^{1/3}$ than before. The initial time dependence was $t^{0.64}$, which may be the same, within experimental and computational error, as that for the unaltered CuS . It appears likely that the alteration previously experienced by this sample of synthetic covellite had been confined to a rim, consistent with petrographic evidence, leaving a leach-refractory core of substantially unaltered covellite.

Scrubber Solids

A total of 14 pressure leach experiments was carried out on scrubber solids, including samples from the December, 1976 field test at The Geysers. The precipitates all had compositions indicative of considerable enrichment with respect to copper content (Table II). The measured range of composition is $\text{Cu}_{1.3}\text{S}$ to $\text{Cu}_{1.9}\text{S}$. The indicated discrepancies between % Cu + % S (by analysis) and 100% (pure Cu_{1+x}S) were the result of unintentional oxidation during preparation for weighing. A closer approach to the true composition is afforded by calculation based on % Cu + % S = 100. For example, analyses of appreciably oxidized samples of washed and dried solids from the long scrubber run at The Geysers gave:

55.0% Cu, 15.7% S, total 70.7%, $\therefore$ 77.8% Cu

52.0% Cu, 14.9% S, total 66.9%, $\therefore$ 77.7% Cu

These results may be compared with analyses of less extensively oxidized samples from the same source: analyzed Cu+S = 92.2%, 92.7% - see Expts. 17, 18 in Table II, where the solids composition is calculated as 77.7%, 77.0% Cu, respectively.

Parameters which were varied include oxygen partial pressure (from 16 psi in air pressure leaching to 100 psi in oxygen pressure leaching), temperature (96 to 144°C), initial H_2SO_4 concentration (10 to 70 g/l) and $(\text{NH}_4)_2\text{SO}_4$ concentration (0 to 220 g/l). At the highest $(\text{NH}_4)_2\text{SO}_4$ concentration employed (Expt. 8), a large amount of $(\text{NH}_4)_2\text{SO}_4$ crystallized out during cooling of the pregnant leach solution to room temperature, in addition to the basic copper sulfate which had formed at reaction temperature. Consequently, quantitative results were not obtained, and Expt. 8 is not analyzed further in this report. In subsequent experiments, the $(\text{NH}_4)_2\text{SO}_4$ concentration did not exceed 120 g/l, well within the room temperature solubility of this substance at the $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ concentrations encountered. Details of solution compositions are given in Table III.

Table II
Compositions of Scrubber Solids

<u>Solids from</u> <u>Runs No.</u>	<u>Used in</u> <u>Leach Expts.</u>	<u>% Cu by</u> <u>Analysis</u>	<u>% S by</u> <u>Analysis</u>	<u>Cu + S</u> <u>total %</u>	<u>% Cu Based</u> <u>on 100%</u>	<u>Formula</u> <u>Cu_{1+x}S</u>
CuS	-				66.46	1.00
Cu ₂ S	-				79.85	2.00
701	3	77.3	20.0	97.3	79.4	1.94
629	4,7	73.0	23.0	96.0	76.0	1.60
722	5,6	69.4	26.1	95.5	72.7	1.34
629	8	61.6	21.1	82.7	74.5	1.47
913/917	9	66.0	19.9	85.9	76.8	1.67
930	10	73.8	21.1	94.9	77.8	1.77
1014	11,12	64.5	25.6	90.1	71.6	1.27
1026	13	66.8	23.8	90.6	73.7	1.41
1215	15	77.6	20.7	98.3	78.9	1.89
Field Slurry		74.0*	19.8	93.8	78.9	
1214/1215	17,18	71.6*	20.6	92.2	77.7	1.72
Composite		71.4*	21.3	92.7	77.0	

*Atomic absorption spectroscopy.

Table III
Solution Compositions

Experiment No. 3

Conditions: 94 psi O₂, 115°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	<u>M</u>	g/l	<u>M</u>	g/l	<u>M</u>
Cu ²⁺	5.1	0.080	7.35	0.116	51.0	0.803
H ₂ SO ₄	71.1	0.726	61.3	0.625	33.1	0.337
(NH ₄) ₂ SO ₄	-	-	-	-	-	-
Total SO ₄						
Analysis	-	-	74.5	0.775	109.5	1.14
Calculated	77.4	0.806	71.2	0.741	109.5	1.14
pH	0.24				0.79	
Density, g/ml	1.06					

Experiment No. 4

Conditions: 94 psi O₂, 115°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	<u>M</u>	g/l	<u>M</u>	g/l	<u>M</u>
Cu ²⁺	1.89	0.030	2.82	0.0444	18.0	0.283
H ₂ SO ₄	-	-	8.55	0.0872	0.922	0.0094
(NH ₄) ₂ SO ₄	-	-	5.42	0.041	5.02	0.038
Total SO ₄						
Analysis	-	-	16.3	0.170	29.8	0.310
Calculated	-	-	16.6	0.173	31.7	0.330
pH	1.42				2.46	
Density, g/ml	1.02					

Table III (continued)

Experiment No. 5

Conditions: 20 psi/100 psi O₂, 108°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	4.98	0.078	15.3	0.240	33.4	0.525
H ₂ SO ₄	70.3	0.717	47.9	0.488	38.0	0.387
(NH ₄) ₂ SO ₄	-	-	-	-	-	-
Total SO ₄						
Analysis	-	-	74.8	0.778	103.6	1.078
Calculated	76.37	0.795	69.9	0.728	87.7	0.912
pH	0.40				0.81	
Density, g/ml	1.05					

Experiment No. 6

Conditions: 25 psi O₂, 130°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	5.03	0.079	21.0	0.331	43.9	0.691
H ₂ SO ₄	70.0	0.714	44.5	0.454	36.0	0.367
(NH ₄) ₂ SO ₄	-	-	-	-	-	-
Total SO ₄						
Analysis	-	-	74.5	0.775	102.3	1.065
Calculated	76.2	0.793	73.3	0.763	80.4	0.836
pH	0.42				0.72	
Density, g/ml	1.05					

Table III (continued)

Experiment No. 7

Conditions: 31 psi O₂, 135°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	0.8134	0.0128	33.1	0.520
H ₂ SO ₄	28.2	0.288	25.0	0.255	4.66	0.0475
(NH ₄) ₂ SO ₄	-	-	-	-	-	-
Total SO ₄						
Analysis	27.9	0.290	24.5	0.255	52.8	0.55
Calculated	27.6	0.288	25.7	0.268	54.5	0.568
pH			0.52		1.64	
Density, g/ml	1.02					

Experiment No. 9

Conditions: 30 psi O₂, 130°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	2.54	0.040	41.3	0.65
H ₂ SO ₄	37.9	0.386	28.1	0.287	5.39	0.055
(NH ₄) ₂ SO ₄	119.0	0.90	95.8	0.725	95.8	0.725
Total SO ₄						
Analysis	108.1	1.125	88.9	0.925	127.8	1.330
Calculated	123.6	1.286	101.0	1.052	137.0	1.43
pH	0.90				1.96	
Density, g/ml	1.07					

Table III (continued)

Experiment No. 10

Conditions: 75 psi O₂, 96°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	0.77	0.012	40.0	0.630
H ₂ SO ₄	24.3	0.248	25.3	0.258	-	-
(NH ₄) ₂ SO ₄	102.4	0.775	83.9	0.635	80.6	0.610
Total SO ₄						
Analysis	94.6	0.985	84.3	0.877	115.7	1.204
Calculated	98.2	1.023	86.9	0.905	119.1	1.240
pH	1.15				3.53	
Density, g/ml	1.06					

Experiment No. 11

Conditions: 76 psi O₂, 144°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	0.66	0.0104	41.73	0.657
H ₂ SO ₄	33.5	0.342	31.1	0.317	4.66	0.0475
(NH ₄) ₂ SO ₄	116.9	0.885	112.3	0.850	116.9	0.885
Total SO ₄						
Analysis	103.2	1.075	99.4	1.035	131.1	1.365
Calculated	117.8	1.227	113.1	1.178	152.7	1.589
pH	0.96				1.87	
Density, g/ml	1.07					

Table III (continued)

Experiment No. 12

Conditions: 65 psi O₂, 116°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	2.09	0.0329	45.9	0.722
H ₂ SO ₄	34.1	0.348	28.7	0.293	2.68	0.0273
(NH ₄) ₂ SO ₄	92.5	0.70	89.2	0.675	92.5	0.700
Total SO ₄						
Analysis	85.8	0.894	83.2	0.866	121.4	1.264
Calculated	100.6	1.048	96.7	1.006	139.2	1.449
pH	0.86				2.0	
Density, g/ml	1.06					

Experiment No. 13

Conditions: 50 psi O₂, 135°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	1.87	0.029	40.8	0.642
H ₂ SO ₄	38.5	0.393	36.0	0.368	12.0	0.122
(NH ₄) ₂ SO ₄	116.9	0.885	116.9	0.885	116.9	0.885
Total SO ₄						
Analysis	109.1	1.135	112.1	1.167	132.1	1.375
Calculated	122.7	1.278	123.2	1.282	158.5	1.649
pH	0.90				1.42	
Density, g/ml	1.07					

Table III (continued)

Experiment No. 15

Conditions: 100 psi O₂, 140°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	Nil	Nil	0.70	0.011	53.8	0.847
H ₂ SO ₄	39.2	0.399	36.8	0.376	2.21	0.023
(NH ₄) ₂ SO ₄	100.4	0.760	100.4	0.760	100.4	0.760
Total SO ₄						
Analysis	104.5	1.088	104.0	1.083	150.1	1.563
Calculated	111.4	1.159	110.1	1.147	156.5	1.629
pH	0.89				2.17	
Density, g/ml	1.06					

Experiment No. 17

Conditions: 16 psi O₂, 135°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	M	g/l	M	g/l	M
Cu ²⁺	3.44	0.0541	6.11	0.096	51.6	0.812
H ₂ SO ₄	39.0	0.398	36.2	0.369	12.44	0.127
(NH ₄) ₂ SO ₄	36.3	0.275	37.6	0.285	42.9	0.325
Total SO ₄						
Analysis	67.7	0.704	68.7	0.715	118.4	1.233
Calculated	69.8	0.727	72.1	0.750	121.5	1.264
pH	0.62				1.20	
Density, g/ml	1.04					

Table III (continued)

Experiment No. 18

Conditions: 19 psi O_2 , 125°C

	Solution Compositions					
	Initial (as made up)		After Heat-Up, t = 0		Final (cooled solution)	
	g/l	<u>M</u>	g/l	<u>M</u>	g/l	<u>M</u>
Cu^{2+}	3.42	0.054	4.74	0.075	52.6	0.828
H_2SO_4	38.9	0.396	35.2	0.359	13.2	0.134
$(NH_4)_2SO_4$	79.2	0.600	77.9	0.590	85.8	0.650
Total SO_4						
Analysis	93.2	0.970	91.5	0.952	140.2	1.460
Calculated	100.9	0.050	98.3	1.023	154.8	1.612
pH	0.80				1.33	
Density, g/ml	1.05					

Included are a) the initial solution, i.e., as made up and before adding the solids (as dry powder, thick slurry, or filter cake), b) the solution in contact with the solids in the pressure reactor after bringing to temperature and before introducing oxygen ($t = 0$), and c) the final solution in the glass liner after cooling the autoclave to room temperature.

In general, the scrubber solids were leached relatively rapidly, their reaction kinetics resembling that of chalcocite more closely than of covellite. A distinctive difference between these copper sulfide precipitates and mineral copper sulfides lies in the absence of elemental sulfur among the products of leaching of the former. Consequently, under conditions which were controlled to prevent formation of basic copper sulfate, the scrubber solids could be pressure leached essentially quantitatively, leaving no significant residue of any kind.

Representative linear plots of the variation of concentration with time are shown in Fig. 4 (oxygen pressure leaching of field scrubber solids) and Fig. 5 (air pressure leaching of field scrubber solids). Unlike in oxygen pressure leaching, a flow of gas out of the autoclave has to be maintained during air pressure leaching in order to offset the depletion of oxygen gas by the reaction. Consequently, upon completion of the leaching, the copper concentration continued to rise, but more slowly, as additional water was removed from the system. The large heat of the oxidation reaction is manifest in the initial temperature rise (Fig. 4) of the reacting slurry. A lesser temperature excursion occurred during air pressure leaching (Fig. 5), consistent with the lower rate of generation of reaction heat and with cooling of the slurry by returning condensate.

Representative log-log plots of extent of reaction versus time are shown in Figs. 6-9. Included is an instance (Fig. 6) of decrease in specific rate (slope) during the course of the leaching. This could come about, for example, if the particle size distribution included a substantial fraction of much finer than median size particles, which would be consumed in the first stage of leaching. See Table III for reaction conditions pertaining to Figs. 6-9.

Fig. 4. Oxygen pressure leaching of field test solids (Expt. 15).
Conditions: 100 g/l $(NH_4)_2SO_4$, 40 g/l H_2SO_4 , 100 psi O_2 .

Fig. 5. Air pressure leaching of field test solids (Expt. 18).
 Conditions: 80 g/l $(\text{NH}_4)_2\text{SO}_4$, 35 g/l H_2SO_4 , 140 psi air.

Fig. 6. Oxygen pressure leaching of scrubber solids (Expt. 3).

Fig. 7. Oxygen pressure leaching of scrubber solids (Expt. 13).

Fig. 8. Oxygen pressure leaching of scrubber solids (Expt. 5).

Fig. 9. Oxygen pressure leaching of scrubber solids (Expt. 9).

Figure 7 shows an example of well-behaved (in a kinetic sense) solids yielding a sensibly constant slope of $\log [1-(1-F)^{1/3}]$ versus $\log t$. These data can be reliably extrapolated to give 245 mins as the time for complete reaction and interpolated to yield 205 mins as the time required for 99% reaction, 170 mins for 95% reaction, etc. for the given conditions (50 psi O_2 , 135°C). On the basis that the system conforms to the assumptions used in deriving the expression $1-(1-F)^{1/3}$, the specific rate increases somewhat more rapidly than t , namely as the 1.24 power. A time exponent greater than unity implies an acceleration of the reaction.

In one leach-regeneration test, the oxygen pressure was intentionally changed midway in the reaction (Fig. 8). Although the specific rate increased as shown, its dependence on PO_2 can not be obtained with any certainty from this experiment alone. For one thing, comparable increases in apparent specific rate occurred in 4 out of 12 runs employing scrubber solids where oxygen partial pressure was not changed during the run. This latter behavior is illustrated in Fig. 9 and could be the result of attrition, or "ungluing", of the dispersed solids, which are known to be aggregates of extremely fine particles.

Comparison of Figs. 6, 7 and 9 reveals a rough correlation between leach rate, as measured inversely by the time required for complete reaction, and the oxygen partial pressure. A statistically more reliable estimation of the dependence of leach rate on oxygen pressure as well as other experimental parameters was obtained by comprehensive analyses of the data, for which purpose details of reaction conditions and results are collected in Table IV.

ANALYSIS OF DATA

Material Balance

Copper balance for the system, including initial solids and solutions, liquid samples, and solid residues, if any, could generally be closed satisfactorily. Sulfate balance was sometimes less satisfactory

Table IV

Summary of Experimental Parameters and Results in the Pressure Leach-
Regeneration of Scrubber Solids

Experiment No.	3	4	5	6	7	9	10	11	12	13	15	17	18
Source of Solids	Run 701	Run 824	Run 722	Run 722	Run 824	Runs 913, 917	Run 930	Run 1014	Run 1014	Run 1026	Field Run 1215	Field Run	Field Run
Initial Treatment	Unwashed	Unwashed	Unwashed	Unwashed	Water Washed	Water Washed	Acid Washed	Unwashed	Unwashed	Unwashed	Unwashed	Unwashed	Unwashed
% Cu	79.4	76.0	72.7	72.7	76.0	76.8	77.8	71.6	71.6	73.7	78.9	77.7	77.7
Formula	Cu _{1.94} S	Cu _{1.60} S	Cu _{1.34} S	Cu _{1.34} S	Cu _{1.60} S	Cu _{1.67} S	Cu _{1.77} S	Cu _{1.27} S	Cu _{1.27} S	Cu _{1.41} S	Cu _{1.89} S	Cu _{1.72} S	Cu _{1.72} S
Slurry Density, g/ml	0.06	0.03	0.06	0.07	0.04	0.05	0.06	0.07	0.07	0.08	0.06	0.05	0.05
Oxygen Partial Pressure, psi	94	94	20 100	25	31	30	75	76	65	50	100	16	19
Total Pressure, psig	104	104	25 105	50	62	55	75	120	75	80	138	171	171
Temperature, °C	115	115	108	130	135	130	96	164	116	135	140	125	135
Maximum Temperature, °C	124	123	114	139	140	132	100	151	120	147	162	144	142
Time to Maximum Temperature, mins.	40	18	17	20	8	5	65	30	20	20	30	20	15
-Δ[H ₂ SO ₄], mol/l	0.288	0.078	0.101	0.087	0.208	0.232	0.258	0.270	0.265	0.245	0.353	0.242	0.224
Δ[Cu ²⁺], mol/l	0.687	0.239	0.285	0.360	0.507	0.610	0.617	0.646	0.689	0.613	0.836	0.716	0.753
Ratio, -Δ[H ₂ SO ₄]/Δ[Cu ²⁺]	0.419	0.326	0.354	0.242	0.410	0.380	0.418	0.418	0.385	0.400	0.422	0.338	0.297
Calculated Formula	Cu _{1.72} S	Cu _{1.48} S	Cu _{1.55} S	Cu _{1.32} S	Cu _{1.69} S	Cu _{1.61} S	Cu _{1.72} S	Cu _{1.72} S	Cu _{1.65} S	Cu _{1.67} S	Cu _{1.73} S	Cu _{1.51} S	Cu _{1.62} S
Copper Solubilized, % of Total	99	80	85	98	99	99	95	93	96	99	98	100	100
Copper in Basic Sulfate, % of Total	-	19	-	-	-	-	4	6	4	-	2	-	-
Copper Unreacted, % of Total	1	1	15	2	1	1	1	1	-	1	-	-	-
Reaction Order (n in Time ⁿ)	0.44	0.35	0.35/ 0.78	0.75	1.20	3.10	0.87	1.14	1.49	1.24	0.50	1.27	1.33
Time for Complete Reaction, mins.	235	290	575	500	245	280	230	90	190	245	150	460	395
Time for 99% Reaction, mins.	130	140	420	360	200	260	170	70	160	205	90	330	330
Time for 90% Reaction, mins.	60	45	250	215	145	230	110	50	125	150	40	280	245

owing to unavoidable analytical inaccuracies. In particular, the accuracy of the determination of $(\text{NH}_4)_2\text{SO}_4$ concentration was fixed by the accuracy of the total NH_3 analysis (gas-membrane electrode). Accurate analysis for sulfate was sometimes difficult because of strong dilution of the test solution resulting from the large volume of wash water required in the copper removal step (cation exchange). In optimum cases, total sulfate calculated as $[\text{Cu}^{2+}] + 1/2 [\text{NH}_3]_{\text{total}} + [\text{H}_2\text{SO}_4]_{\text{free}}$, all as mol/l, agrees well with the direct analytical value (Table III). A check of overall stoichiometry is afforded by comparing sulfuric acid consumed with copper solubilized in the leach reaction. Thus, complete reaction of the copper sulfide solids gives $x/(1+x)$, mol/mol, for the ratio of H_2SO_4 consumed to CuSO_4 produced. These quantities can be approximated by the corresponding changes in concentration between starting ($t = 0$) and final solutions. By use of the latter quantities, i.e., $-\Delta[\text{H}_2\text{SO}_4]$ and $\Delta[\text{Cu}^{2+}]$, reasonable checks of the initial solids composition were generally obtained (Table IV).

Time Dependence

A linear portion of a log-log plot of $G \equiv 1-(1-F)^{1/3}$ versus time ($= t$) has as its slope the time dependence of the specific rate: $\log G = n \log t + b = \log t^n + b$. Curvature indicates that the exponent n is changing as the reaction progresses. When the times for complete reaction, t_{100} , are plotted (Fig. 10) against the slopes n (Table IV, bottom) of the final linear portions of Figs. 6-9 and corresponding graphs for the remaining experiments, there appears a rough trend toward an increase in n with increase in rate (i.e., decrease in t_{100}). Since under the test conditions the rates were most sensitive to oxygen partial pressure, the implication is that the reaction is accelerated by oxygen more than would be indicated by mass transport considerations alone.

If the foregoing implication has validity, it could be the result of the influence of an initial activation of the solids resulting from the release of reaction heat, the rate of release being, of course, determined

Fig. 10. Times for complete reaction and reaction orders in pressure leaching of scrubber solids (all Expts.)

by the reaction rate. On the other hand, the mean exponent of t is 1.12 (13 runs), with an average deviation of 0.45 (40%). If the anomalously high time dependence exhibited in Expt. 9 ($t^{3.10}$, Fig. 9) is eliminated, on the reasonable grounds that the deviation of 3.10 from the mean is 4.4 times the average deviation, the new exponent is 0.95 ± 0.33 (35%). In the absence of contradictory indication from more sophisticated experiments, it is probably reasonable to consider that under fixed conditions of temperature and oxygen mass transport, the rate of pressure leaching of sulfide scrubber solids relative to their accessible surface area is sensibly constant with time (i.e., $\sim t^{1.0}$).

Oxygen Pressure Dependence

When the reciprocal of the time for complete reaction, t_{100} , is taken as a measure of reaction rate, and its logarithm is plotted against the logarithm of oxygen partial pressure, the relationship shown in Fig. 11 is obtained. Appreciable scatter of the points notwithstanding, the rate clearly increases with the oxygen partial pressure, in spite of variations of other experimental parameters within the stated limits. For the two air pressure leach experiments, Nos. 17 and 18, the oxygen partial pressure was calculated from the total air ($N_2 + O_2$) pressure, 140 psi, the gas flowthrough rates and the rates of consumption of oxygen by the leach reaction.

The two lines drawn in Fig. 11 have a slope of -1, presupposing a linear dependence of rate, or t_{100}^{-1} , on P_{O_2} . The majority of data points falls within the band shown. There appears to be no correlation between the magnitude of deviation of a given point from either of the two lines and the chemical composition of the starting material. When the attempt was made to correct the rates for differences in steady temperature, no significant improvement was achieved (Fig. 12).

Of those parameters that have been identified with certainty in this work, over the given ranges of their variations, oxygen partial

Fig. 11. Correlation between time for complete reaction (t_{100}) and oxygen partial pressure.

Fig. 12. Pressure leach rates corrected for temperature variation.
 Reciprocal leach rate (corrected) = $10^{-4} t_{100} / \exp(-1500/T)$.

pressure is the determining parameter of leach rate. Further, the time for complete reaction (or 99%, 95%, etc.) varies at least approximately as the first power of the oxygen partial pressure. This behavior is consistent with rate control by the supply of dissolved oxygen to the solid/solution interface, i.e., mass transport control. One practical implication of this interpretation is that the effectiveness of dispersal of oxygen gas into the agitated slurry is a critical design feature of the pressure reactor. As anticipated for oxygen pressure leach reactions of sulfides, the reaction and, hence, reactor size can be reduced by keeping the mean diffusion distance for dissolved O_2 between dispersed oxygen (or air) bubble and suspended solid particle as short as possible.

Temperature Dependence

There was no perceptible correlation between reaction rate, uncorrected for changes in experimental parameters, and the steady temperature (i.e., following any initial surge due to reaction heat). This negative result merely confirms the relatively low sensitivity of reaction rate to temperature and the circumstance that the range of temperature variation was not great: in terms of absolute temperature, T , the range of $10^3/T$ was only 2.4-2.7. It is clear, however, that the activation energy (ΔE^* in the expression, $\text{rate} = A \exp(-\Delta E^*/RT)$, where R is the universal gas constant) is not large, as would be the case for kinetic control by chemical rate processes.

A trend with respect to temperature dependence was investigated by taking the ratio of leach rate to oxygen partial pressure - actually, the reciprocal quantity $(t_{100} P_{O_2})^{-1}$ was taken as the measure of the relative or "normalized" rate. On an activation energy plot (Fig. 13), the scatter of the experimental points is disappointing. The probable range of ΔE^* appears to be about 5-9 kcal/mol, as illustrated by the slopes of the lines drawn in the figure. By assuming a mid-range value of ΔE^* (6864 cal/mol, slope = 1500°K), and adjusting the specific rates for

Fig. 13. Relative leach rates, $(t_{100} P_{O_2})^{-1}$, versus reciprocal absolute temperature.

temperature variation, the results shown in the previous figure (Fig. 12) were obtained. If anything, the rates were overcorrected by this procedure, so that the true activation energy is probably not greater than 7 kcal/mole. This value is somewhat higher than is typical for pure mass transport control but definitely less than for typical instances for chemical reaction control.

Other Factors

Considerable variability of the starting material in these experiments is a virtual certainty, given the range of conditions of their formation as precipitates and the duration and intensity of subsequent chemical and mechanical influences on their properties. The size distribution of the ultimate particles and the strength of their cohesion into aggregates can be expected to be strongly dependent upon scrubber conditions. The size distribution of the aggregates and of the agglomerates loosely formed from aggregates will also be sensitive to their subsequent history. This means that the specific area (i.e., per unit mass of solid phase) of accessible surface can vary over a wide range for the starting material and, moreover, can change in different ways with time of leaching.

Because the leach reaction under the range of conditions tested appears to proceed as rapidly as oxygen can be supplied to the interface, the role of solids chemistry is not directly ascertainable from their compositions. However, in order for the rate to be limited by the oxygen supply, the precipitates must possess an appreciable inherent chemical reactivity. That the precipitates are unusual in their reactivity is evidenced by the nonformation of elemental sulfur, even at low leach temperatures and acidities.

Evidently, the deviation from a stoichiometric composition and the resultant highly defective crystal structure, alone or in combination with an usually high specific surface area, result in complete oxidation of the sulfide sulfur to sulfate. Changes in the composition of the solid during reaction, as is known to occur with chalcocite (Cu_2S), are not only

possible, but probable. There is evidence that even during oxidation on standing at room temperature, the formation of copper sulfate and basic sulfate is attended by conversion of some solid to covellite, CuS .

The results of attempts to be specific with respect to external influences, other than temperature and oxygen supply, on the leach rates have not been convincing. The conditions of Expt. 4, whose data depart strongly from the plotted composite curves, were unusual. The leach solution in this case was the scrubber solution with which the precipitate has been in contact. No adjustment of composition was made, and the relatively low free acid concentration (room temperature pH 1.4 at start, 2.5 at end) appears to be responsible for stifling the reaction. About 19% of the leached copper reported to a precipitate of basic copper sulfate.

Experiment 10 similarly deviates from average kinetic behavior. Its synthetic leach solution was made up to contain 100 g/l $(\text{NH}_4)_2\text{SO}_4$. The consequently low free acid concentration at reaction temperature evidently retarded the leach rate and led to the formation of basic copper sulfate containing, upon cooling to room temperature, about 4% of the copper. On the other hand, Expt. 3, for which the data cluster with those of Expts. 4 and 10, had no added $(\text{NH}_4)_2\text{SO}_4$; its pH was and remained low during leaching; and no basic copper sulfate was observed to form.

Variability of results is too great to permit quantitative physico-chemical interpretations. However, this was not the purpose of the leach-regeneration studies. The program objectives have been met of establishing the feasibility of leaching actual scrubber solids in an acceptably short time under mild leaching conditions and of determining the overall chemistry of the reaction.

Engineering Considerations

Minimum oxygen requirements in the pressure leaching of copper sulfide precipitate is determined by the composition of the sulfide and

the overall chemistry of the reaction. It has been established in this work that, under conditions of formation in a geothermal stream scrubber and of subsequent regeneration to CuSO_4 by pressure leaching, the sulfide in the scrubber becomes oxidized essentially completely to sulfate:

This being the case, the oxygen requirement in pressure leaching is set by the composition of the copper sulfide. According to the above equation, and relative to the amount of copper returned to solution, minimum oxygen consumption is: $\text{O}_2/\text{Cu} = (4+x)/2(1+x)$ mol/mol, or approximately half (32.00/63.54) this quantity in terms of weight. This relationship is shown in Fig. 14 for the full range of possible precipitate composition, from CuS to Cu_2S .

The corresponding oxygen consumption relative to sulfide is also shown in Fig. 14. It needs to be kept in mind in using this information that the oxygen requirement in leach regeneration relative to the total H_2S scrubbed from the steam is less than that shown because, in forming Cu_{1+x}S from CuSO_4 and H_2S , a portion of the hydrogen sulfide is oxidized and steam-distilled as elemental sulfur out of the scrubber or reports as sulfate to the recirculating scrub solution.

Maximum oxygen consumption rates during the leach-regeneration tests were estimated from the steepest linear portions of plots of solution copper concentration versus time (e.g., Figs. 4 and 5). Thus, for $[\text{Cu}^{2+}]$ in g/l,

$$\frac{1}{63.54} \frac{d[\text{Cu}^{2+}]}{dt} \frac{4+x}{2(1+x)} \frac{1}{P_{\text{O}_2}} = \text{mol O}_2 \text{ consumed/liter/hr/atm O}_2$$

Calculated oxygen consumptions are shown in Table V. The maximum is about 0.25 mol O_2 /l/hr/atm, or about 8 g O_2 /l/hr/atm, while the average is about 0.18 mol/l/hr/atm. This is not a large value for a laboratory pressure reactor. For example, I.H. Warren in the work described above

Fig. 14. Oxygen requirements in the leach-regeneration of copper sulfide scrubber solids.

Table V

Measured Oxygen Consumption Rates in Pressure Leaching of
Copper Sulfide Scrubber Solids

<u>Expt. No.</u>	<u>x in</u> <u>Cu_{1+x}S</u>	<u>O₂/Cu</u> <u>mol/mol</u>	<u>P_{O₂}</u> <u>atm</u>	<u>Rate, Cu</u> <u>g/l/hr</u>	<u>Rate, O₂</u> <u>mol/l/hr/atm</u>
3	0.94	1.27	6.40	71.4	0.22
4	0.60	1.44	6.40	73.1	0.2
5	0.34	1.62	1.36	5.4	0.10
			6.80	5.9	0.022
6	0.34	1.62	1.70	6.5	0.098
7	0.60	1.44	2.11	19.2	0.21
9	0.67	1.40	2.04	18.8	0.20
10	0.77	1.35	5.10	35.0	0.15
11	0.27	1.68	5.17	50.4	0.26
12	0.27	1.68	4.42	22.5	0.14
13	0.41	1.56	3.40	16.9	0.12
15	0.89	1.30	6.80	84.4	0.25
17	0.72	1.36	1.07	8.0	0.16
18	0.72	1.36	1.27	10.5	0.18

obtained an oxygen absorption coefficient, or "sulfite number", of 40 g/l/hr/atm indicating that gas phase mass transfer resistance was not controlling in these tests.

The design of a leach reactor system for the 100,000 lb/hr field test facility must comprehend the requirements to:

- Regenerate the solids produced in the scrubber in a relatively short period of time, nominally within one shift.
- Provide capacity to hold the volume of solution associated with the mass of solids to be leached.
- Provide for control of pressure and temperature during the course of the reaction.
- Provide for sufficient agitation so that the mass transfer of either air or oxygen will not generally limit the reaction rate.

The overall system material balance, determined by the requirements to purge net ammonium sulfate produced and control acid concentrations in both the scrubber and the leach reactor, indicates that the volume of purge slurry fed to regeneration will be between 6700 and 8200 gal/day. A reactor has been specified with a working volume of 3500 gallons, which will require either two or three batches to be treated daily, depending on the purge rate.

A gas dispersion agitator has been specified which will achieve a mass transfer rate of 0.17 g-mol O_2 /l/hr/atm, the average of the maximum rates observed in the lab tests. Since the maximum oxygen requirement is approximately 1050 lb/day, the minimum reaction time required would be 50 min at a nominal oxygen pressure of 50 psi, if gas-phase mass transfer controlled. Since average reaction rates over the course of the run will be lower, it is anticipated that approximately 2-1/2 hr would be required to obtain 95% regeneration at nominal conditions of 230°F, 50 psi oxygen pressure, 3-1/4 hr for 99% regeneration, and 4 hrs for complete reaction.

A reactor feed pump for transferring slurry from the holding tank to the reactor has been sized to permit this operation to take place in

70-80 minutes. Transfer of regenerated solution from the reactor, by autogenous or air pressure, is limited by the ability of the product cooler to reduce the temperature of the copper sulfate solution to the desired level. This cooler has been sized to permit the reactor contents to be drained in less than 3-1/4 to 4 hrs, so that the total regeneration cycle can be carried out in 7-9 hrs under nominal conditions. All components have been designed, and nominal process conditions specified, to permit the cycle to be shortened if required.

While the exothermic leach reaction would raise an adiabatic reaction temperature by 80-100°F, the use of steam might also be required to heat the reactor to its proper initial reactor temperature. Thus, automatic temperature control will be provided for cooling the reactor once the reaction is initiated, and initial heating will be carried out by direct sparging of cleaned steam into the reactor.

When leaching with air, the required flow rate and, therefore, percent excess oxygen will be obtained by controlling the operation of the air compressor. The desired total pressure and, therefore, oxygen partial pressure will be set by a pressure control on the leach reactor vent. This pressure control would also control the flow rate of oxygen, providing make-up on demand to maintain the desired total (and oxygen partial) pressure.

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EIC Corporation
55 Chapel Street
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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730,*000

Final Report on Task A.3

✓ Filter Leaf Test Studies

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SUMMARY

Copper sulfide solids produced by removing low concentrations of hydrogen sulfide from steam by scrubbing with copper sulfate, while composed ultimately of particles of the order of 1 micron, flocculate naturally and settle and filter rapidly. There are no apparent differences in macroscopic properties between material produced in laboratory tests scrubbing simulated geothermal steams and solids produced during field tests on actual geothermal steams.

The solids content of filter cakes produced and pulp densities from settled slurries tend to be rather low, 25 and 15% solids, respectively, due to the floccy nature of the solids produced.

Tight, monofilament filter cloths show excessive tendencies to blind while multifilament cloths require periodic back washing. Spun fabrics show little tendency to blind and give adequate cake release.

Cake specific resistances are low, being approximately equal to media resistances for a 1/2" 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 a batch filter's size would be controlled by solids retention capacity.

Settling rates for purged slurries are rapid, of the order of 1 ft/min, and compressions times are less than one minute.

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 solids settling rates.

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.

BACKGROUND AND PURPOSE

It had been observed in the earliest testing on the small laboratory scrubber that the solids produced when scrubbing simulated geothermal steams with copper sulfate solution showed remarkable tendencies to flocculate naturally and settle rapidly. These solids filtered very rapidly in Buchner funnels and high filtrate clarities were always obtained. However, while liquid solid separation was not perceived to be a critical problem in an integrated process, it was felt that additional data were required to rationally design the liquid solid separation device which would be utilized in the 100,00 lb/hr field test facility. While it was not intended that this operation would necessarily simulate the ultimate commercial technique, sufficient information had to be gathered to insure that the device chosen did not result in the imposition of intolerable operating difficulties during the field test where the emphasis would be on evaluation of scrubbing and regeneration.

In addition, of course, continued testing would give insights into the variability of the filtration behavior of solids produced under various scrubbing conditions and, particularly, the differences - if any - between solids produced from simulated steam scrubbing and solids produced from hydrogen sulfide removed from real geothermal steams. Since small continuous filters would require more or less constant attention during field testing, a preliminary evaluation of possible operating schedules suggested that use of a batch filter would be appropriate. Purged slurry would be accumulated on the second and third shifts and worked off in the batch filter once per day to supply a thickened cake for regeneration by leaching. Thus, a test outline was developed incorporating a schedule of experiments on a one tenth square foot filter leaf.

Subsequent testing indicated the desirability of investigating continuous decantation as an appropriate technique for the 100,000 lb/hr field test facility. Accordingly, a series of one liter cylinder settling and final dilution tests was run to obtain quantitative data on settling rates.

TEST APPARATUS AND PROCEDURES

The test apparatus used in the filter leaf studies, shown in Fig. 1, is based on the apparatus suggested in Dorr Oliver's "Determination of Filtration Characteristics of Any Given Slurry by a Laboratory Leaf Test". Various filter media, supplied by the National Filter Media Corp., were secured to a one tenth square foot test leaf and sealed, if required, with sealing putty. The filtrate pulled through the leaf was conducted to a two liter graduated vacuum flask through 1/2" heavy wall rubber vacuum tubing. A quick shut-off valve and vacuum gauge served to isolate the filter leaf and indicate filtration vacuum respectively. The required vacuum was provided by a small laboratory oil sealed vacuum pump protected with a one liter overflow flask. The solids produced in various scrubbing test were held in a 10 liter slurry bucket and spended with a small variable speed laboratory agitator.

After the new, clean cloth resistance had been determined by filtration tests on water, the medium to be tested was fitted to the test leaf, a vacuum established on the graduated flask and the leaf inserted in the slurry to obtain 2 liters of filtrate. Generally, the cloths were conditioned by a repeated cycle of collecting 10 liters of filtrate, discharging the filter cake, washing and/or back flushing the medium, and repeating the cycle a number of times. Data runs in which cake specific resistance was to be determined were not executed until it had been ascertained that the medium was adequately conditioned and did not show serious tendencies to blind.

All tests were run with a feed slurry at room temperature. Typically, filtrate was collected in two liter increments with the times required to obtain one and then two liters recorded for the given filtration vacuum, filter medium, and slurry being tested. The leaf was withdrawn from the slurry bucket immediately upon obtaining two liters of filtrate, the filtrate was removed and set aside, and the average cake thickness determined.

Fig. 1. Laboratory Set Up - One Tenth Sq. Ft. Leaf Test Program.

Typically, the vacuum was then reestablished at the desired level on the vacuum flask and the test leaf, with cake still adhering, was reinserted in the slurry bucket and the filtration experiment reinitiated immediately. The times were then recorded for the collection of the next two liter increment of filtrate and the procedure was repeated while cumulative volumes and cake thicknesses were recorded. When the cake reached the desired thickness, typically 1/2", it was removed, the filter washed if required, and a filtration rate measurement carried out on water to determine if the medium were blinding.

The filter cake was weighed wet, and a small sample was withdrawn, weighed wet, and dried to determine the cake moisture content.

The slurry settling tests were carried out in liter cylinders and the data analyzed according to the procedures suggested by Coe and Clevenger. Slurries were introduced to liter cylinders and agitated with plunger discs to obtain a uniform suspension. As the discs were withdrawn for the final time, the height of the pulp - clear liquid interface was recorded as a function of time. Typically, the experiments were replicated and the averages of 2-4 tests were reported. Agreement was usually quite good for readings obtained for times greater than 15 sec with considerable scatter in data at shorter times because of the very rapid settling rates involved. For final dilution tests, a rake was inserted in the cylinder and rotated by hand, at approximately 1 rpm, for one minute in each 15 minutes of the test cycle. The rake consisted of a triangular, 3 pronged element attached to an 1/8" diameter rod. At the conclusion of the final dilution tests, the slurry was filtered, dried, and weighed to determine the initial and final slurry solutions.

TEST RESULTS

The media resistances for some of the nonblinding new cloths tested are summarized in Table I. The test data show a relatively low cake resistance and little decrease in resistance as permeabilities increased beyond

Table I

Media Resistance for New Cloths Tested

Medium Style Material Yarn Type Permeability	222-003-00 Polypropylene Spun 1-3	220-005-00 Polypropylene Multifilament 5-8	224-040-00 Polypropylene Monofilament 5-8	222-029-06 Polypropylene Spun 60-70	224-013-20 Polypropylene Monofilament 180-220
$\delta Q/\delta V$, Sec/l					
@ 10" Hg Vac	43		27	25	24.5
@ 15" Hg Vac				20	20
@ 20" Hg Vac	28	20.5	18	17	17
Medium Resistance, Ft^{-1}					
@ 10" Hg Vac	0.43×10^{10}		0.27×10^{10}	0.25×10^{10}	0.25×10^{10}
@ 15" Hg Vac				0.30×10^{10}	0.30×10^{10}
@ 20" Hg Vac	0.56×10^{10}	0.41×10^{10}	0.36×10^{10}	0.34×10^{10}	0.34×10^{10}

5-8 CFM for monofilament cloth. As expected, the lower permeability media, and the multifilament media vis-a-vis monofilament media, showed higher resistances than more open cloths. The relatively sharp increase in medium resistance with filtration vacuum is likely an artifact of the experiment, probably representing an overestimation of the actual pressure drop at the filter. This would be due to the relatively high pressure drop in the vacuum tubing at the high filtration rates usually experienced in these tests.

The media resistances for two conditioned cloths are summarized in Table II. It may be seen that no significant increase in medium resistance, which would be indicative of blinding, occurred over the testing cycles for these cloths.

Filtration rate data on both slurries and water for these media are shown graphically in Figs. 2 and 3, in which a reciprocal filtration rate is plotted against the total volume of filtrate obtained. The water data reported for medium 220-005-00 were obtained after 46 liters of filtrate had passed through the cloth, but no wash cycle was provided after the last slurry filtration. The apparent increase in resistance demonstrates a slight but significant tendency towards blinding for this medium. Far more severe blinding tendencies were observed for monofilament cloths tested which had permeabilities of the order of 1 to 3 CFM. While the open monofilament cloths, with permeabilities approaching 200 CFM, do not show tendencies to blind, cake adherence was poor and, on occasion, poor filtrate clarity was obtained. No such problems were encountered with either multifilament or spun cloths, and these styles would be recommended for commercial applications.

Specific cake resistances calculated from the filtration data presented in Figs. 2 and 3 are summarized in Table III. In general, the data show a pronounced tendency to show higher filtration rates as the total volume of filtrate, and cake thickness, were increased which is contrary to expectations. From the measurements of increase of cake thickness for each

Table II

Media Resistance for Conditioned Cloths

Medium Style	220-005-00	222-029-06
Medium Resistance, $\text{Ft}^{-1} \times 10^{-10}$ New(1)	0.41	0.34
Following Passage of 4 l Filtrate(1)	0.35	
10 l		0.35
14 l	0.36	
18 l		0.35
24 l	0.36	
26 l		0.35
40 l	0.37	0.36
46 l	0.35	0.36

(1) At 20" Hg Vac, each cycle followed by 2 l wash.

Fig. 2. Filtration Rate Curve Medium 220-005-00

- + , $\times$, $\diamond$, ∇ water tests
- $\square$ Water after filtration, without wash
- $\circ$ Run 722 solids, 1/2" Cake
- $\diamond$ Run 722 solids, 5/8" Cake
- $\triangle$ Run 727 solids, 13/32" Cake

Fig. 3. Filtration Rate Curve Medium 222-029-06

x, +, O, Δ, ▽ Water Tests

□ Run 629 Solids, 9/32" Cake

Δ Run 701 Solids, 3/8" Cake

○ Run 824 Solids, 11/32" Cake

Table III

Calculated Specific Cake Resistances

Medium Style	220-005-00	220-005-00	220-005-00	222-029-06	222-029-06	222-029-06
Solids Run No. ⁽¹⁾	727	722	722	701	824	629
Final Cake Thickness, in.	13/32	5/8	1/2	3/8	11/32	9/32
Total Filtrate Vol., l	16	6	16	6	10	10
Initial Slope, Sec/l ²	7.3	5.1(6.1)	4.2(5.8)	8.1	2.6	1.7(4.9)
Cake Resistance ⁽²⁾ , Ft/lb $\times 10^{-10}$	.98	.68(.81)	.56(.78)	1.08	.35	.23(.65)

(1) Scrubbing run during which solids were produced.

(2) At 20" Hg Vac. Solution viscosity = 1.2 centipoise, solids concentration 0.5%.

increment of filtrate obtained however, it was observed that the apparent slurry density was decreasing during the course of the experiment, and, typically, uneven cake formation was noted. It was determined that this behavior was due to the intense agitation required to keep the slurry suspended during the filtration cycle. As the cake thickness built up, the fluid motion induced by the mixer in the slurry bucket tended to wash off the newly deposited cake. Attempts to mitigate this by reducing stirring speeds simply resulted in loss of suspension of the highly flocculated particles and preferential filtering of lower density slurries in any case.

The data on the initial and final slopes of the filtration curves were examined and compared with the initial and final slurry densities calculated from the relation between incremental cake thickness deposited and incremental volume of filtrate obtained and were found to be internally consistent. Therefore, to evaluate the data the initial slopes and initial slurry solid concentrations were utilized in calculating specific cake resistance. The numbers reported in parenthesis in the table reflect estimates of the initial slope of the filtration curves when the intercept at zero volume is not forced to pass through the cake free resistance point. While there is considerable variability in the calculated specific cake resistance, it appears to be more a function of the difficulties in conducting the filtration experiment than with any parameter of the test during which the solids were produced or for the age or previous history of the solids. The high variability of these results, the low cake solid contents obtained, and the floccy nature of the solid suggest that these cakes will be highly compressible and that the calculated specific resistances should not be extrapolated to conditions far different from those tested here.

The calculated and measured cake densities obtained during these filtration experiments are summarized in Table IV. The low cake solid contents are consistent with the floccy nature of the solids and, for most runs, the expected correlation between drying time and cake solids content

Table IV

Filter Cake Solids Contents and Densities

<u>Solids Run No.</u>	<u>Filter Type</u>	<u>Cake Thickness</u>	<u>Drying Time, min.</u>	<u>Cake % Solids⁽¹⁾</u>	<u>Calc. Cake Density⁽²⁾</u>	<u>Measured Cake Dens.⁽³⁾</u>	<u>Ratio Meas./Calc.</u>
701	Buch.		2	30.0	86.9		
722	Buch.		10	31.9	88.7	73.7	.83
722	Leaf	1/2"	2	27.3	84.4	74.1	.88
727	Buch.	5/8"	-	22.8	80.6	77.5	.96
727	Buch.	9/16"	2	26.5	83.7	66.0	.79
727	Buch.	1/2"	10	30.4	87.2	72.6	.83
727	Leaf	13/32"	-	22.3	80.2	69.7	.87
727	Leaf	5/16"	2	26.0	83.2	60.8	.73
824	Buch.	5/8"	10	22.0	79.9	57.1	.71
824	Leaf	11/32"	-	20.1	78.4	61.6	.79

(1) Measured after drying.

(2) From measured % solids and solid and solution densities.

(3) From cake thickness and total wet weight.

was obtained. The measured cake densities were always lower than the calculated ones, with the ratio averaging approximately 80%.

The calculated performance of a continuous filter handling the flow of slurry produced in scrubbing 100,000 lb/hr of geothermal steam is summarized in Table V. The two values of medium and specific cake resistances are the average and high range of values calculated respectively. The calculated submergence times for a rotary vacuum filter are so low for a 1/4" cake that it is unlikely that a suitable standard filter configuration could be obtained. However, it is problematical that a 1" cake could be built up in this type of equipment due to the levels of agitation which would be required to suspend solids. For a 1/2" cake, approximately half the resistance to filtration would still be due to the medium however. The calculated total area requirements are also quite low, even for the highest resistances calculated, and it is likely that acceptable standard filter configurations could be purchased to meet these requirements at either this or full commercial scale.

The calculated performance for a batch filter to remove solids from the purge stream from a 100,000 lb/hr field test facility is summarized in Table VI for both average and high medium and cake resistances. Various filtration time cycles and available pressure drops were investigated to determine the filtration area required. It may be seen that relatively small filters would be required for even long filtration cycles and low pressure drops. However, the cake volume associated with these filtration areas for standard filters is not sufficient to hold the total wet cake which would be produced in a daily cycle. Thus, either a design with wider leaf spacing or a filtration cycle involving multiple batches would be required for the field test facility, which would be inconvenient from an operational point of view.

Thus, while a continuous filter would be a small and manageable size it would also likely require rather more operator attention than desirable and a batch filter, while requiring little attention during operation would

Table V

Calculated Performance of a Continuous Filter

Assumed Value of		
Medium Resistance, Ft^{-1}	0.35×10^{10}	0.36×10^{10}
Specific Cake Resistance, Ft/lb	0.70×10^{10}	1.10×10^{10}
Submergence Time ⁽¹⁾ , Sec		
1/4" Cake	20	24
1/2" Cake	52	67
3/4" Cake	97	129
1" Cake	153	211
% Resistance Due to Medium		
1/4" Cake	70	60
1/2" Cake	53	43
3/4" Cake	43	33
1" Cake	36	27
Filter Area Required ⁽²⁾		
1/4" Cake	7 Ft^2	8 Ft^2
1/2" Cake	9 Ft^2	11.5 Ft^2
3/4" Cake	11 Ft^2	14.5 Ft^2
1" Cake	13 Ft^2	18 Ft^2

(1) Slurry solids content 2 lb/ft^3 , 1.2 cps viscosity, 20" Vac.

(2) 25% submergence, 50% safety factor. Solids produced in scrubbing 100M lb/hr steam.

Table VI

Performance Requirements for a Batch Filter

Assumed Values of

Medium Resistance, $\text{Ft}^{-1} \times 10^{-10}$	0.35	0.35	0.35	0.35	0.36	0.36	0.36	0.36
Specific Cake Resistance, $\text{Ft/lb} \times 10^{-10}$	0.7	0.7	0.7	0.7	1.1	1.1	1.1	1.1
Filtration Cycle Time, hr	6	4	2	2	6	6	4	4
Available Pressure Drop, psi	20	10	20	5	40	20	10	5
Filter Area Required ⁽¹⁾ , Ft^2	90	165	165	360	80	120	225	340
Associated Volume for Cake ⁽²⁾ , Ft^3	11	20	20	45	10	16	28	43

(1) Slurry solids content 2 lb/ft³, 1.2 cps viscosity. Solids produced in scrubbing 100M lb/hr steam. Includes 50% safety factor for handling one day's solids.

(2) Typical for horizontal tank designs, 4" leaf spacing. Total volume of wet cake produced is ~ 100 ft³.

have to be cycled two or three times due to limitations in cake handling capability. These facts suggested that alternative liquid solids separation techniques be evaluated for the field test facility, which required the evaluation of settling data to establish design criteria for either continuous or batch settling equipment. The settling data for solids produced during Run 1026 are shown in Fig. 4 for tests conducted at room temperature and 70°C. As expected, the solids settled somewhat more rapidly at 70°C than at room temperature, due to the decreased solution viscosity. In both cases however the settling rates are rapid, 57 ft/hr at 25°C and 85 ft/hr at 70°C and compression times are short, 60 and 40 seconds, respectively. These curves are, broadly, reflective of all settling data obtained.

The settling rates measured for solids produced in the field testing (Task C.2) are shown in Fig. 5. These solids showed even more rapid settling rates, in excess of 100 ft/hr, and compression times of less than 30 seconds. The data also indicate some tendency for solids which were withdrawn through the purge slurry cooler to settle at a slightly lower rate than those obtained by flash cooling through rapid letdown across a slurry sampling valve. The difference is not so large to be significant. However, it was also observed that the slow cooled solids showed some tendency to be slightly less heavily flocculated and to contain a somewhat greater proportion of fines and settle to slightly lower pulp densities. However, the large floc and settling characteristics associated with the flashed solids could be produced by gently mixing the slow cooled solids, and the ultimate pulp densities obtained were then the same in both cases.

The settling rates and settled pulp densities for solids which had been subjected to intense shear are shown in Fig. 6. The unsheared solids show the typical settling behavior observed for all slurries flash cooled from the laboratory test. After the initial settling experiment, the slurry was subjected to a high rate of shear by agitation in a Waring

Fig. 4. Settling Rates for Run 1026

○ at 25°C

x at 70°C

Fig. 5. Settling Rates of Solids Produced from Real Geothermal Steam

x Flash cooled to 105°C

o Slow cooled to 55°C

Fig. 6. Settling Rate for Run 713

x As purged

O Following high shear agitation

blender at maximum speed for 5 minutes. This was assumed to be reflective of the action to which the slurry might be subjected in repeated circulation through the scrubbing circulating pump prior to withdrawal from the system. While a significant decrease in settling rate and settled pulp density were obtained, the rate is still so rapid as to be quite acceptable for design purposes.

The settling rates of all slurries tested is summarized in Fig. 7, and it may be seen that compression times between 30 and 60 seconds may be easily obtained. The varying final dilutions obtained are due to the differing initial dilutions used in the various test series.

The results of a final dilution test carried out on solids produced during Run 1026 are summarized in Fig. 8. The calculated continuous settling area requirements for room temperature and 70°C are summarized in Table VII. The calculated unit areas for solids settling are very low at all detention times assumed, but the pulp densities increase only slowly. Furthermore, the calculated overflow rates are quite high, as are the pulp heights for the longer detention times. If pulp height is restricted to 3 ft, acceptable overflow rates are obtained with detention times of the order of 1 hour although pulp densities are rather low.

Limited testing was done on laboratory centrifuges to determine if the pulp densities could be increased further. Centrifuging for 5 min at 7000 g increased the pulp densities by only a factor of 2 to 25-30%, which is of the same order as obtained during the filter leaf tests. However, even these low pulp densities still provide for rejection of 80% of the incoming liquid to the clarified stream which is far more than will be required for control of acidity within the system. In fact, a large proportion of this overflow stream would have to be recycled to the regeneration step to control the concentration of the copper sulfate recycled to the scrubber. Thus, low underflow densities do not represent a serious processing problem.

Fig. 7. Settling Rates for Various Slurries Tested

- x Run 1026 70°C
- o Run 1026 25°C
- ▽ Run 824 25°C
- Run 713 25°C
- o Run 713 25°C, High Shear
- o Field Test, Slow Cooled
- o Field Test, Flash Cooled

Fig. 8. Final Dilution Test Run 1026

○ at 25°C

x at 70°C

Table VII

Results of Final Dilution Testing Solids Run 1026

Solids Settled at Room Temperature ⁽¹⁾

Detention Time, Min.	15	30	60	120
Final Dilution, cc/gm	6.85	6.55	6.25	5.95
Pulp Density, wt %	12.1	12.6	13.1	13.7
Unit Area, Ft ² /Ton/Day	1.23	1.23	1.24	1.25
Overflow Rate, GPM/Ft ² (2)	4.17	4.17	4.14	4.10
Pulp Height, Ft	1.73	3.43	6.6	12.62
Unit Area @ 3 Ft Pulp Height		1.41	2.73	5.26
Overflow Rate @ 3 Ft Pulp Height		3.64	1.88	0.97

Solids Settled at Operating Temperature ⁽³⁾

Detention Time, Min.	15	30	60	120
Final Dilution, cc/gm	7.09	6.98	6.69	6.10
Pulp Density, wt %	11.7	11.9	12.3	13.4
Unit Area, Ft ² /Ton/Day	0.80	0.80	0.81	0.82
Overflow Rate, GPM/Ft ² (2)	6.41	6.41	6.33	6.25
Pulp Height, Ft	2.82	5.69	10.89	19.82
Unit Area @ 3 Ft Pulp Height		1.52	2.94	5.42
Overflow Rate @ 3 Ft Pulp Height		3.37	1.74	0.95

(1) 25°C. Initial Dilution 59.5 cc/gm, settling rate 57.3 ft/hr

(2) For a slurry of initial dilution 31 cc/gm, 3 w/o solids.

(3) 70°C. Initial Dilution 58.1 cc/gm, settling rate 85 ft/hr.

DESIGN IMPACT

While either a small continuous filter or thickener could be used for the 100,000 lb/hr field test facility, and modest size units would be required at the full commercial scale, their use is not convenient for the field test program.

Accordingly, a small continuous decanter will be employed to make the primary liquid solid separation in the field test facility. The decanter will be designed with a maximum upflow velocity of less than 30 ft/hr to permit disengagement of solids under the worst anticipated conditions of high purge slurry flow rate and low temperature. A solids detention time of 2 min will be provided. This will limit the attainable under flow density to less than 10%, but this still represents rejection of up to 2/3 of the liquid volume entering the decanter. This provides a safety factor of approximately 2 in the required purge rate and, by limiting pulp density, provides operational flexibility and minimizes the danger of plugging of underflow slurry transfer lines. The decanter will be instrumented and provided with bypass piping to permit its operation to be observed and corrected should temporary upsets occur. In addition, a polish filter will be provided on the clarified overflow stream to collect solids not settled so that its operating characteristics may be determined and the process material balance closed.

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EIC Corporation
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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task A.4

Analytical Technique Development

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SUMMARY

Laboratory testing on simulated purge streams and on purge slurry returned from operation of the 8" scrubber (Task C.2) on geothermal steam have demonstrated that on-line monitoring of pH and monitoring and control of copper content are feasible in this process.

A Swirlclean by-pass filter will remove precipitated sulfide solids from the sample purge stream very effectively. A minimum amount of back-flushing - once per 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, 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. 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 make this control more precise. 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.

BACKGROUND AND RATIONALE FOR INSTRUMENT SELECTION

Control of the copper content of the scrub solution is critical to the proper operation of the copper sulfate process for the removal of H_2S

from geothermal steam. Field tests have shown that a level of at least 0.5 g/l Cu is required to maintain high H_2S removal efficiencies at normal acidities and steam-solution contact times. On the other hand, a large concentration of cupric ion within the scrubber is undesirable because of the consequent greater in-process inventory and loss to the solubles purge.

In addition to serving as the active scrubbing agent, cupric ion serves to passivate austenitic stainless steels by maintaining the system at an oxidizing potential. It has been shown that the corrosion rates of common stainless steel alloys are accelerated dramatically if scrub solution copper contents become depleted. The preliminary control philosophy for the process entailed measuring the copper content of the purge stream and using the output signal of the analyzer to control the flow rate of a concentrated, make-up copper sulfate solution. Such control must be highly reliable: if, for example, the flow of make-up copper sulfate solution is interrupted, the system's inventory will be depleted within about 20 minutes.

Solution acidity is also important in determining corrosion rate and H_2S scrubbing efficiency. Moreover, all geothermal steams of interest contain NH_3 , as well as H_2S , which will be removed in the scrubbing process as $(NH_4)_2SO_4$. For most steams, reaction stoichiometries are such that there will be more H_2SO_4 formed than there is NH_3 present to neutralize it, so that at scrubber conditions, the scrub solution will be a mixture of (mainly) $CuSO_4/H_2SO_4/(NH_4)_2SO_4$. As the purge stream is cooled, the sulfate-bisulfate equilibrium will shift and the pH at temperature will drop. Because of this shift, the measured pH evidently depends on the temperature of measurement as well as on the solution concentrations of H_2SO_4 and $(NH_4)_2SO_4$. The latter can be varied within limits, depending on the composition of the incoming steam and the solution purge rate. It is not clear at this time whether it would be more appropriate or effective to control pH or acidity (i.e., titratable H_2SO_4). However, a change in one will be reflected in the other, unless the ratio of H_2SO_4 to $(NH_4)_2SO_4$ happens to vary in an unusual way from a process point of view. The practical consideration is that pH is easier to measure than acidity, which includes a titration.

Four basic types of instruments were considered for use in measuring and controlling the copper concentration in the system. They are listed, with some advantages and disadvantages of each, in Table I. We searched for a commercially available instrument which could be locally mounted, had a direct, continuous output, did not require pretreatment of the sample prior to measurement, and gave precise, drift-free results in a reliable fashion.

None of the devices investigated met all of the desired criteria. Amperometric instruments were eliminated as being too sensitive to sample conditions, and titrametric devices were rejected as being unnecessarily cumbersome and giving only discontinuous, indirect readings. Direct reading, ion-selective electrodes offer several potential advantages, but it was felt that it would be difficult to obtain consistently accurate readings without excessive drift or frequent recalibration. While indirect-reading photometric devices (i.e., based on formation of a strongly absorbing species with an added reagent), are simply constructed, careful sample preparation is required. A direct reading instrument requires only sample filtration, but special instrument designs are required to obtain the maximum signal strength at the wavelength for maximum absorbance for aqueous cupric sulfate, viz. 825 microns. After reviewing the designs, essentially all "specials" offered by several manufacturers, it was decided that a Model 611LX Photometric Analyzer manufactured by Teledyne Analytical Instrument would be most suitable. This device, featuring a quartz iodide source and silicon diode detector with automatic turbidity compensation, is described in detail in the Appendix.

The photometric analyzer requires a clean sample, however, so the purge slurry will have to be filtered to obtain a filtrate suitable for analysis. It has been shown that solids produced in the scrubber are composed of large agglomerates of micron-size particles which can be filtered rapidly but show some tendency to blind the filter media and form a very low density cake. Thus, a continuous filter was required which would also

Table I

Types and Characteristics of Copper Analyzers

<u>Type of Device</u>	<u>Type of Reading</u>	<u>Advantages</u>	<u>Disadvantages</u>
Photometric	Direct	Flowthrough device Continuous reading Locally mounted Nonambient operation possible	Requires sample filtration Specific wavelength required
Photometric	Indirect	Simpler optics Greater specificity	Requires sample filtration Requires reagents and dilution Remote mounted Ambient operation
Titrametric	Indirect	Very specific Filtration not required	Semicontinuous output Requires reagents Remote mounted Ambient operation
Amperometric	Direct (?)	Very specific Filtration not required Locally mounted	Less precise Hydrodynamic dependent Temperature control required
Selective Ion	Direct	Flowthrough device Continuous reading Filtration not required Locally mounted	Activity, not concentration Subject to interference Drifts
Selective Ion	Indirect	Filtration not required Concentration inferred	Semicontinuous output Reagent required Remote mounted.

be effective in retaining fine particles. After reviewing several sampling filter designs, it was decided that a Swirlklean by-pass filter, manufactured by Collins Products Co., would be an effective device. The characteristics of this unit are described in the Appendix.

It has been pointed out that it is not certain whether acidity or pH is more important for process control: acidity is determined by the process material balance and must be known and controlled. But pH (hydrogen ion activity) may be more important in determining corrosion rate and/or scrubbing efficiency. The former can be measured by a titrametric device (Table I) while the latter can be indicated by a pH meter. Neither type of analyzer can be used at scrub solution temperature and pressure, but pH probes are available for use up to about 120°C.

Three factors led to the decision to select a pH meter to measure hydrogen ion activity rather than acidity directly. First, it is not acidity alone which is important for process control, but both acidity (free sulfuric acid concentration) and total ammonia (ammonium sulfate concentration) since the latter must be controlled to prevent its accumulation. Secondly, corrosion testing has shown that if higher acidities are offset by higher ammonium sulfate concentrations - which serves to raise the pH - corrosion rates can be decreased. Finally, in spite of the acknowledged problems in obtaining consistent results from industrial pH meters, it was felt that it would be only marginally less difficult to obtain trouble-free operation from a titrametric device for acidity or a selective ion device for total ammonia. A review of the characteristics and performance of industrial pH meters led to the selection of a system manufactured by Great Lakes Instruments, a model A60, which has a probe which is temperature compensated and suitable for use at up to 100°C and 100 psi. The instrument is described in detail in the Appendix.

EXPERIMENTAL SETUP AND PROCEDURES

The instruments selected as potentially useful for process control purposes were subjected to laboratory tests with the arrangement depicted

in Fig. 1. The objective of these tests was to determine, insofar as possible in a laboratory environment, the suitability of the instruments for the use proposed. Testing was carried out in bench scale equipment to obtain performance data and to calibrate the instruments as required. It has been assumed that manipulation of the instrument output signals to generate the required control action is state-of-the-art and need not be tested.

Slurry returned from tests in the field scrubber was charged to the surge tank and kept in suspension by the agitator. The slurry was circulated through the test loop by a Marsh pump, and the flow could be directed either through the Swirlklean filter or directly back to the slurry surge tank. The filtrate could be pumped either directly back to the slurry tank or to the analyzer. Slurry and filtrate return lines were flexible so that the effluent of each could be collected and its flow rate measured. The surge tank was covered to control evaporation and access of oxygen, which leached the solids. The slurry piping loop was fitted with control valves and pressure and temperature indicators to control and monitor the flow.

The Swirlklean unit's filtrate was directed through the Teledyne Analyzer's measurement cell, and provisions were made for withdrawing a sample of the stream at this point to independently check the copper content by an off-line analysis. The filtrate then passed through a 2" PVC tee which served as a mounting fitting for the Great Lakes Analyzer's pH probe. A sample of the filtrate leaving the probe mounting was taken to check the indicated pH reading by off-line analysis. Readings were taken periodically of the pressures and temperature in the slurry circulating loop, the flow rates of filtrate and thickened slurry, and instrument response. Samples of filtrate were saved for off-line analyses.

The copper and pH analyzers were calibrated in off-line tests. Standard copper solutions were made up by dissolving known weights of copper wire in acid solution and diluting to the desired concentration with

Fig. 1. Laboratory test set up

distilled water. These solutions were used to calibrate the Teledyne Analyzer and a Bausch and Lomb Spectronic 210 UV spectrophotometer. The latter was used routinely to measure the copper content of the filtrate. Commercially available pH standard buffer solutions (pH 1.0, 2.0, 4.0 and 7.0) were used to calibrate the various pH instruments used. Two laboratory models were used during the course of the testing as "standards" against which the performance of the Great Lakes Analyzer was compared: a Corning Digital 110 and an Instrument Laboratory Deltamatic Model 135A. All samples were allowed to come to room temperature ($23 \pm 1^\circ\text{C}$) before being analyzed, and temperature corrections were made as required to make the results consistent with those obtained on line at operating temperatures ($25\text{--}40^\circ\text{C}$).

TEST RESULTS

Sample Filters

Initial tests on the sample filter were carried out with tap water in the circulating loop and a 10-micron filter element: Initial filtrate rates were acceptable, 44 ml/min at 17 psi pressure drop, but the rate decreased very rapidly to 11 ml/min at 18 psi within 30 min. It was found that the filter element had become covered with a slime, probably hydrous iron oxides, which had penetrated the pores and blinded the filter. The element was replaced with one having a 1.2 micron pore size, and filtrate rates dropped from 80 to 19 ml/min at 14 psi pressure drop in 35 min. This behavior indicated that the finer pore size was more effective in retaining fines, but that some loss of capacity was inevitable and back-flushing would be required to prevent unacceptably low long-term filtration rates, at least for solids of the type occurring in tap water.

Following these scoping tests, slurry from the field tests was introduced to the circulating loop. Since the slurry had been decanted in the field, its density was higher than would normally be purged through the sample filter. Therefore, the slurry was diluted with a solution of

4 g/l Cu, 7 g/l H_2SO_4 , and 35 g/l $(NH_4)_2SO_4$ (approximately the clear filtrate composition) to about 5% slurry density. Tests were initiated, and the same general behavior that was found in the water tests was observed. That is, a high filtration rate would be obtained after back-flushing which would drop off rather rapidly and then decrease more slowly, approaching a near steady state value within about two hours. It was observed that the performance of filter elements with 5 and 10 micron pore sizes were comparable, and most of the test work was carried out with a 10 micron filter.

It was also observed that if the filter assembly were "dead headed" by closing the downstream pressure control valve, filtration rates would subsequently decrease more rapidly. It was felt that this resulted from slurry fines being imbedded into the element, by the pressure surge, where they could not be removed by the unit's hydraulic action. The decrease could be largely restored by back-flushing, but the practice of "dead heading" was avoided in subsequent tests. In all runs, back-flushing was carried out by opening the pressure control valve to reduce the filter back pressure to essentially zero and then forcing a few ml (about 20-50) of filtrate back through the filtrate line with a squeeze bulb. High filtrate rates were obtained immediately upon readjustment of back pressure, with no evidence of fines penetration or leakage past the filter element.

No attempt was made during the initial tests on the slurry to cover the surge tank, and evaporation and slow leaching of the solids caused a steady increase in the copper and ammonium sulfate contents and an increase in pH due to acid consumption. A record of filtration rate over a period of one hundred hours and ten back flush cycles is shown in Fig. 2. selected values of the solution copper content and pH are superimposed and show the effects of evaporation and leaching. After about 50 hours of operation, it was noted that the "steady state" filtrate rate was decreasing and it was postulated that basic copper sulfates were precipitating within the filter. To test this, a quantity of H_2SO_4 was added to the system to reduce its pH to a point where these salts, if they existed, would be soluble.

Fig. 2. Performance of the Swirlclean filter on slurry from field test 1214.

It was indeed found that the filtrate rate rapidly returned to its expected value, indicating that the filter can be cleaned easily by this mechanism as well as by back-flushing. The general type of behavior shown in Fig. 2 was seen in all further tests and accepted as routine. No difficulties were encountered with the operation of the filter, except that it showed a tendency to slowly leak filtrate past its O-ring seals unless very carefully assembled. Since no adverse effects were subsequently found in operation of the copper and pH analyzers, we conclude that this device will be an effective tool for the sample treatment required.

Copper Analyzer

It had been determined in the laboratory spectrophotometer that the expected linear correlation between CuSO_4 concentration and absorbance existed and that it was essentially unaffected by $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 concentration in the regions of interest. The calibration, however, was found to be sensitive to temperature, and in a direction opposite to that which would result from density changes. Thus, in operation of an analyzer, careful control of sample temperature must be maintained or a calibration factor must be established to correct for the effect of temperature (and composition, if necessary).

The effect of temperature and solution composition on the indicated copper concentrations for the laboratory spectrophotometer and the Taledyne Analyzer are shown in Figs. 3 and 4. The slope of the indicated concentration as a function of temperature is the same for both instruments, the readings increasing about 0.55% above the true concentration for each degree centigrade above room temperature ($23 \pm 1^\circ\text{C}$). Within the accuracy of the readings and for the temperature range of interest the slopes are constant at each copper concentration and conform to a common temperature coefficient, which eases the calibration problem. The effects of $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 concentrations on the indicated copper concentrations are not great and are not strong functions of temperature, as shown in Fig. 4. At room temperature, increasing $(\text{NH}_4)_2\text{SO}_4$ concentration from 50 to 125 g/l results in a

Fig. 3. Sensitivity of indicated concentration to sample temperature for the B & L spectrophotometer.

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decrease in the indicated copper concentration of about 2.5%, while at 50°C the decrease is only about 1.5%. The absolute deviations are lower for solutions containing lower copper contents and are difficult to read since the smallest meter division is 0.05 g/l, but the relative errors are probably about the same. It is anticipated that the variation in $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 concentrations in an integrated process will be far less than tested here so that this effect is a second order correction and need not be made routinely.

The Teledyne Analyzer was calibrated at the factory at room temperature and the calibration was confirmed in the laboratory. The instrument had excellent stability, showing very little tendency for the zero or span calibration to drift once it had warmed up. A minor mechanical modification was required to prevent the span filter from shifting position on its shaft when moved in and out of the light path by a solenoid activated drive. It only remained to be determined, then, whether the instrument was stable over a long period in the contact with filtrate derived from scrubbing real geothermal steam. The solutions might, for instance, contain components which slowly coated the sample cell windows.

The results of a long term test are depicted in Fig. 5. The Analyzer output is recorded both in terms of the concentrations read directly, at temperature of about 25-40°C, and for values corrected to room temperature. It can be seen that, when the temperature correction is made, the correspondence is excellent over the course of the test. The increase in copper content was the result of slow leaching of the solids. At the conclusion of the tests, rechecking the zero and span calibrations showed a drift of less than .05 g/l. The indicated stability would permit a weekly recalibration schedule to be carried out.

The results of a shorter test in which the filtrate temperature was deliberately varied and the instrument output corrected to room temperature concentrations by adjusting the span calibration setting are shown in Fig. 6. It is seen that the span adjustment for temperature compensation is essentially

Fig. 5. Response of Teledyne Analyzer in filtrate from field test 1214.

Fig. 6. Span adjustment setting required to maintain true copper concentration reading.

independent of copper concentration in the range of interest, which would simplify calibration procedures greatly. It may be possible to eliminate the apparent differences between setting when increasing and decreasing sample temperatures by replacing the potentiometer with a less sensitive one.

Confirmation of the instrument's resistance to drift in the presence of refreshed solutions will require additional field testing. However, it is clear that readings can be obtained with an accuracy of better than ± 1 g/l, at least for periods between recalibration, which should perhaps be of the order of a week. This is well within the range required to spot sudden changes in operating conditions and take corrective control actions, and will not impose material balance errors of more than $\pm 5\%$.

pH Analyzer

The standard Great Lakes Analyzer Model 60 pH probe is filled with a pH 7 buffer solution and is normally calibrated in a pH 7 buffer and then spanned to a buffer in the range of interest. In preliminary laboratory tests, it was found that if the instrument were spanned to pH 2.0, it would give accurate, linear response above this range and fair response down to about pH 1.5, but was highly nonlinear below this range. Errors of up to 0.2 pH unit were common and considerable difficulty was experienced with drift and reproducibility. Attempts to alleviate the problem by calibrating and spanning within the range pH 1.0-2.0 were only partially successful, and highly nonlinear results were then obtained outside of this range. After consultation with the manufacturer, it was determined that better results might be obtained if the "standard" internal buffer in the probe were replaced by one which was closer to the range of interest and the instrument then calibrated to this lower value.

In initial attempts to do this, a pH 2.0 HCl buffer was used and the results were worse! Not only was the response still nonlinear (in systems with sulfate acidity), but the instrument response time was increased

dramatically and drift problems increased. For subsequent attempts, "standards" for pH were made by titrating H_2SO_4 into solutions containing 100 g/l $(\text{NH}_4)_2\text{SO}_4$, with the required acidity determined by measuring the solutions' pH with a carefully calibrated laboratory pH meter. "Standard" solutions were made up in this manner to pH 2.0 and 1.0, and the pH 2.0 standard was used as a reference solution in the probe. This approach largely solved the problem, as can be seen in Fig. 7, although some non-linearity is still present, especially at low $(\text{NH}_4)_2\text{SO}_4$ concentrations where the buffer capacity is less. It should be noted that the smallest scale division on the Analyzer is 0.1 pH units.

The shape of the acidity - pH curves obtained by use of the Analyzer, Fig. 8, are as expected: higher acidities are needed to reach a given pH as the $(\text{NH}_4)_2\text{SO}_4$ content is increased. The slopes of these curves in the region of interest are not great, and the Analyzer's scale cannot be consistently read with a precision greater than about ± 0.05 pH units. Thus, it will not be possible even for a known $(\text{NH}_4)_2\text{SO}_4$ concentration, to infer changes of acidity less than about $\pm 3-4$ g/l, which represents a relatively large error. Accurate values of acidity and total ammonia contents for determining the process material balances will have to be obtained in off-line analyses, and the pH Analyzer's output will be monitored to determine principally if changes have occurred in the purge stream compositions.

The resistance of the Analyzer to fouling and drift in solutions returned from the field test was investigated over a 100-hour run at the same time the Teledyne Analyzer was tested, and the results are shown in Fig. 9. The pH scale has been expanded to accentuate any monotonic changes due to fouling or drift. Based on the data shown in Fig. 7, an offset of about 0.15 pH units between the two sets of readings would be expected for this solution, whereas the observed difference is only about 0.1. The observed slow increase in pH was due to leaching, and the correspondence over the course of the test was good.

Fig. 7. Calibration of Great Lakes Instruments pH Analyzer.

SOLUTION pH AT ROOM TEMPERATURE

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Fig. 9. Response of Great Lakes Analyzer in filtrate from field test 1214.

At the end of the run, the instrument was recalibrated and respanned. A slight change ($\leq .05$ units) was found in the calibration and span settings indicating that recalibration might be required week'y. It was also observed that the Analyzer time constant had increased somewhat, from about 6 to about 12 seconds, which may be related to the drift problem and due to partial blockage of the probe's porous plug. While this is an appreciable rate of drift, there was little apparent systematic increase in the discrepancy between the lab pH meter and the Analyzer reading so that the severity of the drift problem could not be ascertained in tests of this duration.

Since the Analyzer probe is temperature compensated, no temperature correction need be made during the course of this run. However, the probe's temperature compensation thermister is buried within its plastic body and is well insulated. Thus, the time constant for response to step changes in temperature is fairly long, 10-15 min, and rapid changes in solution temperature would introduce significant errors in the indicated pH.

MODIFICATIONS REQUIRED FOR FIELD USE

All of the components of the sampling and analysis system will require some modification for field use. The Swirlclean filter will be fitted with an automatic back-flush system, which is available as a standard component, to insure high filtrate rates and minimize sample lag time. In addition, a modified sealing system will be developed, if possible, to minimize filtrate leakage.

The entire Teledyne Analyzer system - its source box, sample box, photodiode box, and receiver/analyzer - will be mounted in purged enclosures to protect the instruments' electronics from deterioration due to attack by atmospheric H_2S . In addition, it will be desirable to change the span potentiometer to one which will be somewhat less coarse, thereby easing calibration and temperature compensation problems.

As in the case with the copper analyzer, the Great Lakes Analyzer will have to be enclosed to protect its electronics. Its span calibration potentiometer will also be replaced, if possible, to permit more precise range adjustment at low pH's.

In summary, all components of the sampling and analysis system, when modified as indicated, should give reliable field service in the use for which they are intended. Fairly careful control of sample temperature will be required, however, to obtain consistent results. This will be achieved by installing an oversized cooler on the filtrate line.

APPENDIX

DESCRIPTIVE LITERATURE ON

Swirlklean Filter

Teledyne Analyzer

Great Lakes Analyzer

COLLINS PRODUCTS COMPANY

P. O. Box 382

Phone 713 327-4200

LIVINGSTON, TEXAS 77351

THE COLLINS SWIRLKLEAN BYPASS FILTER

The Collins Swirlklean bypass filter was developed to remove small micron and sub-micron size particles from both liquid and vapor samples. Small pore membrane filter are used in the filter. Membrane filters are thin (0.005 in. thick) porous structures composed of polymeric materials. These filter elements have uniform pore size for good surface retention of particles.

HAVE YOU TRIED THE COLLINS SWIRLKLEAN BYPASS FILTER
IN YOUR ANALYZER SAMPLING SYSTEM?

THOSE WHO HAVE, LIKE THE CLEAN SAMPLES TO THEIR ANALYZERS.

- SAMPLING SYSTEM AND ANALYZER MAINTENANCE IS REDUCED
- USES MEMBRANE FILTER ELEMENTS FOR SURFACE FILTRATION
- TANGENTIAL ENTRY OF BYPASS CREATES SWIRLING ACTION
KEEPS FILTER ELEMENTS CLEAN - PARTICLES ARE RETURNED
TO PROCESS
- IDEAL FOR CONTROL APPLICATIONS, BECAUSE SMALL INTERNAL
VOLUME GIVES UP-TO-DATE SAMPLE
- AVAILABLE IN CORROSION RESISTANT MATERIALS

THE COLLINS SWIRLKLEAN BYPASS FILTER HAS BEEN INSTALLED AND PROVED TO BE AN EXCELLENT ANALYZER FILTER BY A NUMBER OF LARGE CHEMICAL AND PETROLEUM COMPANIES. REPLACE THOSE EXISTING FILTERS THAT HAVE A TENDENCY TO PLUG SHORTLY AFTER BEING PLACED IN SERVICE. THE COLLINS SWIRLKLEAN IS EVEN RECOMMENDED FOR DIRTY STREAMS CONTAINING IRON SULFIDE, IRON RUST, CATALYST, AND OTHER FINE PARTICLES. STANDARD FILTER ELEMENTS HAVE A 0.5 MICRON PORE SIZE. OTHER PORE SIZES ARE AVAILABLE.

SPECIFY THE COLLINS SWIRLKLEAN IN YOUR NEXT ANALYZER INSTALLATION FOR CLEANER SAMPLES AND MORE TROUBLE-FREE OPERATION.

SWIRLKLEAN Features

- Filter elements are inexpensive.
- Remove particles to the sub-micron range.
- Remove water droplets from vapor samples.
- Filter element change requires about five minutes.
- Remove entrained water from liquid hydrocarbon streams.
- Filter body, base, and cap can be made from corrosion resistant material.
- Effective in removing iron sulfide and other small particles without frequent filter plugging.

Removes

**RUST
IRON SULFIDE
FINE CATALYST AND
OTHER SMALL PARTICLES
FOR CLEAN SAMPLE**

TO: Chromatographic Analyzers
Reid Vapor Pressure Analyzers
Four Point Analyzers
Infrared Analyzers

THE COLLINS SWIRLKLEAN BYPASS FILTER

SPECIFICATIONS

	Model I	Model II
• BODY MATERIAL		
Standard:	303, 316 Stainless Steel	303 Stainless Steel
Special Orders:	Other Materials	Other Materials
• FILTER ELEMENTS		
Type:	Membrane	Membrane
Pore Size:		
(Standard)	0.5 Microns	0.45 Microns
(Available)	10, 5, 3, 1.2, 0.8, 0.5, and 0.3 Microns	10, 5, 3, 1.2, 0.8, 0.5, and 0.3 Microns
Total Filter Surface:	22 Sq. Cm.	126 Sq. Cm.
Element Material:	Depends on Application	Depends on Application
• INTERNAL VOLUME		
Bypass Side:	25 Cu. Cm.	160 Cu. Cm.
Analyzer Sample Side:	4 Cu. Cm.	10 Cu. Cm.
• RECOMMENDED FLOW RATES-LIQUID		
Bypass Stream:	1 To 2 GPM Minimum	2 To 6 GPM Minimum
Analyzer Sample:	50 Cu. Cm./Min.	275 Cu. Cm./Min.
• RECOMMENDED FLOW RATES-VAPOR		
Bypass Stream:	2000 Cu. Cm./Min.	0.5 To 1 CFM
Analyzer Sample:	To 1000 Cu. Cm./Min.	To 1 CFM
• PRESSURE TESTED TO:	5000 PSIG	2500 PSIG
• MAXIMUM TEMPERATURE:		
Standard Element:	To 200°C 120°C	To 200°C 120°C
• PROCESS CONNECTIONS	1/4" FPT	3/8" FPT
• ANALYZER CONNECTION	1/8" Tube Standard 1/4" Tube Available	1/8" Tube Standard 1/4" Tube Available

Model I

Model II

144

Patented

The GLI Model 60 Analyzer for pH, ORP (oxidation reduction potential) or conductivity measurement is intended for use in process and pollution applications. By selecting the proper options, the user can obtain almost any display or control function required. These analyzers are Factory Mutual approved for General Purpose applications. Some outstanding features are:

1. Differential input reduces ground loops and signal noise.
2. One hundred percent solid state circuitry on plug-in cards provides high reliability and easy access.
3. NEMA - 4 enclosure is standard.
4. Six inch meter movement is standard. Optional displays include 2-1/2" strip chart recorder or digital meter in lieu of meter.
5. Analog outputs and range expand are available with or without isolation.
6. Dual-relay controllers are available for alarms or ON/OFF control.
7. Two-mode controller for proportional control loops is available with as much as eight minutes deadtime.
8. Probe and analyzer can be separated by as much as 3,000 feet.
9. FM approved, Intrinsically safe system is optional.

SPECIFICATIONS

Maximum Range	pH: 0-14 ORP: ± 2000 mv
Stability (analyzer and Model 60 Probe)	0.03 pH units per day
Ambient Temperature	-30 to 40°C., 99% R.H.
Power Requirements	120 VAC $\pm 15\%$, 50-60 Hz, less than 10 VA
Response Time	0.1 to 1.0 seconds user selectable
Meter Presentation	6" scale length standard
Recorder Presentation	2.5" chart width (optional)
Digital Presentation	3-1/2 digit display (optional)
Case	Anodized aluminum, Model A60-W-X-Y-Z or fiberglass; Model A65-W-X-Y-Z Nema - 4 enclosures.
Consult Specification Sheet S60PD-AO/515	
Panel mount model A60-W-X-Y-Z

Surface mount model A65-W-X-Y-Z

GREAT LAKES INSTRUMENTS, INC.

MODEL 60 PROBE ASSEMBLY
Supersedes S60P/874

The GLI Model 60 Probe incorporates more outstanding features than any other commercially available pH sensor. The major features are:

1. The GLI Standard Electrode is used instead of a reference electrode. This means that no filling solutions, crystals, reservoirs or pressurization schemes are needed for this probe.
2. The GLI Differential Electrode Technique* eliminates ground loops and noisy signals while maintaining fast response time. The output signals from the probe electronics are strong enough to be sent over a mile of inexpensive cable without degradation.
3. Small size and light weight simplify mounting, handling and calibration.
4. Complete encapsulation eliminates problems due to leaking or high humidity. Combined with the low power levels in the probe, the encapsulation allows the probe to be safely used in hazardous atmospheres.
5. Temperature compensation is internal and automatic.

The net result is a small but rugged probe that requires virtually no servicing while providing exceptional performance and reliability even in the really tough industrial applications.

The Model 60 Probe can be used with the Model 60 and Model 70 Analyzers. Combined with a GLI Interface Module, the Model 60 Probe can be used with most other manufacturers analyzers.

*Patented

MODEL 60 pH PROBE

SPECIFICATIONS

Range	0-14 pH units
Stability	0.03 pH units per day
Sensitivity	0.001 pH units
Output Impedance	1 Ohm
Temperature Limits	-5 to +95°C Derakane ** -5 to +65°C Epoxy **
Pressure Rating	To 100 psi**
Wetted Materials	Standard: Epoxy, Ceramic, Glass, Titanium Palladium Alloy *** Optional: Derakane in lieu of Epoxy
Interconnect Cable	Belden 8786

DIMENSIONS***

FLOW THRU
P60L - 2 - 1
(STAINLESS TEE)

FLOW THRU
P60L - 3 - 1
(PVC TEE)

TANK MOUNT
P60L - 4 - 1

Caution: Mount these probes on a vertical axis (electrodes down) to 75° from the vertical. Other mountings may cause erratic readings.

**For different ratings and special materials of construction, consult factory.

***For other probe configurations and mounting hardware consult Specification Sheet S60PMH/274.

photometric analyzers

SERIES 600

features

- Ratio Measurement
- Optics Separated from Electronics
- Variable Optical Path
- Photo Tube Detector
- Proportional Temperature Control
- Readout is Linear
- Stable Electronics
- Choice of Readout Devices
- Sample Pre-Heater
- Custom System Design

TELEDYNE
ANALYTICAL INSTRUMENTS

Method of Analysis: The TAI Series 600 Photometric Analyzer monitors continuously the concentration of one component in a composition of liquids (or gases) by measuring the radiation absorbed in a selected band in the ultra-violet or visible spectral region. The ultra-violet analyzer compares unique spectral peaks found within wavelengths between 2000 and 4000 Angstroms. Any liquid or gas having a characteristic absorption spectrum in this region can be measured by the analyzer. Analysis can also be made in the visible region: indication is the ratio of two different colors or the transmission of one color compared to total transmission.

**OIL IN WATER
POLLUTION OR PROCESS CONTROL**

**QUALITY CONTROL
MONITORING PRODUCT PURITY**

**REACTION RATES
MONITORING A REACTANT TO
PROCESS COMPLETION**

**CONTAMINANTS
MONITORING PROCESSES FOR
BUILDUP OF UNDESIRABLES**

instrumentation features

RATIO MEASUREMENT compensates for lamp aging and cell deposits.

OPTICS SEPARATED FROM ELECTRONICS for ease of maintenance.

VARIABLE OPTICAL PATH allows flexibility of application.

SIMPLE PHOTOTUBE provides long, stable life.

PROPORTIONAL TEMPERATURE CONTROL

of optics & cell to $\pm .05^\circ\text{C}$ available for critical applications.

READOUT IS LINEAR with concentration.

STABLE ELECTRONICS - All solid state modular construction.

READOUT DEVICES - Customer's choice of RECORDER, METER or TRANSMITTER for pneumatic, voltage or current output signal.

SAMPLE PRE-HEATER - Thermistor regulated proportional temperature controlled sample heater for sensitive measurement.

CUSTOM SYSTEM DESIGN - Experienced system engineering for design of sample systems.

physical characteristics

The analyzer consists of four sections, the source, sample and detector modules, and a remote control module. Separating the electronics from the optics and sample prevents accidental leaks from destroying the electronic components.

MODEL 610. Contained in three aluminum explosion-proof conduits, coupled together on two parallel iron channels for bulkhead, wall or pipe rack mounting.

MODEL 611. Contained in three sheet steel enclosures, coupled together on two parallel iron channels for bulkhead, wall or pipe rack mounting.

regulating transformer

To eliminate spurious readings due to line voltage variations, a regulating transformer is furnished with the analyzer for most applications.

solid state electronics

An all solid state electronic section combines good stability with high sensitivity. Assures low long term drift. Eliminates both phototube and vacuum tube matching and noise associated with tube type amplifiers. Printed circuit board construction allows ease of maintenance and modular replacement of electronic sections. Features, such as automatic zero control, E to I and E to E converters and high and low alarms, can be added with a minimum of trouble at a later date.

logarithmic amplifier

A stable and highly reliable all solid state, temperature regulated logarithmic amplifier, yields an output signal which is linear with sample concentration. Use of all solid state components eliminates the need for tube matching and drift associated with vacuum tubes.

ratio measurement

The electronics are arranged to subtract the logarithms of the reference and sample signals. The result is a ratio measurement which cancels out the effects of dirt in the sample, deposits on the cell windows or darkening of the lamp.

automatic zero

Automatic zero can be added, if required, without modification of recording or controlling equipment.

recorders and indicators

DC millivolt output signal standard. Control unit meter and current output (1-5, 4-20 and 10-50 ma DC) optional.

alarms

One or two electronically adjustable SPDT alarm contacts optional.

single cell, dual beam

A single beam of energy passes through the sample cell and then alternately through two rotating interference filters. Pulses of radiation at the selected wavelengths strike a phototube which converts the pulses of radiation into electrical pulses. The level of the alternate pulses is proportional to the energy transmitted through the sample at the two different wavelengths. These pulses are amplified and the logarithm taken. The pulses are separated by a magnetically operated mercury switch into a reference signal and a measuring signal. The two signals are then transmitted to the remote control module where the logarithms are subtracted to yield a ratio output which is linear with sample concentration.

dual cell, dual beam

A single beam of energy is divided into a reference beam and a sample beam using a beam splitter. Each of the beams passes through a selected filter and a sample cell to a phototube. The phototube conducts a current proportional to the energy received. Each signal is amplified for transmission to the remote control module. The logarithm of each signal is taken and then subtracted to yield a ratio output which is linear with sample concentration.

In addition to the Model 600 Photometric Analyzer, Teledyne Analytical Instruments also manufactures thermal conductivity analyzers, near infrared analyzers, flame ionization analyzers, ultraviolet analyzers and the industry's most complete and comprehensive line of oxygen analyzers.

Performance specifications vary with the application. Specifications listed are typical

NOISE:	Less than $\pm 1\%$	SENSITIVITY	.02 to 3 absorbance units
DRIFT:	Less than 1% per day	REPRODUCIBILITY:	$\pm 2\%$ of scale or better
DIURNAL:	Less than 1% per 20°F	ELECTRONIC RESPONSE:	90% in 1 second
ACCURACY:	$\pm 1\%$ full scale possible	FILTER WAVELENGTH:	210 to 1000 millimicrons
AMBIENT:	40°F to 120°F	SAMPLE PRESSURE:	Quartz window: 400 psi
SAMPLE CELL:	Stainless steel with Quartz window standard. Other materials available.	ENCLOSURE	General Purpose-sheet steel Hazardous Duty - conduit
CELL LENGTH:	.01 to 40 inches	READOUT:	Strip or Circular Chart Recorder or Meter. Pneumatic or electric transmitter available
FLOW RATE:	50 to 1500 cc/min	SAMPLE TEMPERATURE:	40°F to 125°F Normal (Others available)
LIGHT SOURCE:	Tungsten Lamp, Mercury, Deuterium Arc		
POWER RATING:	115 volts, 60 cycle Approx. 200 watts		

general information

TAI's Series 800 instruments can measure any compound having a specific absorbance within the ultra-violet or visible spectrum. The background components must not have any interfering absorbance at the specific wavelength of interest.

The pass band of the measuring filter is selected at a wavelength of strong absorbance by the component of interest and little or no absorbance by the components of the background. The pass band of the reference filter is selected at a wavelength where none of the components of the sample absorb appreciably.

applications

oil in plant effluent	chlorine purity
oil in boiler feed water	bromine purity
turbidity	mercury vapor
phenol in water	COLOR OF OILS
solvents in water	- Astm
SO ₂ in stack gas	- Saybolt
H ₂ S-SO ₂ ratio in sulfur plants	- Rosin
aromatics in paraffins	- Apha

partial list of other compounds

acetal	ethylene bromide
acetaldehyde	formaldehyde
acetone	furfural
isoamyl alcohol	hydrogen sulfide
aniline	isoprene
benzaldehyde	mercury vapor
benzene	methyl ethyl ketone
bromine	nickel carbonyl
1,3 butadiene	nitrobenzene
carbon disulfide	ozone
carbon tetrachloride	perchloroethylene
chlorine	phenol
cyclohexane	phosgene
dimethyl amine	sulfur dioxide
dioxane	toluene
ethyl benzene	vinyl acetylene

TELEDYNE ANALYTICAL INSTRUMENTS

333 West Mission Drive
San Gabriel, California 91776
(213) 283-7181

EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158

CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task B.1

Materials Testing

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SUMMARY

A series of tests has been carried out to determine the resistance to corrosion and stability of various materials under conditions which simulate operation of process steps other than steam scrubbing. A variety of alloy materials, composites, and elastomers were 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°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°C, and 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 inconclusive. 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 the first two conditions were present in the 8" and 4" scrubbing column systems, where little crevice corrosion was observed, the results suggest that it may be possible to design around the problem in a commercial system.

BACKGROUND

The results of a companion series of tests, Task A.1, to determine materials of construction suitable under scrubber operating conditions have already been reported. Briefly, it was found that in the presence of a minimum concentration of cupric ion (>1 g/l) and controlled acidity (<25 g/l H_2SO_4 @ 100 g/l $(\text{NH}_4)_2\text{SO}_4$, $\text{pH} \gtrsim 1.1$) austenitic stainless steels were passivated, and would be suitable materials of construction (corrosion rate $\lesssim 5$ mills/year). To provide for protection in upset situations, e.g., a high acidity excursion, the use of a high alloy austenitic stainless, C20Cb3, was specified, with titanium specified as a more costly but essentially totally passive back-up material. No evidence was found in these tests of stress corrosion cracking ($\text{Cl}^- \leq 25$ ppm), weld attack, or substantial occurrence of pitting, but all alloys tested proved to be susceptible to crevice corrosion attack. It was postulated that this was due to a local depletion in copper concentration.

No other point in the system will be subjected to as severe operating conditions as the scrubber. It is of necessity at the highest temperature ($\sim 175^\circ\text{C}$), and since for essentially all geothermal steam compositions of interest the ratio of ammonia-to-hydrogen sulfide is less than two (mole basis), the consequence of the scrubbing reaction is a decrease in copper concentration and an increase in acidity.

The purged scrubbing solution (slurry) is cooled rapidly after being removed from the scrubber by countercurrent exchange with makeup copper sulfate solution which is high in copper and low in acidity. The thickened slurry may be reheated significantly prior to regeneration, but the fast kinetics of this step insure a rapid increase in copper content with a corresponding decrease in

acidity, since acid is consumed in the regeneration step for leaching of enriched solids (Cu_nS , $n>1$). In the neutralization and purge copper removal steps temperatures will be lower and acidities greatly reduced or at least controlled.

It is well known from operating practice in the copper industry that austenitic stainlesses are suitable materials of construction at much higher acidities ($\text{H}_2\text{SO}_4 \sim 50 \text{ g/l}$, $\text{pH} \sim 0.7$) if temperatures are held below about 60°C . While less information is available as to specific materials, it is also known that engineering plastics, particularly fiberglass reinforced materials (composites), have found wide use at these temperatures. While even less operating data are available on the suitability of trim materials, e.g., gaskets, O-rings, mechanical seals, valve trim, etc., there are indications from manufacturers' literature that standard materials are generally suitable at temperatures below $50\text{--}60^\circ\text{C}$.

The objectives of the materials testing work, Task B.2, were to determine the suitability of all candidate materials under process conditions external to the scrubber. Manufacturers' data would be used wherever possible as a guide to screen candidate materials, and only those thought suitable would be subjected to test. Only limited test work was to be carried out on austenitic stainless steels, for which operating history exists, with the major effort devoted to composite materials since they are likely to show cost advantages at a commercial scale for certain system components, e.g., surge tankage.

Accordingly, a series of tests was programmed for solutions with compositions simulating those expected under process conditions. The major independent variables in these tests were to be materials composition, test duration, and

solution temperature. Operations at four temperatures simulated key operating conditions: ambient temperature (25°C); 50°C, representing partially cooled solutions' storage temperatures; the solutions' normal boiling point, 105-110°C, representing the maximum possible temperature in an unconfined state; and leach reactor conditions, ~ 130°C, for metals only. In the leach reactor tests, oxygen over pressures would also be applied.

Since the results of Task A.1 indicated that susceptibility to crevice corrosion might be a major concern if austenitic stainless steels were used in the scrubber, the Task B.1 test plan was modified to include additional work in this area. These tests were, of course, carried out under scrubber operating conditions and were directed towards determining the influence of liquid velocity, gasket material, anodic-to-cathodic area, and crevice style and tightness on the extent of crevice corrosion.

TEST APPARATUS AND PROCEDURES

Crevice Corrosion Studies at Scrubber Condition

Coupon testing was carried out as a modified Huey test according to procedures specified in NACE Standard TM02-70 "Laboratory Corrosion Testing of Metals on the Process Industries".

The testing was carried out in stirred and unstirred autoclaves using approaches and procedures described in the preliminary report for Task A.1, and will not be repeated here. Solutions were made up and test coupons were evaluated in the same manner. Immersible parts in the stirred autoclaves, initially made from 316 stainless steel, were replaced with titanium in the final experiments. In one test $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was used instead of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Several different types of crevices were studied during the course of these tests. In some tests, crevices were made simply with two similar or different alloy flat plates bolted or held together with thin wall Teflon spaghetti tubing. Gasketed crevices were made by placing Teflon or asbestos sheets in between two samples. In one test, copper sheets were used to enclose asbestos gasketing to prepare the creviced sample. A systematic study of the effect of percent area creviced was carried out using Teflon rods of various areas which bore on metal samples. The metallic samples used for test were 1" x 1" x 1/8" C20Cb3 alloy flat plates with a 3/8" hole at the center. A 3/16" clearance hole was drilled at the center of the Teflon rod for 3/16" titanium bolts. The flat face of Teflon rod was machined smooth and a 1/2" deep hole was drilled axially at a diameter sufficient to obtain the desired crevice area. Two 3/16" through-holes were drilled radially to allow liquid circulation to the inside edges of the crevice. The metallic sample was then placed between two similar Teflon rods and the assembly was tightened with titanium bolts. In some tests, the surfaces of the metallic samples were machined, either on one or both sides.

In other tests, with Teflon envelope gaskets, the effects of various bolting torques on crevice corrosion rates were examined. Samples used for the holes were 1" x 1" x 1/8" C20Cb3 alloy flat plates with fully gasketed surfaces. Crevices were made up with between 5 and 60 inch pound torque applied to the bolts.

Since the majority of these tests were carried out in the unstirred autoclave, a brief series of tests was also performed to determine the effect of solution velocity on crevice corrosion susceptibility. In these tests,

smaller samples of C20Cb3 (1/2" x 1/2" x 1/8") with Teflon gaskets were bolted to the agitator paddles. The agitator was run at a low speed, sufficient to move the samples through the solution at 1'/sec.

At the conclusion of all tests, the autoclaves were quenched and opened. The state of the coupons, the appearance of the solution and the solution copper content and pH were then recorded. The coupons were cleaned, inspected for evidence of attack and reweighed. Corrosion rates were calculated from the observed weight loss, the known coupon density, immersed area and test duration, and directly from the depth of crevices observed in the metal and the test duration.

Corrosion Studies at Leach Reactor Conditions

These tests were carried out in a stirred autoclave using apparatus and procedures described in the preliminary report for Task A.1. An atmosphere of nitrogen was maintained in the autoclave during heat up, and prior to admitting oxygen the nitrogen was vented by purging with autogeneous steam.

When the system was at the autogeneous steam pressure corresponding to the desired temperature, the stirrer was started and the system pressure was increased to the desired total pressure by admitting compressed oxygen. The desired oxygen partial pressure was maintained by controlling the total pressure and system temperature. At the end of test, the autoclave was quenched and opened. Corrosion rates were then calculated from the observed weight loss and known coupon density, immersed area, and test duration.

Metals Testing at the Normal Boiling Point

These tests were carried out in a glass reflux reactor. The reactor consisted of a one liter resin flask, a reflux condenser and a glass

thermometer. The temperature of the reactor was controlled by adjusting a Variac setting to control voltage input to heating tapes wrapped around the flask.

The coupons were prepared in the same way as for corrosion studies at scrubber conditions. The dimensions and state of the coupons were noted prior to each test, and they were weighed on an analytical balance before being immersed in the test solution. The test solution was made up in the same way as for tests at scrubber conditions and the copper content and pH were checked before and after the test.

After the samples had been immersed in the one liter resin flask filled with about 700-800 ml of test solution, the system was closed and brought to temperature as rapidly as possible. At the conclusion of the test, the reactor was removed from its heat source, cooled, opened, and the level of coupon immersion, the state of the coupons and the appearance of the solution recorded. The coupons were cleaned, inspected under a metallograph if they showed evidence of attack, and reweighed. Corrosion rate was calculated from the observed weight loss and known coupon density, immersed area, and test duration.

Materials Testing of Composites at the NBP, 50°C and Ambient Temperatures

The tests at the NBP were carried out in the same reflux reactor and followed the same procedures used for metal testing. The samples tested include different kinds of plastic, e.g., including Hetrion, Duracor, Derakane, and Arlak and elastomers such as Viton and EPR and were weighed on an analytical balance. The samples and their thicknesses was measured at several spots before they were immersed in the test solution.

At the end of the test the samples were cleaned and reweighed, and the percent weight gain with test duration was calculated. It was noted that the

weight of the samples decreased with time following the test with exposure of the samples to the atmosphere. After a series of tests had been carried out, it was determined that the weight loss was the same each time, and undoubtedly reflected loss of water adsorbed or wicked up during the immersion period. Accordingly, the convention was established of basing weight gain (or loss) calculations on weights determined two days after removal from the solution.

The testing of composites at 50°C was also carried out in a reflux reactor. The temperature was maintained by means of a constant temperature bath, and sample weights before and after the immersion period were used to calculate the percent weight gain with time.

Ambient tests were carried out by immersing the samples in solutions which were held at room temperature for extended periods of time. Percent weight gains and dimensional changes were determined in the same way as for tests at the boiling point and 50°C. In general, tests at ambient temperatures were carried out for the longest period of time, with the 50°C tests for shorter and the boiling tests being run for the shortest period.

Stress-Deflection Testing for Composite Materials

The response of samples of composite materials to applied stresses was determined before and after exposure to the test solutions. The equipment employed in this study included a simple specimen support fixture, a sharp edged steel knife, a scale for measuring applied load and a feeler gauge for measuring deflection. The test set-up is shown in Fig. 1.

The test specimen, whether new or exposed to test solutions, was weighed on an analytical balance and placed on the specimen support fixtures. The edge of the steel knife was then placed vertically at the middle of the

Fig. 1. Apparatus for measuring deflection of composite specimens.

specimen. A weighing scale, suspended by a chain from two ends of the knife, was used to measure the load applied to the specimen. The load was applied by means of a rope connected to the other end of the scale. A feeler gauge was carefully placed directly underneath the knife edge and a zero deflection reading obtained before the load was applied. Then, deflection was recorded as a function of the load applied to the specimen. When the test was completed the specimen was turned over, and deflection and loads recorded for stresses applied to the opposite side. The variation observed on new samples served as a measure both of the variability inherent in the test procedure and the inhomogeneity of the samples.

TEST RESULTS

Resistance of Metals

Corrosion rates for various metals in simulated purge stream solutions at ambient temperature and at the normal boiling point, and for solutions under leach reactor conditions are summarized in Tables I-III respectively.

Measured corrosion rates at ambient temperature for T304 and T316 stainlesses were of the order of .01 mills/year. No evidence of weld attack, pitting, or crevice corrosion was observed and since the samples were exposed for almost eight months, it may be concluded that these materials will give excellent service in this application. There appears to be little advantage in selecting T316 over the less expensive T304 material. One test was performed on a porous sintered stainless which had been considered as a sample line filter material. This material had a very high specific surface and significant weight losses were found, although penetration rates calculated for solid surfaces at these rates would still be small, of the order of 1 mill/year.

Table I

Corrosion Rates for Stainless Steels in Purge Solutions at Ambient Conditions

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
B.1-1	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	New	2 g/t Cu	.05	No visible effect.
	316-10	.059	12.32	17.33	2.63		W, $\frac{1}{2}$	New	pH 1.38	.05	No visible effect.
	316L-8	.03	13.39	17.6	2.05		W, $\frac{1}{2}$	New	100 g/t $(\text{NH}_4)_2\text{SO}_4$ 24 g/t H_2SO_4 5 ppm Cl^- 700 hrs	.03	No visible effect.
B.1-7	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-1	2 g/t Cu	.005 (.029)	No visible effect.
	316-10	.059	12.32	17.33	2.63		W, $\frac{1}{2}$	See B.1-1	pH 1.38	.01 (.029)	No visible effect.
	316L-8	.03	13.39	17.6	2.05		W, $\frac{1}{2}$	See B.1-1	100 g/t $(\text{NH}_4)_2\text{SO}_4$ 24 g/t H_2SO_4 5 ppm Cl^- 670 hrs (total 1370 hrs)	- (.017)	No visible effect.
B.1-10	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-7	2 g/t Cu	.017 (.021)	No visible effect.
	316-10	.059	12.32	17.33	2.63		W, $\frac{1}{2}$	See B.1-7	pH 1.38	.011 (.019)	No visible effect.
	316L-8	.03	13.39	17.6	2.05		W, $\frac{1}{2}$	See B.1-7	150 g/t $(\text{NH}_4)_2\text{SO}_4$ 24 g/t H_2SO_4 5 ppm Cl^- 1160 hrs (2530 hrs)	.014 (.014)	No visible effect.
B.1-13	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-10	2 g/t Cu	.009 (.019)	No visible effect.
	316-10/	.059/	12.32/	17.33/	2.63/		W, $\frac{1}{2}$, C	See B.1-10	pH 1.38	.017/ (.019/	No visible effect.
	316L-8	.03	13.39	17.6	2.05				100 g/t $(\text{NH}_4)_2\text{SO}_4$ 24 g/t H_2SO_4 5 ppm Cl^- 770 hrs (3300 hrs)	.013 .014)	No visible effect.

W = welded, C = with crevice, $\frac{1}{2}$ = half immersed.

Table I
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
B.1-17	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-13	2 g/l Cu	(.016)	No visible effect.
	316-10/	.059/	12.32/	17.33/	2.63/		W, $\frac{1}{2}$, C	See B.1-13	pH 1.38	.005 (.013/	No visible effect.
	316L-8	.03	13.39	17.6	2.05				100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 620 hrs (3920 hrs)	.016)	No visible effect.
B.1-19	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-17	2 g/l Cu	(.016)	No visible effect.
	316-10/	.059/	12.32/	17.33/	2.63/		W, $\frac{1}{2}$, C	See B.1-17	pH 1.38	(.013/	No visible effect.
	316L-8	.03	13.39	17.6	2.05				150 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 960 hrs (4880 hrs)	.016)	No visible effect.
B.1-23	304-7	.055	8.4	18.34	0.11		W, $\frac{1}{2}$	See B.1-19	2 g/l Cu + 2.9 g/l Cu	.0034 (.0194)	No visible effect.
	316-10/	.059/	12.32/	17.33/	2.63		W, $\frac{1}{2}$, C	See B.1-19	pH 1.38 + 1.07	.020/ (.013/	No visible effect.
	316L-8	.03	13.39	17.6	2.05				100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 673 hrs (5553 hrs)	.0136 .016)	No visible effect.

W = welded, C = with crevice, $\frac{1}{2}$ = half immersed.

Table I
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
B.1-20	5 μ M	316 SS (porous sintered)					P,1	New	2 g/l Cu		Disintegrated.
	10 μ M	316 SS (porous sintered)					P,1	New	pH ~ 1.1		86.6 mg/yr (1.0%/yr) wt loss.
	20 μ M	316 SS (porous sintered)					P,1	New	100 g/l $(\text{NH}_4)_2\text{SO}_4$		131.0 mg/yr (2.7%/yr) wt loss.
	40 μ M	316 SS (porous sintered)					P,1	New	24 g/l H_2SO_4		204.2 mg/yr (2.4%/yr) wt loss.
	100 μ M	316 SS (porous sintered)					P,1	New	5 ppm Cl^- 393 hrs		377.4 mg/yr (3.4%/yr) wt loss.

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P = plain, I = completely immersed.

Table II

Corrosion Rates for Materials in Purge Solutions at the Normal Boiling Point

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
B.1-5	304-8/9	.05	8.4	18.34	.11		W, 1/2, A	New/New	2 g/l Cu	0.22/0.54	No visible effect.
	316-8/7	.059	12.32	17.33	2.63		W, 1/2, A	New/New	pH 1.13	0.04/0.04	No visible effect.
	C20-Cb3-7/8	.03	33.08	19.37	2.19		P, 1, A	New/New	100 g/l (NH ₄) ₂ SO ₄	0.10/0.03	No visible effect.
	EB26-1-11/14	.01max	.3max	26 nom	1 nom		P, 1/2, A	New/New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 96 hrs, 109°C	- /0.01	No visible effect.
B.1-14	304-14/15	.05	9.1	18.5	-		P, 1/2, C	See B.1-4	2 g/l Cu	0.02/0.10	Light etching.
	C20-Cb3-5/8	.03	33.08	19.37	2.19		S/P, 1/2, C	See 23/ B.1-5	pH 1.18 100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 426 hrs, 108°C	0.63/0.63	Light etching.
B.1-16	304-14/15	.05	9.1	18.5	-		P, 1/2, C	See B.1-14	2 g/l Cu	1.02/0.06 (.59/.08)	Light etching.
	C20-Cb3-5/8	.03	33.08	19.37	2.19		S/P, 1/2, C	See B.1-14	pH 1.18 100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 554 hrs (total 980 hrs), 108°C	0.06/1.77 (.30/1.07)	Light etching.
B.1-21	304-14/15	.05	9.1	18.5	-		G(T), 3/4	See B.1-16	2 g/l Cu	0.1/0.43	(.29/.29) Pitting, green stain
	C20-Cb3-5/8	.03	33.08	19.37	2.19		G(T), 3/4	See B.1-16	pH 1.10 100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 1504 hrs (total 2484 hrs), 108°C	0.056/0.028 (.15/.44)	Light etching.

P = plain, W = welded, S = stressed, C = with crevice.

1 = Completely immersed, 1/2 = half immersed, 3/4 = three-fourths immersed.

G(T) = designates samples gasketed with Teflon, A = activated.

Table III

Corrosion Rates for Materials under Leach Reactor Conditions

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	NI	Cr	Mo	Others					
B.1-2	304-18	.07	9.05	18.1	.26		W _{1/2}	New	2 g/l Cu	0.3	No visible effect.
	304L-18	.028	10.08	18.63	.19		W _{1/2}	New	pH 1.10	0.1	No visible effect.
	316-7	.059	12.32	17.33	2.63		W _{1/2}	New	100 g/l (NH ₄) ₂ SO ₄	0.6	No visible effect.
	316L-9	.03	13.39	17.6	2.05		W _{1/2}	New	24 g/l H ₂ SO ₄	0.7	No visible effect.
	D20-3	.039	27.83	19.2	2.05		P ₁	New	5 ppm Cl ⁻	0.1	No visible effect.
	C20-Cb3-4	.03	33.08	19.37	2.19		W _{1/2}	See Test 19	96 hrs	0.8	No visible effect.
	EB26-1-10	.01mx	.3mx	26 nom	1 nom		P _{1/2}	New	40 psi O ₂ , 110°C	0.2	No visible effect.
	Ti-2	.012	-	-	-	>99.8Ti	P _{1/2}	New		0.6	Light etching.
B.1-3	304L-18	.026	10.08	18.63	.19		W _{1/2}	See B.1-2	2 g/l Cu	1.4	No visible effect.
	316L-9	.03	13.39	17.6	2.05		W _{1/2}	See B.1-2	pH 1.04	1.0	No visible effect.
	D20-3	.039	27.83	19.2	2.05		P ₁	See B.1-2	100 g/l (NH ₄) ₂ SO ₄	0.4	No visible effect.
	C20-Cb3-4	.03	33.08	19.37	2.18		W _{1/2}	See B.1-2	36 g/l H ₂ SO ₄	0.9	No visible effect.
	304-18/11	.07/	9.05/	18.1/	.26/		W _{1/2} /	See B.1-2	5 ppm Cl ⁻	2.3/	No visible effect.
		.05	9.1	18.5			S _{1/2} ,C	New	94 hrs (1)	0.6	No visible effect.
	116-7/3	.059/	12.32/	17.33/	2.63/		W _{1/2} /	See B.1-2/	40 psi O ₂ , 110°C	1.3/	No visible effect.
		.018	11.67	16.84	2.14		S _{1/2} ,C	New		0.7	No visible effect.
	EB26-1-10	.01mx	.3mx	26 nom	1 nom		P _{1/2}	See B.1-2		0.4	No visible effect.
	Ti-2	.012	-	-	-	>99.8Ti	P _{1/2}	See B.1-2		0.2	No visible effect.
B.1-4	304-12	.05	9.1	18.5			P _{1/2}	New	2 g/l Cu	0.9	No visible effect.
	316-5	.018	11.67	16.84	2.14		P _{1/2}	New	pH 0.84	3.6	Light staining.
	304-14/15	.05	9.1	18.5	-		P _{1/2} ,C	New/New	75 g/l (NH ₄) ₂ SO ₄	1.0/0.9	No visible effect.
	304-13/	.05/	9.1/	18.5/	-		P _{1/2} ,C	New/New	36 g/l H ₂ SO ₄	0.9/	No visible effect.
	316-6	.018	11.67	16.84	2.14				5 ppm Cl ⁻	2.1	Light staining.
	C20-Cb3-1	.03	33.08	19.37	2.19		P _{1/2}	See 22	91 hrs	1.5	No visible effect.
	EB26-1-13	.01mx	.3mx	26 nom	1 nom		P _{1/2}	New	90 psi O ₂ , 115°C	0.8	No visible effect.

P = plain, W = welded, S = stressed, C = with crevice.

1 = completely immersed, 1/2 = half immersed.

(1) = loss of level during testing decreased immersion time.

Table III
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
B.1-6	304-10	.07	9.05	18.1	.26		W, $\frac{1}{2}$	See B.1-3	20 g/l Cu	1.1	No visible effect.
	316L-9	.03	13.39	17.6	2.05		W, $\frac{1}{2}$	See B.1-3	pH 2.05	0.8	No visible effect.
	304-15/11	.05	9.1	18.5	-		P, $\frac{1}{2}$	See B.1-4/	100 g/l $(\text{NH}_4)_2\text{SO}_4$	0.4/	No visible effect.
							S, 1, C	See B.1-3	10 g/l H_2SO_4	0.2	No visible effect.
	316-5/3	.018	11.67	16.54	2.14		P, $\frac{1}{2}$	See B.1-4/	5 ppm Cl^-	0.7/	No visible effect.
							S, 1, C	See B.1-3	75 hrs (1)	0.7	No visible effect.
	C20-Cb3-1	.03	33.08	19.37	2.19		P, 1	See B.1-4	50 psi O_2 , 125°C	0.5	No visible effect.
	E826-1-10	.03mm	.3mm	26 nom	1 nom		P, $\frac{1}{2}$	See B.1-3		2.3	No visible effect.

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P = plain, W = welded, S = stressed, C = with crevice.
1 = completely immersed, $\frac{1}{2}$ = half immersed.
(1) = loss of level during testing decreased immersion time.

As expected, corrosion rates measured at the purge solutions' normal boiling point were somewhat higher. While rates approaching 2 mills/year were found in one test, it is likely that the long term rate is less than 0.5 mills/year for either T304 or C20Cb3 stainlesses. No evidence of crevice corrosion or weld attack was found in these tests, and corrosion was not accelerated when the samples were "activated" by rubbing them with zinc. These samples were exposed to test conditions for about three and one half months, and although some evidence was seen of surface attack, the measured corrosion rates are so low that either T304 or C20Cb3 may be considered well suited for this service. The former would be preferred in view of its substantially lower cost.

The first three tests under leach reactor conditions, Table III, were carried out in solutions with high acidity and low copper content simulating initial conditions when the solutions would be most corrosive. The final test simulates conditions at the end of the leach where the copper contents were higher, acidities lower, but temperatures would also be higher, ~ 125°C vs. 110-115°C. The first three tests show the expected general increase in corrosion rate with acidity, and the same order of passivity found in the Task A.1 work, i.e., EB26-1 > C20Cb3 > T304 ~ T316. The results of the final test are of considerable interest: acidities were lower than for the first test by a factor of ten but corrosion rates were higher, apparently because the temperature was 15°C higher. In the temperature-composition range of interest, then, corrosion rates for T304 and T316 stainlesses ranged from 0.2 to 1.4 mills/year and averaged about 0.7 mills/year, and C20Cb3 was essentially the same. These are low enough to permit

these materials to be used with a corrosion allowance of 1/64" for the expected commercial life. Again, T304 stainless would be preferred in terms of cost.

Resistance of Composite Materials

The composition and sample designations of non-metallic materials tested are summarized in Table IV. The amount of weight each sample gained over the course of their exposure to solutions at ambient temperature, 50°C, and the normal boiling point are shown in Figs. 2-4 respectively.

The materials chosen for test were selected after screening a wide range of possible choices. Teflon, Viton, and EPR are all high quality, general purpose materials suitable for gaskets, O-rings, and seals. Weight gains are within limits specified by manufacturers, and no swelling or softening was noted on any samples tested. Two classes of composite materials were tested: fiberglass reinforced vinyl esters and chlorinated polyesters. Samples of several formulations were obtained from various manufacturers to determine the range of properties which might be encountered. The results shown in Figs. 2-4 are generally as expected, in that there is significant variability from formulation to formulation within a resin class and the materials pick up more weight, and do so more rapidly, at higher temperatures. While the chlorinated polyesters showed somewhat lower weight gains at higher temperatures, they also showed somewhat more tendency to delaminate and wicking was much more pronounced. However, they were dimensionally stable, and much of the problem apparently stemmed from less than adequate edge sealing by the sample supplier. The reason for the high initial weight gain and subsequent (relative) weight loss was not apparent, and may have been an artifact of the experiment since it is known that samples did loose weight on standing following the tests.

Table IV

Identification of Nonmetallic Materials Tested

<u>Sample Designation</u>	<u>Trade Name</u>	<u>Composition</u>	<u>Form Tested</u>
Q-1	Teflon	Fluorocarbon	O-Ring
Q-2	Viton	Fluorocarbon	O-Ring
Q-3	EPR	Ethylene-Propylene Rubber	O-Ring
R-1	Epoxy	Epoxy	Coupon
R-2	Derakane	Vinyl Ester	Coupon
D-411	Derakane	Vinyl Ester	Coupon
D-470	Derakane	Vinyl Ester	Coupon
D6000-6	Duracor	Vinyl Ester	Coupon
197/3-382-20	Hetron	Chlorinated Polyester	Coupon
72L-6-7,8,9	Hetron	Chlorinated Polyester	Coupon
A-382	Atlak	Chlorinated Polyester	Coupon

Fig. 2. Weight gain of samples at ambient temperature

Fig. 3. Weight gain of samples at 50°C.

Fig. 4. Weight gain of samples at normal boiling point.

The response of the composite samples tested to applied stresses before and after testing in solutions at the normal boiling point is shown in Figs. 5. These curves show stress-strain behavior only qualitatively: the samples tested had widely varying dimensions, edging and perhaps other fabrication procedures were such that the materials' properties were not isotropic, and limitations of the test procedure were such that it was difficult to obtain highly reproducible results. The data points reported are the averages of deflections obtained as stress was first increased then decreased; while no hysteresis was observed consistently, readings might vary by $\pm .002$ " from point to point. The differences in deflection for a given sample when placed label up or label down are a measure of the nonisotropic nature of the material. Deflection readings obtained after immersion in boiling test solution could not be considered changed unless they fell outside the range of uncertainty defined by the untested sample.

Hetron 197/3-382 and 72L-6 (chlorinated polyester) samples were tested new and after exposure to boiling purge solutions for 300 and 600 hours, although different samples of each material were tested in this sequence. Figures 5A and 6A show that there was a definite loss in flexural strength for Hetron after 300 hours of testing, although the magnitude was not great. Figure 5B does not show further loss of strength on testing to 600 hrs - note the label down results - but the results of Fig. 6B are quite definite. After 600 hours there was a distinct loss of strength and, in fact, the sample cracked with an audible snap when tested in the label up position.

The magnitude of the deflections in the sample of Duracor D6000 are lower than for Hetron at a given applied stress because the sample piece was

Fig. 5A. Stress-deflection behavior of Hetron 197/3-382.

Fig. 5B. Stress-deflection behavior of Metron 197/3-382.

Fig. 6A. Stress-deflection behavior of Hetron 72L-6

Fig. 6B. Stress-deflection behavior of Heltron 72L-6.

Fig. 7. Stress-deflection behavior of Duracor D6000

thicker, so the scale has been expanded by a factor of five to accentuate the results. The results do not show a significant loss of flexural strength; indeed, in the label down position the sample appears to have been stiffened somewhat. However, since the magnitude of the changes are less than the magnitude of the deflection differences for the unexposed sample in the label up and label down positions, it is not possible to conclude unequivocally that a loss or gain in strength has occurred.

These tests, and the weight gain tests reported above, are useful primarily for indicating the general behavior of classes of materials in the intended service. The behavior of process equipment in a given case reflects the skill of the fabricator and the care taken in the design and installation of the equipment and auxiliaries to a much greater extent than is the case for alternative, metallic construction materials. Of all possible materials surveyed, the vinyl esters and chlorinated polyesters typified by Derakane[®] (Dow Chemical) and Hetron[®] (Asland Chemical) resins are most likely to be most serviceable in this application, especially at temperatures above 50°C. And of these, the vinyl esters appear to retain superior mechanical properties after exposure to solutions at their normal boiling points.

Crevise Corrosion Studies

The results of an extensive series of autoclave tests, under simulated scrubber conditions, which were directed towards gaining a better understanding of the crevice corrosion phenomena in this system are summarized in Table V.

All tests except Nos. 48(a) and 49 took place in an unstirred, closed autoclave, and, except for tests No. 43, 47 and 48 were carried out in the "standard" test solution which contained, nominally, 2 g/l Cu, 25 g/l H₂SO₄,

Table V

Crevice Corrosion Test Log

Test No.	Sample Designation	Sample Composition, %					Sample Heat	Sample History	Solution Comp. Test Duration	Corrosion Rate, MPY	Comments
		C	Al	Cr	Mo	Others					
35	51-Ti-1	.012	-	-	-	>99.8 Ti	G(T), 1/4	See 31	1.96 g/l Cu + 1.85	0.75	Light crevice corrosion
	51-Ti-2	.012	-	-	-	>99.8 Ti	G(T), 1/4	See 34	pH 1.13 + 1.12	13.6	Light crevice corrosion, pitting
	FP-11	Commercially pure titanium.					P, 1/2	New	100 g/l (NH ₄) ₂ SO ₄	0.043	No effect
	Ti-Pd	(Ti-0.20% Pd Nom)					P, 1/4	New	5 ppm Cl ⁻	0.086	No effect
36	Ti-50-1	(Ti-50A Nom)	-	-	-	N, .03 O, .015 H, .015 Fe, .2	G(T), 3/4	New	2.29 g/l Cu + 1.97	-	Light etching under gasket
	Ti-50-2	(Ti-50A Nom)	-	-	-	N, .03 O, .015 H, .015 Fe, .2	G(A), 3/4	New	pH 1.12 + 1.26	0.88	Light etching and pitting under gasket
	Ti-Pd-1	(Ti-0.20% Pd Nom)	-	-	-	Pd, .15 N, .25 O, .015 H, .015 Fe, .15	G(A), 3/4	New	100 g/l (NH ₄) ₂ SO ₄	-	Light etching under gasket
	Ti-Pd-2	(Ti-0.20% Pd Nom)	-	-	-	Pd, .15 N, .25 O, .015 H, .015 Fe, .15	G(T), 3/4	New	5 ppm Cl ⁻	0.060	Light etching under gasket
	Ti-12-1	TIMET Ti-CODE-12	-	-	-	-	G(A), 3/4	New	160 hrs	-	Light etching, red scale under gasket
	Ti-12-2	TIMET Ti-CODE-12	-	-	-	-	G(T), 3/4	New	175°C	0.096	Light etching under gasket
	Ti-71	Commercially pure titanium.	-	-	-	-	P, 1/4	See No. 35	-	-	No effect
	Ti-10	Ti-0.20% Pd, See above	-	-	-	-	P, 1/4	See No. 35	-	-	No effect
	51-Ti-1	.012	-	-	-	>99.8 Ti	G(T), 3/4	See No. 35	-	0.199	Etching, pitting under gasket
	51-Ti-2	.012	-	-	-	>99.8 Ti	G(A)	See No. 35	-	-	Etching, pitting under gasket
	316-1	.01	33.08	19.39	2.19	Cr+Ti, 8	G(A), 1	See No. 33	1.99 g/l Cu + .033	64.7	Crevice corrosion
	316-2	.03	33.08	19.39	2.19	Cr+Ti, 8	G(T), 1	-	pH 1.11 + 1.19	206	Crevice corrosion
	316-3	.03	33.08	19.39	2.19	Cr+Ti, 8	G(Cu), 1	See No. 34	100 g/l (NH ₄) ₂ SO ₄	202	Crevice corrosion
	316-7	.059	12.32	17.33	2.63	-	G(Cu), 1	-	5 ppm Cl ⁻ 175°C	223	Crevice corrosion
									48 hrs		

1 = fully immersed, 1/2 = half immersed, 0 = unimmersed.
P = P in (stretched), N = welded, C = stretched, G = with crevice.

G(1) = designation gasketed sample with Teflon

G(2) = designation gasketed sample with Asbestos

G(Cu) = designation gasketed sample with Copper

corrosion rates of gasketed samples based on exposed area.

Table V
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Comp. Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
38	51-Ti-1	.012	-	-	-	>99.8 Ti	G(T),1	See No. 36	2.2 g/l Cu + 2.09	.014	No visible effect
	51-Ti-2	.012	-	-	-	>99.8 Ti	G(A),1	See No. 36	pH 1.19 + 1.33	.055	No visible effect
	Ti-Pd-1	(Ti-0.20% Pd Nom) 0.8	-	-	-	Pd, .15 N, .25 O, .015 H, .125 Fe, .15	G(A),1	See No. 36	100 g/l (NH ₄) ₂ SO ₄	.041	No visible effect
39	Ti-Pd-2	(Ti-0.20% Pd Nom) 0.8	-	-	-	Pd, .15 N, .25 O, .015 H, .125 Fe, .15	G(T),1	See No. 36	304 hrs	.014	No visible effect
	Ti-50-2	(Ti-50A Nom) .08	-	-	-	N, .03 O, .25 H, .015	G(T),1	See No. 36	5 ppm Cl ⁻	-	No visible effect
	Ti-50-1	-	-	-	-	-	G(A),1		175°C	-	No visible effect
39	C20-Cb3-14	.07max	29 nom	20 nom	2 min		G(T),1	New	2 g/l + < .02	345	Crevice corrosion
	C20-Cb3-15	.07max	29 nom	20 nom	2 min		G(T),1	New	pH 1.15 + 1.24	402	Crevice corrosion
	C20-Cb3-16	.07max	29 nom	20 nom	2 min		G(A),1	New	100 g/l (NH ₄) ₂ SO ₄	846	Crevice corrosion
	C20-Cb3-17	.07max	29 nom	20 nom	2 min		G(Cu),1	New	5 ppm Cl ⁻	467	Crevice corrosion
	C20-Cb3-18	.07max	29 nom	20 nom	2 min		P,1	New	110 hrs, 175°C	92.9	Dark staining
40	C20-Cb3, Tube 1	.07max	29 nom	20 nom	2 min		G(T),1	New	2 g/l Cu	85.9	Corrosion rate for crevice area, crevice corrosion, light staining
	C20-Cb3, Tube 2	.07max	29 nom	20 nom	2 min		G(T),1	New	pH 1.10	79.7	Corrosion rate for crevice area, crevice corrosion, light staining
	C20-Cb3, Tube 3	.07max	29 nom	20 nom	2 min		P,1	New	100 g/l (NH ₄) ₂ SO ₄ 5 ppm Cl ⁻ 110 hrs, 175°C	1.5	Light staining

Table V
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
		C	Ni	Cr	Mo	Others					
41	C20-Cb3-19	.07mx	29 nom	20 nom	2 nom		P,1	New	2.1 g/l Cu pH 1.20	2.8	Light stain on face and sheared edges.
	C20-Cb3-20	.07mx	29 nom	20 nom	2 nom		C(10X),1	New	100 g/l (NH ₄) ₂ SO ₄	2.0	Corrosion rate for uncrevice area, light stain on faces, sheared edges, under crevice.
	C20-Cb3-21	.07mx	29 nom	20 nom	2 nom		C(10X),1	New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 64 hrs, 175°C	2.9	Corrosion rate for uncreviced area, no visible effect.
42	C20-Cb3-22	.07mx	29 nom	20 nom	2 nom		P,1	New	2.15 g/l Cu	1.9	No visible effect.
	C20-Cb3-23	.07mx	29 nom	20 nom	2 nom		C(10X),1	New	pH 1.14	1.9	Corrosion rate for uncreviced area, no effect.
	C20-Cb3-24	.07mx	29 nom	20 nom	2 nom		C(10X),M(P),1	New	100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 164 hrs, 175°C	1.5	Corrosion rate for uncreviced area, no visible effect.
43	31-71-1	.012	-	-	-	>99.8Ti	P,1	See 38	2.00 g/l Zn	-	No visible effect.
	C20-Cb3-5	.03	33.08	19.37	2.19		S,1	See 21	pH 1.15	117	Dark stain.
	19-124-7	.055	.84	18.34	.11		W,1	See B.1-23	100 g/l (NH ₄) ₂ SO ₄	2600	Welded area attacked more severely than the rest.
	316-10	.059	12.32	17.21	2.63		W,1	See B.1-23	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 39 hrs, 175°C	1200	Heavy etching.
44	C20-Cb3-25	.07mx	29 nom	20 nom	2 nom		P,1	New	2.21 g/l Cu + 0.89	3.4	No visible effect.
	C20-Cb3-26	.07mx	29 nom	20 nom	2 nom		C(222),1	New	pH 1.17 + 1.16	75	Corrosion rate for crevice area.
	C20-Cb3-27	.07mx	29 nom	20 nom	2 nom		C(562),1	New	100 g/l (NH ₄) ₂ SO ₄		Dark stain under crevice rim.
	C20-Cb3-28	.07mx	29 nom	20 nom	2 nom		C(562),1,M(B)	New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 141 hrs, 175°C	103 182	Corrosion rate for crevice area. Corrosion rate for crevice area.

C(C) = % crevice, P = plain, S = stress, W = welded, C(T) = designates gasketed sample with Teflon.
M(F) = Machined (front), M(B) = machined (both side), 1 = full immersed.

Table V
(continued)

Test No.	Sample Designation	Sample Composition, %					Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	
		C	Ni	Cr	Mo	Others					
45	C20-Cb3-29	.07mx	29 nom	20 nom	2 nom		P,1	New	2.17 g/l Cu + 2.07	2.5	No visible effect
	C20-Cb3-30	.07mx	29 nom	20 nom	2 nom		C(13%),1	New	pH ~1.20 + 1.15	75	Corrosion rate for creviced area.
	C20-Cb3-31	.07mx	29 nom	20 nom	2 nom		C(16%),1	New	100 g/l (NH ₄) ₂ SO ₄	23	Corrosion rate for creviced area.
	C20-Cb3-32	.07mx	29 nom	20 nom	2 nom		C(59%),1	New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 110 hrs, 175°C	32	Corrosion rate for creviced area, edges undercut > 1000 MPY.
46	C20-Cb3-33/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/O	New	2.15 g/l Cu + 17 ppm	360/	Crevice corrosion. Lightly bolted.
	C20-Cb3-34	.07mx	29 nom	20 nom	2 nom		G(T),1,C/O	New	pH 1.16 + 1.30 100 g/l (NH ₄) ₂ SO ₄	320	Cut at edges of metal. Crevice corrosion. Lightly bolted.
	C20-Cb3-35/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/O	New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻	160/	Cut at edges of metal. Crevice corrosion. Tightly bolted. Cut at
	C20-Cb3-35	.07mx	29 nom	20 nom	2 nom		G(T),1,C/O	New	91 hrs, 175°C	120	edges of metal. Clean under gasket. Crevice corrosion. Tightly bolted. Cut at
47	C20-Cb3-37	.07mx	29 nom	20 nom	2 nom		P,1	New	4.84 g/l Cu + 1.64	2.2	No visible effect.
	C20-Cb3-38/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/R	New	pH 1.19 100 g/l (NH ₄) ₂ SO ₄	75/	Crevice corrosion. Lightly bolted (torque:
	C20-Cb3-39	.07mx	29 nom	20 nom	2 nom		G(T),1,C/R	New	24 g/l H ₂ SO ₄ 5 ppm Cl ⁻	150	5 inch-pound), cut at edges of gasket. Crevice corrosion. Lightly bolted, (torque:
	C20-Cb3-40/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/R	New	91 hrs, 175°C	140/	5 inch-pound), cut at edges of gasket. Crevice corrosion. Tightly bolted. (torque:
	C20-Cb3-41	.07mx	29 nom	20 nom	2 nom		G(T),1,C/R	New		80/	60 inch-pound), cut at edges of gasket. Crevice corrosion. Tightly bolted. (torque:

C(X) = X crevice, P = plain, G(T) = designated gasketed sample with Teflon, 1 = full immersed,
C/O = with crevice, gasket overlap. C/R = with crevice, gasket recessed.

Table V
(continued)

Test No.	Sample Designation	C	Ni	Cr	Mo	Others	Sample State	Sample History	Solution Composition Test Duration	Corrosion Rate, MPY	Comments
*48(a)	C20-Cb3-42/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/B	New	5.30 g/l Cu + 90 ppm pH 1.18 + 1.24	390	Crevise corrosion, cut at edges of metal.
	C20-Cb3-43/	.07mx	29 nom	20 nom	2 nom		G(T),1,C/B	New	100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 94 hrs, 175°C	300	Crevise corrosion, cut at edges of metal.
	C20-Cb3-44/	.07mx	29 nom	20 nom	2 nom		G(T),1,C	New		390/	Crevise corrosion, cut at edges of metal.
	C20-Cb3-45	.07mx	29 nom	20 nom	2 nom		G(T),1,C	New		26.6	No visible effect.
48(b)	C20-Cb3-46/	.07mx	29 nom	20 nom	2 nom		G(T),1,C	New	5.30 g/l Cu pH 1.18	115/	Crevise corrosion, cut at edges of metal.
	C20-Cb3-47	.07mx	29 nom	20 nom	2 nom		G(T),1,C		100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ + 5 ppm Cl ⁻ 94 hrs, 175°C	2.2	No visible effect.
*49	C20-Cb3-48	.07mx	29 nom	20 nom	2 nom		G(T),1,C/B	New	2.18 g/l Cu + 0.93 pH 1.20 + 1.19	3.3	No visible effect
	C20-Cb3-49	.07mx	29 nom	20 nom	2 nom		G(T),1,C/B	New	100 g/l (NH ₄) ₂ SO ₄ 24 g/l H ₂ SO ₄ 5 ppm Cl ⁻ 64 hrs, 175°C	710	Crevise corrosion, cut at edges of metal.
	C20-Cb3-50/	.07mx	29 nom	20 nom	2 nom		G(T),1,C	New		1200/	Crevise corrosion, cut at edges of metal.
	C20-Cb3-51	.07mx	29 nom	20 nom	2 nom		G(T),1,C	New		430	Crevise corrosion, cut at edges of metal.

G(T) = designates gasketed sample with Teflon, 1 = full immersed. C = with crevice.

C/B = with crevice mounted on stirrer blade.

*Test No. 48(a), and 49 in stirred autoclave.

100 g/l $(\text{NH}_4)_2\text{SO}_4$, and 5 ppm Cl^- . Tests were carried out at 175°C with durations ranging from 48 to 304 hours. While some testing was carried out on titanium and T304 and 316 stainlesses, C20Cb3 samples with varying types of gasketing arrangements were the subject of most tests. Tests No. 48(a) and 49 took place in a stirred autoclave, and for tests No. 47 and 48 a 5 g/l copper solution was tested while 2 g/l zinc was used in test No. 43.

Tests No. 35, 36, and 38 were directed towards reverifying the suitability of titanium in this service, and various alloys and gasketing materials were tested. With one exception, test No. 35, sample Ti-2, there were only the lightest evidences of corrosion in the crevices and the relatively severe (for Ti) corrosion found in this test did not reoccur in subsequent tests of even longer duration. There is no evidence, based on these tests, that either one alloy or one gasket material is to be preferred: all have shown acceptable service under the conditions tested. Test No. 43 illustrates the importance of the cupric ion in this system in passivating austenitic stainless steels; zinc would be effective in removing H_2S but does not maintain the scrub solution's potential high enough to passivate the stainless.

The variables investigated in the remaining tests include gasket material, percent area gasketed, bolting torque, and solution velocity. In general, the results of these tests are so highly variable that it is not possible to draw unequivocal conclusions as to the mechanisms involved.

The effect of gasket material, if any, is not systematic (see tests No. 37, 39), and Teflon was used in the majority of the remaining tests. It had been observed that, qualitatively, crevices which were poorly or loosely made up seem to corrode more severely than tightly made up ones. While the

results of tests No. 46 and 47 appear to be equivocal on the effects of bolting torque, it was observed that the extent of corrosion under the gasket was, in fact, lower for the highly torqued samples. Most of the weight loss in these tests occurred in relatively deep cuts, with penetration rates which exceeded 1000 mills/year by direct measurement, at the edge of the gasket-metal interface.

Creviced samples were mounted on stirrer blades (tests No. 48(a), 49) to determine whether or not high solution velocities by the edge of a crevice would reduce or prevent corrosion. The results show that turbulence alone is not sufficient, although one sample (C20-48) was unaffected and another (C20-43) showed no visible sign of attack. The test series in which the percent area creviced was varied, Nos. 40-45, was carried out to determine if a high ratio of cathodic-to-anodic area would produce (require) current densities which were high enough to prevent corrosion. No (or very light) corrosion was observed in two tests at low (10%) fraction areas creviced, while in the other tests the corrosion rates under the creviced areas were of the order of 100 mills/year for creviced areas which ranged from 20-60%. While high, this is at least an order of magnitude lower than observed in other tests where crevice corrosion was severe at the gasket-metal interface.

It is useful at this point to recall the results of uncontrolled corrosion experiments which have taken place during the operation of the 4" laboratory and 8" field scrubber units. Both of these units, their auxiliaries and piping are assembled in ways that result in the formation of many crevices throughout the system. The slurry circulatory piping on the 8" unit contained both gasketed and screwed joints, and the 4" column contained numerous

screwed joints and compression fittings, all presenting excellent locations for crevice corrosion. The laboratory scrubber has been in service intermittently for a period which has totaled a few hundred hours, and field testing on the 8" column totaled 50 hours with the final campaign lasting for 30 hours. In autoclave tests, corrosion has been initiated in less than 48 hours (see Test No. 37). Solutions compositions varied from more to less corrosive than the "standard" solutions used in most autoclave tests, but probably contained somewhat less acidity on a time weighted bases. One feature of operation in these scrubbers, however, which differed from the autoclave tests was the intermittent presence of oxygen, admitted on shutdown; oxygen which was removed by a N₂/steam purge in laboratory coupon testing.

Both scrubbers have been thoroughly examined, and no evidence of the type of crevice corrosion found in the autoclave tests was observed. Flanged joints on the 8" column piping were not attacked either under the gasket or at the gasket-metal interface. Even poorly made up, slowly leaking screwed joints on the 4" column and its piping were not corroded. Isolated evidence of attack in confined spaces on the Greylok[®] flanges, in the 8" columns' downcomer seal, and on a corrosion monitoring probe (!) shows that corrosion by such a mechanism is always possible, but perhaps not likely in an operating system which is correctly designed. In the face of this experience on "real" systems, it might be concluded that the frequent and often severe crevice corrosion observed in autoclave tests was an artifact of the experimental technique. Unfortunately, only longer term testing under stable conditions in a "real" system can provide the necessary data to resolve the problem.

Impact on the Design of a Commercial System

These material suitability tests have shown, as anticipated, that austenitic stainless steels will be generally suitable for use in equipment external to the scrubber. Type 304 stainless will be suitable for use in pumps, piping and valves, tankage, heat exchangers, agitators, and as the major material of construction for the regeneration reactor at temperatures up to at least 125°C.

Where its use will present cost advantages, composite materials such as Derakane (fiberglass reinforced vinyl esters) are suitable for long term use at temperatures up to at least 50°C, and are able to tolerate excursions up to the normal boiling point for shorter periods of time without adverse effect. Materials savings of approximately 50% are possible vis-a-vis the use of T304 stainless steel in a 50,000 gal atmospheric pressure storage tank, for example.

Standard, high quality elastomers and gasket materials (Teflon, Viton, etc.) will be generally suitable up to the maximum temperature recommended by manufacturers.

The mechanisms governing crevice corrosion of austenitic stainless steels at scrubber conditions are not well understood. Laboratory and field tests in 4" and 8" scrubbers, though discontinuous and of short duration, suggest that it may be possible to design around the problem. The incentives for demonstrating this are obvious; C20Cb3 is considerably less expensive than titanium. Furthermore, if it can be shown that crevice corrosion is not an unmanageable problem with C20, and the system control and operating philosophy is effective in maintaining low acidity and high copper contents under all conditions, the use of the less expensive T304 or T316 alloys may be possible at significant savings.

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EIC Corporation
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Newton, Massachusetts 02158

CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task B.2

Roast Regeneration Studies

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SUMMARY

Sufficient laboratory work has 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 and 300°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 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. It is anticipated that conditions can be established to effect rapid and complete roasting without encountering appreciable volatilization of SO₂ and SO₃, thereby eliminating the need for secondary scrubbing.

GENERAL CONSIDERATIONS

The roast alternative to the regeneration of copper sulfate from copper sulfide scrubber solids has the possibility of lower capital costs as compared with the pressure leach alternative. This is especially possible for a very large installation treating solids from several industrial-scale scrubbers. Operating costs, particularly as influenced by yields and acid neutralization and energy requirements, will also figure importantly in the comparative overall economics. Thus, a technical feasibility study of roast regeneration with use of small laboratory equipment is warranted, even though regeneration by pressure leaching has been shown capable of rapid and essentially quantitative conversion to copper sulfate under mild operating conditions.

As has been shown, the scrubber solids typically settle rapidly but form a relatively low-density cake. Owing to their microporous nature, complete drying is difficult, and removal of water even to the minimum degree necessary to permit autogenous (self-sustained) roasting may require more energy than would be desirable.

With respect to yields, it is important that loss of copper be kept to a minimum since, otherwise, reagent and associated costs would become unacceptable. It may not be as important to react the copper sulfide completely to oxidized copper because of the possibility of recycling small amounts of unreacted sulfide. The feasibility of this will depend upon the requirements for a solids purge to counter the buildup of "rock dust" from the underground formation, acid-insoluble impurities in the purchased copper sulfate, and other fine "debris."

Acid neutralization considerations are very important. For geothermal steams within the anticipated range of compositions and accounting for the co-scrubbing for the major portion of the ammonia, the process is a net producer of acid. Thus, acid that would be required for dissolving the oxidized copper from roasting should clearly be provided by scrub solution (about 0.3M in H_2SO_4) rather than by purchased sulfuric acid, insofar as possible.

The composition of the copper sulfide has a strong influence on the acid requirements for roast regeneration. At one extreme, sulfation roasting of CuS should consume the minimum amount of acid:

In industrial practice, however, sulfation roasting produces appreciable oxide, with formation of SO₂,

so that a mixture of oxide and sulfate is obtained. At the Cu₂S extreme of composition, to which scrubber solids correspond more closely, sulfate cannot even in principle be the sole reaction product in the absence of acid. This is because of insufficient sulfur in relation to copper:

In wet roasting in the absence of acid, the sulfation reactions would be similar except that thermal hydrolysis in the solution could result in the formation of solid copper sulfates, most probably antlerite, 2Cu(OH)₂·CuSO₄, or brochantite, 3Cu(OH)₂·CuSO₄. These basic copper sulfates are acid-soluble at lower temperature, so that in the wet roasting of Cu₂S in the presence of acid, the reaction should result in an entirely acid-soluble product mix.

It may be supposed that, in wet roasting, the solution should preferably be confined to a thin film of liquid covering the solid, i.e., a moistened solid, rather than a slurry. Otherwise, relatively slow mass transport in the liquid would limit the rate of oxidation. Furthermore, accumulation of soluble reaction products in the liquid layer would require that the liquid be replaced frequently or continuously by fresh solution. Finally, there is the consideration that above 100°C,

vaporization of water from the added solution can impose heavy heat requirements.

With the foregoing perspectives as background, the laboratory study was designed to ascertain the critical parameters and reaction conditions in roast regeneration. No attempt was made to assemble and operate a roaster capable of holding quantities of solids large enough to provide even preliminary design information. This gap in information is scheduled to be filled by use of a vendor's equipment with scrubber solids that will become available in quantity during operation of the large field unit.

EXPERIMENTAL APPROACHES

It was considered outside the scope of Task B.2 to set up and operate a fluid-bed roaster. Rather, effort was focused on broadly characterizing the chemistry and kinetics of the roasting of scrubber solids. Accordingly, results are limited to those obtained in static experiments conducted in a laboratory oven or tube furnace. This approach dictated that, for the most part, thin layers and, hence, gram-size samples of solid be employed.

The minimum pretreatment of scrubber solids consisted of removing initially present oxidation products by dissolution with 1M H_2SO_4 . This operation was generally carried out by use of a Millipore filter assembly which accommodated 4.7-cm diameter filter paper. Active filter area was 9.6 cm^2 . Relatively coarse (10- μm pore size), Teflon filters were found most suitable with respect to filtration speed, chemical resistance and residual mechanical strength.

The extent of reaction was determined by measuring the copper concentration of a solution of the oxidation product. Analysis was usually by direct spectrophotometry at the near-infrared absorption peak (825 nm) of $Cu^{2+}(aq.)$. The basis for this estimation was the total copper in the sample as given by the sum of dissolved copper in successive samples plus the analysis for copper in the unreacted solids, if any.

In all roast experiments involving interim sampling for oxidized copper, the filter cake was left intact on the filter paper, which was

transferred out of the oven to the filter flask as required. The operation of interim acid washing necessitated that the sample be out of the oven for about 3 min. A time out of the oven of 30-45 sec was generally sufficient for periodic solution addition during wet roasting.

Roast experiments in the tube furnace were carried out with use of porcelain boats having an inside bottom area of 8.0 cm^2 . In this case, interim sampling was not performed on a given charge of solids; instead, a number of boats was used to permit a sequence of reaction times under substantially identical conditions. The ID of the quartz furnace tube was 60 mm; its length was 120 cm, so that approximately 20 cm of tube projected out of each end of the furnace. The samples were located well within the heated zone of the 80-cm long furnace, so that the temperature should have been the same for all samples.

With the exception of a few comparison roast tests with synthetic CuS , the source of copper sulfate samples was a drum of decanted scrubber solids from the December 1976 field test at The Geysers. This slurry was also the source of scrub solution in selected wet roasting experiments.

Four major variants of fixed-bed roasting were investigated to varying degrees of detail. These include:

- a. Continuous dry roasting, wet or dry charge (mainly the latter).
- b. Interrupted dry roasting, with periodic removal of oxidation products.
- c. Wet roasting with intermittent addition of solution and with periodic removal of oxidation products.
- d. Wet roasting with continuous addition of solution.

The major experimental emphasis was on wet roasting with intermittent addition of solution and on continuous dry roasting.

WET ROASTING

Reproducibility

The experimental techniques employed would not, one would suppose, lend themselves to providing quantitative kinetic data. Nevertheless,

in two tests addressed to this question, the results were sufficiently reproducible to give confidence, in this study generally, to indicated trends with changes in experimental parameters. Data for the two tests under consideration, one at 150°C (Expt. 9) and the other at 160°C (Expt. 17), are summarized in Figure 1. In all four runs shown, the conditions included removal of oxidation products by acid washing and water rinsing once per hour, with intermediate moistening of the residues with 1-ml portions of distilled water at 20-min intervals (i.e., 2 ml H₂O per hour per sample).

In Expt. 9, the difference between the duplicate runs amounted to about 12%. The observed difference is in the direction expected for different initial thicknesses of filter cake (48 and 51 mg Cu/cm² for Runs A and B, respectively). On the other hand, the initial amounts of solids were closely similar in Expt. 17 (83 and 82 mg Cu/cm² for Runs A and B, respectively), and the measured difference was still about 10%. Therefore, the results of the two experiments may be taken as indicative of the reproducibility of the technique.

Although the experiments to be described in the next section, from which temperature coefficient of rate was estimated, involved wet roasting with sulfuric acid rather than with water, the data of Figure 1 are consistent with a relatively small temperature coefficient (over the limited interval 150-160°C).

Temperature Coefficient

The activation energy has been estimated for the case of wet roasting with intermittent addition of solution. Results of four runs having significant parameters substantially the same, except for temperature, are plotted in Figure 2. The experimental conditions were:

- Initial solids in the range 0.38-0.66g Cu (40-69 mg Cu/cm²).
- Acid removal of oxidation products and water washing once per hour.

Fig. 1: Results of duplicate wet-roast experiments with water moistening. Quantities in parentheses are weights of contained copper in the initial filter cakes.

Fig. 2: Rates of wet roasting with 1M H_2SO_4 at 90°C (Expt. 23), 150°C (Expt. 6A), 160°C (Expt. 7B) and 200°C (Expt. 18).

- Addition of 1 ml of 1M H_2SO_4 to the acid- and water-washed solids at 20-min intervals beginning just prior to reinsertion into the oven, i.e., 3 ml/hr.

The operations of removing oxidation products by acid washing and adding solution to the unreacted residue were performed outside of the oven and evidently quenched the sample temperature at intervals. The result was that the time-average reaction temperature was less than the oven temperature. The rate information summarized in Figure 2 should be viewed with this inherent experimental limitation in mind.

The reaction rates are seen qualitatively to vary in the expected way with oven temperature. The fall-off in amount of copper oxidized per unit time (the slopes in Figure 2) is at least partly due to a decrease in interfacial area as the number and average size of the particles decreases during the course of the reaction. This effect can often be demonstrated by employing the function $1-(1-F)^{1/3}$, where F is the fraction reacted. This function, plotted versus F in Figure 3, is derived for a collection of isotopically reacting, uniform particles of regular geometry. In practice, the function can often be used to account semi-quantitatively for the variation of the specific reaction rate (amount reacted per unit interfacial area per unit time) of irregularly shaped particles with extent of reaction. A replot of the data of Figure 2 as $1-(1-F)^{1/3}$ versus t on a log-log graph substantially conforms to this experience (Figure 4).

Scanning electron microscopy (described below) of unreacted sulfide residues from partially wet-roasted solids revealed significant consolidation of the high-porosity starting material into denser, smoother surfaced and more crystalline particles. Consequently, the inferred decrease in surface area in those cases probably resulted as much or more from this mechanism as from the assumed decrease in average size of the reacting particles. Thus, the utility of the function $1-(1-F)^{1/3}$ in describing the kinetics of roast-regeneration of scrubber solids is primarily one of normalization and extrapolation and not necessarily indicative of a shrinking particle size.

Fig. 3: Nature of the function $1-(1-F)^{1/3}$, commonly employed to correct the extent of reaction, F , for decreasing interfacial area of solid particles undergoing reaction.

Fig. 4: Log-log plots of normalized fraction reacted vs. time of wet roasting with 1M H_2SO_4 . Upper left: replots of data of Fig. 2 (same symbols). Lower right: $\circ$ = Expt. 19; $\odot$ = Expt. 21. See Table 1 for temperatures.

With the foregoing qualification concerning detailed interpretation, a slope of unity in a plot of $\log[1-(1-F)^{1/3}]$ vs. $\log t$ means that the specific reaction rate, as measured by the time derivative of $1-(1-F)^{1/3}$, is sensibly constant. The kinetic data of Figure 4 correspond approximately to a constant specific reaction rate (zero order with respect to time), although the two-segment nature of Run 23 data is evident in both graphs. When the data points of Figure 4 are connected with lines of assumed unit slope, extrapolated times for complete reaction, t_{100}^* , are obtained as listed in Table 1.

TABLE 1
KINETIC DATA FOR ESTIMATING ACTIVATION ENERGY
FOR WET ROASTING (1M H_2SO_4)

Expt.	T, °C	t_{100}^* , hr	$\ln (100/t_{100}^*)$	$1/T, ^\circ K^{-1}$
18	200	6.6	2.72	0.00211
7B	160	9.7	2.33	0.00231
6A	150	10.3	2.27	0.00236
23	90	26.7	1.32	0.00275
19	160	5.2	2.96	0.00231
21	140	6.5	2.73	0.00242

t_{100}^* = extrapolated time for complete reaction,
based on assumed linear reaction kinetics.

On taking the reciprocal of time for complete reaction as a measure of specific reaction rate, the Arrhenius plot shown in Figure 5 is obtained. From the slope of the straight line fitted to the points, an activation energy of 4.3 kcal/mol is calculated. This value is rough and is probably a lower limit, owing to the greater temperature-quenching effect at higher oven temperatures. Additional results are consistent with this estimated low value of the activation energy. Thus, for Expts. 19 (160°C) and

Fig. 5: Log rate vs. reciprocal temperature correlation of wet-roast data. T is absolute temperature, $^{\circ}K$; t_{100}^* is extrapolated time for complete reaction (Fig. 4 and Table 1).

21 (140°C), the supplemental data shown in Figure 4 were obtained. Extrapolation with assumed unit slope, as above, leads to the two points above the line in Figure 5. The oxidation rates were higher, evidently because conditions were different (0.57 and 0.55g Cu in the initial charge, but acid-moistening at the greater frequency of 0.5 ml of 1M H₂SO₄ each 10 min, i.e., 3 ml/hr). Significantly, the slope over this very limited interval of temperature is fully compatible with that for the wider temperature range.

The temperature coefficient of reaction rate in wet roasting is clearly of lesser magnitude than values typical of chemical reaction control (≥ 10 kcal/mol). In low temperature roasting under the specified conditions, the rate is evidently controlled by mass transfer processes. Consequently, at temperatures between the normal boiling point of water and the temperature of geothermal steam, other conditions can be expected to have an appreciable influence on the time required for roast-regeneration to copper sulfate. The effects of nonthermal parameters are scoped in the following sections.

Effect of Filter Cake Thickness

As anticipated, the accessibility of the solid surface to the fluid reactants (namely, oxygen and acid) is a determinant of reaction rate. This parameter was varied by changing the initial thickness of filter cake. Filter cake thickness may be roughly estimated as follows. In two tests with amounts of solids in the range employed in the wet-roast experiments, the weight relationships were:

$$\left. \begin{array}{l} 0.74\text{g solids after drying: liquid/solid} = 1.43 \text{ g/g} \\ 2.49\text{g solids after drying: liquid/solid} = 1.28 \text{ g/g} \end{array} \right\} \begin{array}{l} \text{average ratio} \\ = 1.36 \text{ g/g} \end{array}$$

For typical scrubber solids, Cu_{1.9}S, the percentage of copper is about 79%, and the solids density is about 5.5 g/cm³ (as estimated by interpolation between the densities of CuS, 4.6 g/cm³ and Cu₂S, 5.6 g/cm³). The volume of copper sulfide corresponding to 1g of Cu is, then,

$1/(0.79 \times 5.5) = 0.23 \text{ cm}^3$, and the volume of liquid filling the pores is $1.36/0.79 = 1.72 \text{ cm}^3$, or a total volume of 1.95 cm^3 . Given a filter area of 9.6 cm^2 , the effective cake thickness is estimated as $1.95/9.6 = 0.20 \text{ cm}$, or 2.0 mm .

Actually, since excess liquid was in every case removed by aspiration through the filter, some amount of air-filled voids doubtless existed within the cake. Granting this, the rough figures 2.0 mm/g contained copper and $0.65 \text{ g solids/g cake}$ are likely too low and too high, respectively. Consistent with this reasoning, the thickness of a filter cake containing 3.0 g Cu was visually estimated to be $12\text{--}15 \text{ mm}$, rather than the 6 mm one would calculate on the basis of negligible void volume. Roughly, then, actual cake thickness in these experiments can be considered to be about 4 mm per g of contained copper or, more generally, about 4 cm per g of contained copper per cm^2 of filter area.

In wet-roasting of thin filter cakes, other parameters being the same, results consistently showed a strong inverse correlation between oxidation rate and filter cake thickness. This behavior is illustrated for three experiments in Figure 6. In Expt. 6, the times for complete reaction were almost exactly proportional to the initial amounts of solids. While this is probably a fortuitous result, the data of Expts. 5 and 22, 24 also indicate the reaction rate to correlate with filter cake thickness.

The experimental conditions not explicitly shown in Figure 6 are:

- Expt. 5: Acid wash each hour; moisten with 1 ml of $1 \text{M H}_2\text{SO}_4$ midway during the hour roast interval (i.e., 1 ml/hr), 125°C .
- Expt. 6: Same, except moisten with 1 ml of $1 \text{M H}_2\text{SO}_4$ at 20 and 40 min into the roast interval (i.e., 2 ml/hr), 150°C .
- Expts. 22 & 24: Acid wash and water rinse each half hour; moisten with 0.5 ml of $1 \text{M H}_2\text{SO}_4$ at the beginning of and at 10-min intervals during each half-hour roast period (i.e., 3 ml/hr), 160°C .

Fig. 6: Apparent effect of cake thickness in wet roasting of thin filter cake. Initial thickness, mm (approximate): Expt. 5A (2.8), 5B (1.2); 6A (2.4), 6B (1.4); 24 (2.7), 22 (1.2). Other conditions are given on p. 15.

Considering that, in addition to filter cake thickness, the rate of addition of acid and the frequency of removal of oxidation products were also varied in these experiments, the effects of the latter parameters are not directly separable. In a subsequent section, the results of experiments addressed to these parameters will be considered.

The foregoing data pertain to initial solids loadings in the range 40-95 mg/cm², or filter cake thicknesses in the range 1-3 mm. With heavier solids loadings, beginning at about 130 mg/cm², or ca. 4-mm cake thickness, modified behavior was observed (Figure 7). The initial rate (i.e., to the first sampling point) was slower for the thicker cake in terms of percent reacted, as anticipated. Subsequently, however, the oxidation rate accelerated and, for a time, exceeded that of the thinner cake. However, in operationally significant terms of amount of copper sulfide oxidized per unit time per unit area of filter, that measure of rate was higher for the thicker cake even in the first hour.

Additions of acid in Expt. 25 (Figure 7) were intended to be roughly in proportion to the initial sample weight, thus:

Expt. 25A (0.325g Cu initially): 0.5 ml 1M H₂SO₄ x 4 hr⁻¹

Expt. 25B (0.994g Cu initially): 2.0 ml 1M H₂SO₄ x 4 hr⁻¹

With this schedule, the amount of solution added relative to the amount of unreacted sulfide increased strongly with time.

A follow-up experiment was carried out to confirm the appearance of an inflection in the rate curve for thicker cakes. In Expt. 26 (Figure 8), initial cake thicknesses were roughly 3 and 12 mm. The cakes were left moistened with fresh 1M H₂SO₄ following acid washing and were moistened with 1M H₂SO₄ at 15-min intervals during the 1-hr roasting periods, i.e., 3 hr⁻¹. A departure in procedure involved reducing the volume of acid addition each hour to maintain rough proportionality to the amount of sulfide remaining. Initial addition volumes during roasting were 1.0 ml for the thinner cake and 4.0 ml for the thicker cake. For the

Fig. 7: Apparent effect of cake thickness in wet roasting, intermediate range. Initial thickness, mm (approximate): Expt. 25A (1.3), 25B (4.0). Other conditions are given on p. 17.

Fig. 8: Effect of cake thickness in wet roasting with additions of 1M H_2SO_4 proportioned to amounts of residual sulfide. Initial thickness, mm (approximate): Expt. 13B (3.0), 14 (11.1). Other conditions are given on p. 20.

latter, an acceleration in oxidation rate was again observed after about the first hour (Figure 8).

An explanation of the anomalous kinetic behavior observed for the heavier filter cakes under acid moistening would, at this time, involve a high degree of speculation. One factor may be a variation in the amount of added H_2SO_4 which decomposes thermally as compared with that which reacts with the solids. It is significant that if the wet-roast reaction is taken to completion, a 1-cm cake can evidently be converted to copper sulfate as rapidly as a 1-mm cake.

An additional pair of experiments (13B and 14) has pertinence for the consideration of cake thickness effects. Scrub solution, which contained $(NH_4)_2SO_4$ and $CuSO_4$ as well as H_2SO_4 , was employed for interim moistening during oven roasting. The oxidation rates at $160^\circ C$ were lower (about 50% reaction in 5 hrs) than for roasting with acid moistening under otherwise similar conditions, as discussed more fully in the next section. Scrub solution additions were:

Expt. 13B (0.76g Cu initially): 0.5 ml solution $\times$ 3 hr^{-1}

Expt. 14 (2.77g Cu initially): 1.0 ml solution $\times$ 3 hr^{-1}

The significant result is that for initial cake thicknesses of ca. 3 and 11 mm, respectively, the oxidation rate for the thicker cake was only about 10 percent less than for the thinner cake. In relation to the amount of solution available for reaction, the rate of oxidation (e.g., g Cu/hr) is actually greater for the larger sample.

It can be concluded that in wet roasting, provided the reaction is not starved for solution, the fraction of copper oxidized per unit area of filter per unit time is not strongly dependent on cake thickness except for impractically thin and, probably, for relatively thick cakes.

Composition of Added Liquid

During wet roasting, solids were generally moistened with one of three compositions of liquid, including distilled water and 1 molar sulfuric

acid. The third liquid employed was scrub solution from the field test, whose ammonium sulfate concentration had been augmented to a nominal 75 g/l. The overall composition of this modified scrub solution is given in Table 2. Except for the copper concentration, which is high owing to oxidation of the stored slurry from the field test, the composition is more or less what one would anticipate at steady-state in an integrated operation (i.e., including regeneration and recycle).

TABLE 2
COMPOSITION OF MODIFIED SCRUB SOLUTION

	<u>g/l</u>	<u>Molar</u>
Cu^{2+}	4.56	0.072
H_2SO_4	39.9	0.406
NH_4^+	-	1.10
$(\text{NH}_4)_2\text{SO}_4$	73	0.55
Total SO_4^{2-} (material balance)	-	1.03
Total SO_4^{2-} (analysis)	103.3	1.075

It is apparent that, without the presence of acid in the water used to moisten the filter cake during wet roasting, the oxidation reaction becomes very slow after several hours (compare Figure 1 with Figures 2 and 6). Following the initial period of relatively rapid oxidation while, presumably, the specific surface area of the solid phase is still large, the rate becomes and remains very slow. An example of this behavior is given by data of Expt. 17A in Figure 9. In this same figure, the dramatic effect of switching to 1M H_2SO_4 to moisten the residual filter cake is shown by the data of Expt. 13A.

The conditions, including initial thickness of filter cake, for the first (H_2O) segment of Expt. 13A are the same as those for Expt. 17A

Fig. 9: Data illustrating slow kinetics of wet roasting with water. After 4 hr into Expt. 13A, moistening with 1M H_2SO_4 commenced.

(previously specified in the section on reproducibility), except that water addition during the former was at the rate 0.5 ml, twice per hour, whereas 1 ml additions were used in Expt. 17. Acid addition during the second segment of Expt. 13A was at the rate of 0.5 ml of 1M H_2SO_4 , three times per hour. The rate of oxidation during this second, faster segment was sensibly constant (Figure 9), suggesting that the detailed mechanism had become essentially independent of interfacial area. Similar behavior, although with slower kinetics, was obtained at the outset during wet roasting of synthetic CuS with 1M H_2SO_4 (Figure 10).

Given that hydrogen ion is necessary for the rapid wet roasting of scrubber solids, a lower reaction rate would be expected with the scrub solution (about 0.4M H_2SO_4 , Table 2) than with 1M H_2SO_4 . The results for Expts. 7B and 13B in Figure 11 bear out this expectation. Initial amounts of solids were reasonably similar (69 and 79 mg Cu/cm^2), and liquid volumes were approximately the same: ca. 0.75 ml 1M $\text{H}_2\text{SO}_4 \times 2 \text{ hr}^{-1}$ for Expt. 7B and ca. 0.5 ml scrub solution $\times 3 \text{ hr}^{-1}$ for Expt. 13B. Times for complete reaction, to the nearest 0.5 hr, were 7.5 hr and 13.5 hr (extrapolated*) for H_2SO_4 concentrations of 40 g/l and 98 g/l, respectively.

It would not be valid to conclude from the foregoing comparison that the rate of wet roasting is nearly proportional to H_2SO_4 concentration over the range considered, because the major constituent of the scrub solution is ammonium sulfate. Subsequent comparison experiments (19 and 20, Figure 11) revealed that the presence of major amounts of this salt significantly slowed down the reaction for the same H_2SO_4 concentration. Initial amount of solids was 59 mg Cu/cm^2 in each case, and solution additions were as follows:

Expt. 19: 0.5 ml 1M $\text{H}_2\text{SO}_4 \times 6 \text{ hr}^{-1}$

Expt. 20: (0.5 ml 1M $\text{H}_2\text{SO}_4 + 75 \text{ g/l } (\text{NH}_4)_2\text{SO}_4) \times 6 \text{ hr}^{-1}$

* After 10 hr of roasting, the residual solids were acid-moistened, and the resulting acceleration of oxidation rate led to complete reaction in 13 hr.

Fig. 10: Results of wet roasting of synthetic covellite, CuS.

Fig. 11: Comparison of H_2SO_4 , $H_2SO_4 + (NH_4)_2SO_4$ and scrub solution, used to moisten residual solids during wet roasting. Conditions given on p. 23.

The corresponding times for complete reaction are 4.5 and 9 hr, or a factor of 2 difference. This is a larger effect than anticipated and makes evident that, in the range 40-98 g/l H_2SO_4 , the retarding effect of $(NH_4)_2SO_4$ predominates over any presumed accelerating effect of H_2SO_4 . A major physical difference resulting from the presence of $(NH_4)_2SO_4$ in the solution used to moisten the solids is the formation of a layer of this salt (possibly as a sludge) upon evaporation of the water. The expected consequence is a more restricted access of oxygen to the unreacted sulfide. Consideration of quantitative differences between the results of Expts. 19 and 7B (Figure 11) is taken up in the next section.

A comparison test with synthetic CuS also showed a reduced oxidation rate at $160^\circ C$ with scrub solution (Figure 10). It is significant that the composition of the sulfide remained at $Cu_{1.00}S$ during wet-roasting with H_2SO_4 but was altered to $Cu_{1.43}S$ by reaction with scrub solution for 9 hr. This alteration was the result of a secondary enrichment analogous to that occurring in the scrubber. In the limiting case, the reaction with aqueous cupric ion is

Operation of the secondary enrichment mechanism should ensure that residual scrubber solids remain near Cu_2S in composition during wet roasting, as observed.

Addition Rate and Volume Effects

At temperatures of $200^\circ C$ and below, wet roasting was demonstrated to be faster, in general, than dry roasting. Furthermore, the oxidation rate with acid moistening was found consistently to be greater than for water moistening. Therefore, some effect of the amount of acid added in relation to the amount of solids undergoing wet roasting was to be anticipated.

The results of Expts. 25 and 26 (Figures 7 and 8) are broadly indicative of an enhancement of the rate of wet roasting with greater

availability of acid. The initial rates of addition of 1M H_2SO_4 for the four runs in question, in relation to total copper in the solids, were:

Expt. 25A, 6.2 ml/g/hr; Expt. 25B, 8.0 ml/g/hr

Expt. 26A, 3.7 ml/g/hr; Expt. 26B, 4.0 ml/g/hr

Furthermore, as noted earlier, the volumes added during Expt. 26 were adjusted downward hourly to maintain the same ratio of H_2SO_4 to unreacted solids.

Additional pertinent data are summarized in Table 3. The significant difference in conditions between Expts. 19 and 24 is that, for the latter, acid washing for dissolution of oxidized solids was carried out each half hour, rather than hourly. Experimental points for Expt. 19 were found essentially to coincide with alternate points for Expt. 24. The conclusion is that there was little effect of the more frequent removal of oxidation products. If there was a small effect, it was probably largely compensated by the longer total times out of the oven and, hence, lower mean temperatures for the Expt. 24 samples.

TABLE 3

CORRELATION BETWEEN OXIDATION RATE AND ACID ADDITION
IN SELECTED WET-ROAST EXPERIMENTS AT 150°C

Run No.	7B	25A	19	24*
Figure No.	11	7	11	6
Initial Cu, g	0.66	0.33	0.57	0.68
Time between H_2SO_4 additions, min	20	15	10	10
H_2SO_4 addition rate, ml/hr	1.5	2.0	3.0	3.0
Time for complete reaction, t_{100} , hr				
Observed (see graphs)	7.5	≤ 4	4+	4
Extrapolated [†]	9.7	5.1	5.2	5.1

* Removal of acid-soluble copper twice per hour.

[†] On a plot of $\log [1-(1-F)^{1/3}]$ vs. $\log t$, with the assumption of unit slope.

For the sequence 7B, 25A, 19, the rate of addition of acid (as given by the product of volume added and frequency of addition) increased from 1.5 to 3 ml/hr. The order of wet-roast rates, as measured by the reciprocal time for complete reaction, t_{100}^{-1} , was $7A < 25A = 19$ (Table 3). However, on comparing the initial rates of addition of acid relative to copper in the samples (2.3, 6.1, 5.3 ml/g/hr, respectively) a more consistent pattern of behavior emerges. This pattern, moreover, suggests that for thin filter cakes, the inverse relationship between rate and initial cake thickness, noted above, was largely a consequence of relatively greater supply of H_2SO_4 provided to the thinner filter cakes.

Two runs were carried out with continuous addition of H_2SO_4 during roasting. The experimental arrangement required that the roast temperature be kept relatively low. Reaction rates were also low; e.g., 40% after 8 hr at $85^\circ C$ (estimated time for complete reaction 28 hr). Since there was no significant accelerating effect of continuous as opposed to intermittent addition of acid (cf. Table 1) and, moreover, the experimental arrangement was cumbersome, this approach was not investigated further.

In the Table 3 experiments, the total added H_2SO_4 (exclusive of that used in acid washing) ranged from 18 to 24 ml/g copper or, closely enough, 1.8 to 2.4 g/g. These quantities are considerably in excess of the minimum acid requirement for the overall reaction

namely 0.772g H_2SO_4 /g Cu. Typically, samples removed from the oven were dry, so that the excess sulfuric acid had presumably been volatilized (as SO_3 and H_2O). In fact, the odor of SO_3 was sometimes detected on opening the oven. Of course, the experimental setup and procedure were such as to promote excess acid consumption, especially as residual solids decreased during a run.

In industrial application of wet roasting, the excess H_2SO_4 would have to be recovered, even if only for suitable disposal. The possibility

of effecting overall process acid balance by control of excess acid consumption during wet roasting has to be weighed against the costs of acid recovery and disposal and of incremental heat requirements for water and sulfuric acid volatilization. It may be noted that minimum acid requirements do not change greatly for solid compositions in the range $\text{Cu}_{1.8}\text{S}$ to Cu_2S . Thus,

for which $\text{H}_2\text{SO}_4/\text{Cu} = 4/9$ (mol/mol), rather than $1/2$.

Characterization of Products in Wet Roasting

A number of experiments focused on determination of the chemical compositions of the products of wet roasting. All three solution compositions employed in the kinetic studies were encompassed, namely, water, sulfuric acid and scrub solution. In several runs, analytical data were sufficiently comprehensive to permit detailed material balances to be calculated.

The determination of hydroxide (or oxide) and sulfate in the reaction products was accomplished by dissolution in a known volume of standard perchloric acid, HClO_4 . Titration of the unneutralized HClO_4 then gave the amount of hydroxide. Sulfate was determined, after copper removal by cation exchange, by titration with $\text{Pb}(\text{ClO}_4)_2$ to a Pb^{2+} -specific electrode end point. The determination of NH_4^+ was accomplished by alkali addition and analysis for the resulting $\text{NH}_3(\text{aq.})$ by means of an NH_3 -specific membrane electrode.

• Wet Roasting with Water

In the case of wet roasting with water, the sole source of sulfate in the oxidation products is the sulfide contained in the scrubber solids. Since Cu_{1+x}S contains insufficient sulfide in relation to copper to form CuSO_4 exclusively, the oxidation product must contain some hydroxide

(or oxide). With no loss of sulfur (as SO_2 or SO_3) by decomposition, the reaction stoichiometry in the general case would be

The corresponding molar composition of the reaction products is $\text{Cu}:\text{OH}:\text{SO}_4 = 1:2x/1+x$, or $1:1:0.5$ if Cu_2S is the starting material. For scrubber solids of composition $\text{Cu}_{1.9}\text{S}$, the limiting product stoichiometry is $1.000:0.947:0.526$. For $\text{Cu}_{1.8}\text{S}$, it would be $1.000:0.889:0.556$.

Actual analyses for separate experiments at 150°C are given in Table 4. The physical arrangement involved larger than typical amounts of starting solids, contained within Petri dishes for convenience in analyzing products. The kinetic data are, accordingly, not directly comparable with those obtained with filter cakes. The product analyses in Table 4 are consistent with a starting composition close to Cu_2S and relatively little loss of sulfur due to decomposition. Direct measurement of sulfur loss in these experiments showed the average sulfur loss to be essentially zero, within the reliability of the assumed composition of the initial scrubber solids.

TABLE 4
COMPOSITION OF OXIDATION PRODUCTS IN WET ROASTING
WITH WATER, 150°C

Expt.	%	Mol Ratios			
		Cu	OH	SO ₄	
8A-1	42	1	0.89	0.49	} average Cu:OH:SO ₄ = 1:0.93:0.55
8A-2	39	1	0.94	0.65	
10A	72	1	0.97	0.57	
11B	80	1	0.93	0.49	

Phase identification of water-roasted scrubber solids (Expt. 10B-2) by x-ray diffraction (Debye-Scherrer photographs) revealed the principal crystalline oxide phase to be antlerite, $2\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4$. The probable overall composition of the oxidation product suggests that copper sulfate was also present (although not necessarily well crystallized, owing to hydration/dehydration of $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$). In a separate wet-roast experiment (15B) employing the standard filter-cake technique, it was found that 9% of the (acid-soluble) oxidation products was soluble in water at about 5% copper sulfide reacted.

The unreacted sulfide phase which accompanied the antlerite in Expt. 10B-2 yielded the diffraction pattern of digenite, approximately $\text{Cu}_{1.8}\text{S}$. Chemical analyses of unoxidized residues from other wet-roast experiments ranged from $\text{Cu}_{1.8}\text{S}$ to $\text{Cu}_{2.0}\text{S}$, and averaged $\text{Cu}_{1.90}\text{S}$. Prolonged roasting with water (Expt. 17A, 20 hrs) led to appreciable regrowth of the initially microporous solids, although the difference was strikingly apparent only at high magnification, cf. Figures 12 and 13.

● Wet Roasting with Sulfuric Acid

If adequate H_2SO_4 is supplied to the reaction, the oxidation product should be copper sulfate, with no basic sulfate. The latter can form if H_2SO_4 is in insufficient supply. The copper sulfate product at the time of observation could be hydrated to an extent depending upon thermal history and H_2O partial pressure: CuSO_4 and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ are the expected forms at roast temperature, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or an intermediate hydrate may form on cooling.

Experimentally, a rough correlation was found between the proportion of hydroxide in the oxidation products and the extent of reaction (see Table 5). In a separate experiment (15C), the water-soluble fraction of the oxidation products comprised >99% of the total acid-solubles at about 15% reacted. However, full sulfation is evidently the limit reached when H_2SO_4 is present in sufficient amount to neutralize basic sulfate

200X

20,000X

Fig. 12: Scanning electron photomicrographs of copper sulfide scrubber solids as dried preparatory to roasting. Left: low magnification showing size distribution of agglomerates. Right: high magnification showing microporous nature of individual particles.

200X

20,000X

Fig. 13: Low (left) and high (right) magnification scanning electron photomicrographs of scrubber solids after wet roasting with water for 20 hr at 160°C (Expt. 17A).

which might otherwise form. X-ray diffraction analysis (Expt. 10B-2) revealed $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and some $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to be present, along with unreacted sulfide (digenite pattern).

TABLE 5
COMPOSITION OF OXIDATION PRODUCTS IN WET ROASTING
WITH SULFURIC ACID, 150°C

Expt.	% Reacted	Cu	OH	SO ₄	SO ₄ Loss, %*
8B-1	44	1	0.47	0.72	41
8B-2	39	1	0.51	0.94	xx
11A-1	94	1	0.014	0.95	59
11A-2	89	1	0.005	0.91	62
12A-1	91	1	0.00	0.99	68
12A-2	93	1	0.00	1.01	65

*Based on added H_2SO_4 .

A significant feature of wet roasting with sulfuric acid, as here carried out, is volatilization of the acid (as SO_3). The loss of sulfate by this mechanism was estimated by calculating the sulfate which would be formed from the amount of sulfide oxidized (assuming $\text{Cu}_{1.9}\text{S}$ starting material), combining this figure with the amount of sulfate added as H_2SO_4 , and comparing the sum with analytically determined sulfate in the reaction product.

It is seen in Table 5 that a loss of sulfate corresponding to about 60% of the added H_2SO_4 was incurred. The practice of acid-moistening by periodic additions of relatively large volumes of solution is clearly not efficient in terms of acid utilization. Evidently, substantial H_2SO_4 can be decomposed at temperatures in the vicinity of 150°C before it becomes fixed by reaction with the solids.

● Wet Roasting with Scrub Solution

It is unlikely that purchased acid would be used in the wet roasting of scrubber solids, because the scrubber reaction generates excess H_2SO_4 which, in the general case, must be neutralized by purchased base. The acid solution of choice in wet roasting would be scrub solution, although it has been shown that the ammonium sulfate content of the scrub solution slows down the oxidation rate appreciably. In a pair of experiments (12B-1 and B-2) in which scrub solution (composition given earlier) was employed, ammonium was measured in the reaction products (Table 6), which in this case were water-soluble and presumably consisted of $CuSO_4$ and $(NH_4)_2SO_4$. This, however, is not a typical result, and a short-time follow-up experiment yielded an oxidation product which was only 76% water soluble (Expt. 15A, Table 6).

TABLE 6
COMPOSITION OF OXIDATION PRODUCTS IN WET ROASTING
WITH SCRUB SOLUTION

Expt.	Temp. °C	Time	% Reacted	Mol Ratios			SO ₄ Loss, %	NH ₄ Loss, %
				Cu	SO ₄	NH ₄		
12B-1	150	8-1/2 hr	58	1	1.70	1.19	16	15
12B-2	150	8-1/2 hr	63	1	1.58	1.02	20	23
15A	160	1 hr	25	76% water-soluble				
14	160	1 hr	24	52% water-soluble				
		2 hr	32	85% water-soluble				
		3 hr	36.5	98% water-soluble				
		4 hr	42	98% water-soluble				
		5 hr	48	99% water-soluble				

In a fourth pertinent experiment, the water-soluble fraction of the oxidation products was found to increase with extent of reaction

(Expt. 14, Table 6). This is a reasonable result when account is taken of the periodic increase in the ratio of solution to solids as oxidation products were removed by acid washing. Scanning electron microscopy at high magnification (Figure 14) again revealed significant regrowth of the unreacted sulfide solids.

The percentage loss of sulfate by decomposition was less than for wet-roasting with H_2SO_4 , but still significant. Moreover, some decomposition of the ammonium sulfate must also have occurred in order to account for the loss of ammonium. Since the percentage losses of NH_4 and SO_4 were comparable for the two runs from which material balances were extracted, these limited results suggest a common source of loss by volatilization, namely decomposition of $(\text{NH}_4)_2\text{SO}_4$ into NH_3 and SO_3 . Process implications will be considered subsequently.

DRY ROASTING

For the reasons given above, dry roasting was not studied in as much detail as wet roasting. Given the exothermic nature of the roast reaction and the observed general reactivity of scrubber solids toward oxidation, one can be confident of finding reasonable conditions for effecting rapid dry roasting. Therefore, greater interest centered about the nature of the oxidation products. These were determined semi-quantitatively by their solubility behavior. Thus, by sequential treatment of the same sample,

water soluble	= sulfate, CuSO_4
cold acid soluble	= oxysulfate, $\text{CuO} \cdot \text{CuSO}_4$
hot acid soluble	= oxide, CuO
insoluble	= unreacted sulfide

Preliminary dry-roast experiments gave slow kinetics for temperatures of 200°C and below. At 160°C , for example, the extent of reaction for an initially water-moistened sample containing 0.66g Cu was 10% after 10 hr (vs. 5% for synthetic CuS) and 15% after 17 hr. With more frequent

5,000X

20,000X

Fig. 14: Scanning electron photomicrographs of scrubber solids after wet roasting with scrub solution for 5 hr at 160°C (Expt. 14).

sampling for acid-soluble copper, the overall rate increased, as expected. For example, a companion sample of scrubber solids that was treated hourly for determination of acid-soluble copper and left acid-moistened each time reacted to the extent of 83% in 10 hr. Here, of course, one is dealing with conditions intermediate between wet and dry-roasting, and not of great practical interest.

A continuous roast experiment at 200°C, commencing with a dry charge and conducted in the tube furnace, gave the results shown in Table 7.

TABLE 7
SOLIDS COMPOSITIONS IN DRY ROASTING AT 200°C

	initial copper	= 0.4833g	
after 7-1/2 hours	{ water soluble copper	= 0.0482g	} total = 0.132g or 27% reaction
	{ (additional) cold-acid soluble copper	= 0.0781g	
	{ (additional) hot-acid soluble copper	= 0.0057g	

Roughly speaking, the distribution of copper among the oxidation products of continuous dry roasting at 200°C for 7-1/2 hours was 37% as sulfate, 59% as oxysulfate and 4% as oxide. Thus, with no attempt to maintain SO₂ and SO₃ partial pressures (the furnace tube was open to the atmosphere at both ends), over one-third of the oxidized copper was in the sulfate form. This result is in general accord with investigations by others of cuprous sulfide oxidation at considerably higher temperatures, where co-existing products included: digenite, Cu₂O, CuSO₄, CuSO₄·H₂O and CuO.

In a subsequent dry roast experiment at 300°C, a time profile was obtained by employing six sample boats containing similar quantities of dry solids. The boats were charged simultaneously into the furnace and withdrawn consecutively over a span of 5 hr. As shown by the results in Table 8, oxidation was approximately 90% complete after 1 hr. From 1 to 4 hr roast time, little further change occurred but, subsequently, a slow

TABLE 8

SUMMARY OF DATA FOR DRY ROASTING OF SCRUBBER SOLIDS IN AIR AT 300°C

<u>Roast Time, hr.</u>		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
		<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>
Initial wt. of solids		0.6152		0.6283		0.6005	
Wt. of roasted solids		0.7244		0.7519		0.6178	
Wt. gain of solids, %			17.8		19.7		18.2
Analysis of products							
Water soluble Cu		0.1169		0.1249		0.1170	
			33		34		32
Add'l cold-acid soluble Cu		0.2315		0.2515		0.2455	
			66		65		67
Add'l hot-acid soluble Cu		0.0041		0.0020		0.0042	
			1		0.5		1
Total Cu oxidized		0.3525		0.3784		0.3667	
Wt. Cu in residue		0.0354		0.0354		0.0349	
Extent of oxidation, %			87.2		91.4		91.3
							76.1
							79.6

change apparently took place in the composition of the solids. The observed change was in the direction of a decrease in the sample weight gain.

A slow loss of weight of a partially oxidized sample after four hours in the furnace at 300°C might be attributed to decomposition of sulfate and oxysulfate to oxide, with loss of SO₂ and SO₃. This explanation has been applied in the past to weight changes during sulfation roasting of Cu₂S and CuS. However, the solubility characteristics of the 5- and 6-hr roast residues (Table 8) are not entirely compatible with this interpretation. Nor is there an evident reason why the apparent percent of copper oxidized should decrease, unless the oxide formed is incompletely soluble in hot 1M H₂SO₄. Apart from the indicated discrepancies, which occurred only for times much longer than the minimum required roast time, dry roasting can be seen to be relatively rapid at 300°C. The distribution of copper among oxidized forms is not grossly different from the slower, 200°C roast: about one-third of the oxidized copper was water soluble, and the remaining two-thirds was acid soluble.

In an effort to learn more about the rate, as opposed to the extent, of dry roasting, a similar experiment was carried out at the intermediate temperature of 250°C. The collected data in Table 9 show that by 2 hours at temperature, the reaction rate had become very slow. As was the case at 300°C, the percent weight gain and percent oxidation appear to have fallen off after about 4 hr. Prior to that time, the average composition of the oxidation products, as indicated by solubility behavior, corresponded to about one-third sulfate and two-thirds oxysulfate and oxide. The indicated change in composition between 4 and 7-hr roast time (Table 9) may be real, with the water-soluble fraction having increased and the cold-acid soluble fraction having decreased.

There was the expected trend in the extent of reaction with the temperature of dry roasting, as shown in Table 10. The reaction appears to become retarded by an accumulation of reaction products or by some change in the nature of the unreacted solids, or both. Retardation sets in at an extent of reaction which increases rapidly with temperature.

TABLE 9

SUMMARY OF DATA FOR DRY ROASTING OF SCRUBBER SOLIDS IN AIR AT 250°C

<u>Roast Time, hr.</u>	<u>1</u>		<u>2</u>		<u>3</u>		<u>4</u>		<u>7</u>	
	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>
Initial wt. of solids	0.6141		0.6541		0.6088		0.6307		0.6058	
Wt. of roasted solids	0.6859		0.7761		0.7246		0.7616		0.6959	
Wt. gain of solids, %		11.7		18.7		19.0		20.8		14.9
Analysis of products										
Water soluble Cu	0.0431		0.0552		0.0638		0.0635		0.0618	
		38		29		36		30		41
Add'l cold-acid soluble Cu	0.0678		0.1333		0.1072		0.1448		0.0817	
		60		69		61		68		54
Add'l hot-acid soluble Cu	0.0019		0.0034		0.0047		0.0042		0.0077	
		2		2		3		2		5
Total Cu oxidized	0.1128		0.1919		0.1757		0.2125		0.1512	
Wt. Cu in residue	0.3898		0.3316		0.3026		0.2936		0.3362	
Extent of oxidation, %		22.4		36.7		36.7		42.0		31.0

Mineralogical examination of dry roasted solids produced by reaction with air at 250°C yielded essentially no information, owing to extreme fineness of the particles. Consequently, wet chemical analysis of products was employed for the concluding experiments on dry roasting.

TABLE 10

SELECTED CHARACTERISTICS OF THE DRY ROASTING (FIXED BED)
OF SCRUBBER SOLIDS IN AIR AT 200, 250 and 300°C

Dry Roast Temperature	200°C	250°C	300°C
Extent of Oxidation, %	27 (7-1/2 hr)	42 @ 4 hr 31 @ 7 hr	91 @ 4 hr 80 @ 6 hr
Analysis of Oxidation Products			
Soluble in water, %	36.5(7-1/2 hr)	33(1-4 hr)	33(1-4 hr)
Soluble in cold 1M H ₂ SO ₄ , %	96 (7-1/2 hr)	98(1-4 hr)	99(1-4 hr)
Balance (cold acid insoluble), %	4	2	1

A shorter required residence time in the roaster than that indicated by the data at 300°C would be advantageous. An estimate of reaction time at 400°C (still a low temperature by comparison to those of typical roasting operations) was made as follows. A zero-order reaction was assumed, and a rate constant, k , was calculated according to the expression $1-(1-F)^{1/3} = kt$, for the 1-hr and 2-hr data points. Depending upon how the 200°, 250° and 300°C points on a plot of $\ln k$ vs. $1/T$, °K⁻¹, are connected by a straight line, the activation energy is 16-22 kcal/mol, or an average of 19 kcal/mol. Extrapolation to 400°C gives $k_{400} \approx 5.3 \text{ h}^{-1}$, or a time for complete reaction ($t_{100} = 1/k$) of 0.19 hr, or 11 min, at this temperature.

That estimate for 400°C was found to be not far off the mark, as shown by the data in Table 11. For samples in the given size range, there was no convincing trend with reaction time in either the percent weight gain (theoretical for $\text{Cu}_2\text{S} + \text{CuO} \cdot \text{CuSO}_4$ is 50.3%) or in the percent reacted. The indication is that observed differences are random, accessible solid particles being

essentially completed reacted in the shortest (15 min) time interval. Percent reacted in Table 11 was determined by comparison of copper dissolved in standard 3.75M HClO_4 with the analyzed copper content of the undissolved residue. Hot-acid (1N H_2SO_4) soluble copper was in some instances, but not consistently, greater than cold- HClO_4 soluble copper. This may be due to further aqueous oxidation of the unreacted Cu_2S in the former case.

Analysis of the HClO_4 solution for Cu^{2+} , for O^{2-} (by back-titration of HClO_4 with NaOH) and for SO_4^{2-} gave the molar compositions shown in Table 11. Note that, in mole units, the sum of O^{2-} and SO_4^{2-} must equal Cu^{2+} if no other ionic species are present. The average of $\text{O}^{2-} + \text{SO}_4^{2-}$ was 2.11 relative to $\text{Cu}^{2+} = 2.00$ mol. Accordingly, within the limits of reliability of the chemical analysis, the composition of the roast product was essentially $\text{CuO} \cdot \text{CuSO}_4$ in each case. There was no definitive trend in composition with time in the furnace.

The likelihood that accessible particles had completely reacted within the first 15-min period was tested in a second experiment by employing a range of initial sample weights. The data of Table 12 show an inverse relationship between extent of reaction, as measured by percent weight gain and by percent acid-soluble copper, and initial sample weight or bed thickness. Fluidized bed roasting would presumably yield complete reaction in air at 400°C in less than 15 mins residence time.

The product analyses of Tables 11 and 12 revealed no correlation between $\text{O}^{2-}/\text{Cu}^{2+}$ and percent reacted or percent weight gain, and similarly for $\text{SO}_4^{2-}/\text{Cu}^{2+}$. The overall average value of $\text{O}^{2-}/\text{Cu}^{2+}$ in 8 samples was 0.94, and the overall average value of $\text{SO}_4^{2-}/\text{Cu}^{2+}$ for the same samples was 1.18. This gives a ratio of SO_4^{2-} to O^{2-} in the product of 1.25, average. This ratio could be obtained by the oxidation of $\text{Cu}_{1.8}\text{S}$ to 0.8 CuO and 1.0 CuSO_4 . However, the same data give $(\text{O}^{2-} + \text{SO}_4^{2-})/\text{Cu}^{2+} = 1.06$. The analytical and experimental uncertainties implied by this somewhat anomalous result, as well as by the relatively large (10%) average deviations in the values of $\text{O}^{2-}/\text{Cu}^{2+}$ and $\text{SO}_4^{2-}/\text{Cu}^{2+}$, cast doubt on this interpretation.

TABLE 11

RESULTS OF DRY ROASTING IN AIR AT 400°C FOR VARIOUS TIMES

Time, hr	Initial wt., g	Wt. Gain %	Percent Reacted	Hot-Acid Soluble, %	Composition of Product, mol		
					Cu ²⁺	O ²⁻	SO ₄ ²⁻
0.25	0.6885	37.7	84.2	92	2.00	1.00	1.20
0.50	0.6526	44.7	80.6	92	2.00	1.02	0.95
1.0	0.6017	42.8	78.9	90	2.00	1.18	1.14
2.0	0.7333	44.4	91.1	88	2.00	0.97	1.10
4.0	0.7121	45.6	88.5	90	2.00	0.86	1.14

TABLE 12

RESULTS OF DRY ROASTING FOR 15 MINS IN AIR AT 400°C FOR VARIOUS
INITIAL SAMPLE WEIGHTS

Initial wt., g	Approx. Bed Thickness, mm	Wt. Gain %	Percent Reacted	Composition of Product, mol		
				Cu ²⁺	O ²⁻	SO ₄ ²⁻
1.1994	6	36.3	73.3	2.00	0.75	0.96
0.6268	3	44.9	93.4	2.00	0.89	0.97
0.3174	1.5	49.5	99.3	2.00	0.88	1.04
1.2252	6	32.6	83.2	2.00	N.A.	0.99*
0.6017	3	47.4	99.6	2.00	N.A.	1.12*
0.3208	1.5	50.8	100	2.00	N.A.	1.14*

*Gravimetric by precipitation as BaSO₄.

Direct information that the deviation of the initial solids composition from Cu_2S was considerably smaller than 10 percent copper deficiency is given by analyses for copper and sulfur in the samples of starting material (Table 13). The average composition of scrubber solids employed in the 250°C and 400°C experiments was evidently very close to Cu_2S .

Three samples of roast product, including the assumedly small percent of unreacted residue, were analyzed for sulfur by the same Leco combustion procedure as applied to unreacted solids. An average value of $13.3 \pm 0.2\%$ S (Table 13) was obtained in this way, as compared with 14.8% S calculated from the above wet chemical analyses. Theoretical for $\text{CuO} \cdot \text{CuSO}_4$ is 13.4% S. One can be confident that the product of air roasting at 400°C was close to $\text{CuO} \cdot \text{CuSO}_4$ and that, consequently, little or none of the original sulfur had been lost for periods up to 4 hrs.

When the cumulative data for 250, 300 and 400°C were plotted as percent weight gain vs. percent reacted, as measured by hot-acid soluble copper, the anomalous nature of the results obtained at 300°C became apparent (Fig. 15). The deviation of the 300°C data from the stoichiometry corresponding to the oxidation of Cu_2S to $\text{CuO} \cdot \text{CuSO}_4$ can most simply be explained by a considerable (inadvertent) initial oxidation of the charge. Calculated copper contents of the Table 8 samples support this interpretation. Thus, percent copper in the original six samples, as calculated from the sum of soluble copper and copper in the insoluble roast residue, ranged from 64.5 to 66.7%. This is clearly not representative of the Cu_nS starting material.

A repeat roasting sequence at 300°C (Table 14 and Figure 15) removed the apparent anomaly. Extent of oxidation was 86-91% at 1/2 hr, increasing to 93-95% at 1 hr. Between 1 and 2 hr roast time, the weight gain and the measured extent of reaction perceptibly decreased, as occurred previously in the 250°C and 300°C sequences. The most likely explanation for a concomitant decrease in weight and decrease in acid-soluble copper for the extensively oxidized sample is some loss of SO_2 , with the formation of a leach-refractory oxide. If a similar phenomenon occurred within 4-hr roast time at 400°C, it was not discernible from the data (Table 11).

TABLE 13
COPPER AND SULFUR ANALYSES OF DRY-ROASTED SOLIDS,
250° AND 400°C

Temp.	Samples	Roast Time	% Cu	% S	Remarks
250°C (Table 9)	(4) Cu_nS	-	$\begin{cases} 79.6_6 \\ 78.3_5 \end{cases}$	$\begin{cases} 20.8 \\ 20.0 \end{cases}$	$\text{Cu}_{1.95}\text{S}$ (100% Cu + S basis)
	Cu_nS	-	80.1 ₃	19.6	$\text{Cu}_{2.06}\text{S}$ } (100% Cu + S basis)
	Cu_nS	-	80.4 ₅	20.1	
400°C (Table 11)	Product	0.25 hr	-	13.3	Initial wt. 0.3869 g
	Product	1.0 hr	-	13.6	Initial wt. 0.4423 g
	Product	4.0 hr	-	13.0	Initial wt. 0.4365 g

*Average weight chosen to give same average bed depth (in smaller porcelain boats) as for companion samples reported in Table 11.

TABLE 14

DRY ROASTING OF SCRUBBER SOLIDS IN AIR AT 300°C (REPEAT)

<u>Roast Time, hr.</u>		<u>0.5</u>		<u>0.5</u>		<u>1</u>		<u>1</u>		<u>2</u>		<u>2</u>	
		<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>	<u>g</u>	<u>%</u>
Initial wt. of solids		0.6010		0.5962		0.6355		0.6199		0.6196		0.6133	
Wt. of roasted solids		0.8774		0.8517		0.9302		0.9123		0.8639		0.8393	
Wt. gain of solids, %		46.0		42.9		46.4		47.2		39.4		36.9	
Analysis of products													
Water soluble Cu		0.1512				0.1629				0.1438			
		34.5				34.6				35.9			
Add'l cold-acid soluble Cu		0.2845		*0.3957		0.3056		#0.4706		0.2532		†0.3772	
		65.0		95.9		64.9		98.9		63.2		99.2	
Add'l hot-acid soluble Cu		0.0023		0.0171		0.0022		0.0052		0.0034		†0.0030	
		0.5		4.1		0.5		1.1		0.9		0.8	
Total Cu oxidized		0.4380		0.4128		0.4707		0.4758		0.4004			
Wt Cu in residue		0.0427		0.0676		0.0332		0.0243		0.0925		0.443	
Extent of oxidation, %		91.1		85.9		93.4		95.1		81.2		76.9	
% Cu in original solids		80.0		80.6		79.3		80.7		79.6		80.6	

* Leached with 15 ml cold scrub solution, 27°C.

Leached with 15 ml warm scrub solution, 55°C.

† Leached with 15 ml hot scrub solution, 80°C.

Fig. 15. Collected dry roast data. $\bigcirc$ = 200°C, $\bigcirc$ (dashed) = 300°C (see text), $\square$ = 400°C.

The opportunity was taken with the repeat roasting experiment at 300°C to ascertain that target copper loadings (about 30 g/l) could be obtained by leaching the calcine with scrub solution, rather than barren H_2SO_4 . Accordingly, alternate calcine samples were treated with simulated scrub solution, 25 g/l H_2SO_4 + 100 g/l $(NH_4)_2SO_4$, as detailed in Table 14. The requisite copper loading was obtained with scrub solution whose temperature ranged from room ambient to 80°C.

PROCESS SIGNIFICANCE

The practical significance of our findings with respect to the roasting of scrubber solids can best be understood in the context of how roast-regeneration relates to the overall H_2S removal process. The circulating scrubber slurry is made up of a solution containing mainly ammonium sulfate, sulfuric acid, copper sulfate and boric acid, and solids consisting principally of copper sulfide. It is necessary to reconvert the copper sulfide, as by roasting, essentially quantitatively to a strong copper sulfate solution for makeup to the scrubber. It is also necessary to treat the solution for acid neutralization and for removal of other solutes, in order to offset their buildup. In so doing, liquid volume must be conserved in the scrubber.

The foregoing process requirements indicate that a side-stream of scrubbing slurry will be subjected to a liquid/solid separation. The solids, in the form of a denser slurry or filter cake, will pass to a roast step where they will be converted to sulfate (or other oxidized form which, upon treatment with sulfuric acid, will be reacted to copper sulfate). A purge will be taken of the liquid stream and treated for ammonium sulfate and boric acid removal; soluble copper will be recovered from this purge stream. The main liquid stream will be neutralized, made up to strength in copper sulfate (30-50 g/l) and adjusted in liquid volume to become the scrubber liquid makeup stream.

Partial neutralization of the liquid side-stream will be effected simultaneously with copper makeup by using it to dissolve the solids produced in roasting. There would be an advantage in deriving as much acid neutralization

capacity as possible from the roast step. In essence, however, this translates to increasing the formation of oxide relative to sulfate in the oxidation products, with rejection of an equivalent amount of sulfur. If the sulfur content of the scrubber solids were to be converted to SO_2 , a process addition and associated equipment would be required to scrub the SO_2 .

Elemental sulfur is the desired form of sulfur for rejection from the process, but it does not seem feasible to produce elemental sulfur by roasting copper sulfide. Accordingly, other directions need to be considered for deriving the maximum acid neutralizing capability from the roast step. In wet roasting in the laboratory with sulfuric acid or scrub solution, some of the added sulfate was volatilized, presumably as SO_3 . This is not a practically useful result because, at temperatures high enough for decomposition of H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ to be appreciable, the vapor pressure of water is high. If pressure reactors need to be resorted to, then one may as well go the pressure-leach route. Furthermore, recovery of the H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ volatilized in wet-roasting would be difficult.

Wet roasting could be conducted in an open reactor at a temperature well below the normal boiling point, but approximately one day's reaction time is estimated for the most favorable conditions, other than temperature (i.e., an order of magnitude slower than the fastest rate achieved at 160°C , namely, complete reaction in ca. 2.5 hr). Simpler means of oxidizing the scrubber solids, such as sparging air through the hot slurry, would suffice if long reaction times were acceptable. One inference to be drawn is that the potential advantage of wet over dry roasting in avoiding the energy-intensive drying of the scrubber solids would not be realized in practice because of the high temperature needed to sustain reasonably fast kinetics.

Dry roasting also has problems in the area of energy consumption in that still higher temperatures than for wet roasting will apparently be required to effect complete reaction as well as rapid kinetics. These would be temperatures of the order of 300°C or higher and would not be attainable by heat exchange with the geothermal steam. An estimate of maximum water

content for autogenous roasting of scrubber solids can be obtained from thermochemical data, namely, the exothermic heat of formation of $\text{CuO} \cdot \text{CuSO}_4$ from Cu_2S (Eq. 3) and the heat capacities of H_2O , air and Cu_2S . Over the temperature interval 300-700°K, $-\Delta H$ is close to 200 kcal/mol Cu_2S (Barin & Knacke, 1973). This is sufficient heat to bring the wet copper sulfide charge and the combustion air, assuming 50% excess O_2 is supplied (i.e., 3.6 kg air/kg Cu_2S), to a reaction temperature of 700°K (427°C) and to convert the contained water to steam at this temperature, when the slurry density is about 50% solids or greater. In comparison, filter cakes produced from scrubber slurry by conventional filter equipment had a maximum of about 25% solids.

A discussion with F. M. Stephens, Jr. of Hazen Research, Inc. concerning the probable amenability of scrubber solids to fluidized sulfation roasting provided some further information and predictions based on his experience with roughly similar sulfides. For example, a water content of less than 35% may be required for autogenous roasting under practical conditions. Some improvement in the dewatering requirements could be achieved by a) using the hot off-gases to preheat the charge, b) preheating the combustion air or c) adding fuel during roasting. Mr. Stephens suggested that in large-scale roasting, one should aim for 80-90% conversion and accept a recirculating load of solid sulfide.

An inert sand bed would likely be required to prevent the finely divided charge from being swept out of the roaster. Mr. Stephens suggested that the addition of about 1% of Na_2SO_4 (in relation to the $\text{CuO} \cdot \text{CuSO}_4$) would aid in agglomeration of the product. The presence of $(\text{NH}_4)_2\text{SO}_4$ and H_3BO_3 in the feed slurry would probably not accomplish the desired result because of their volatility.

In spite of probably unfavorable energy balance when the feed consists of low-density cake, dry roasting at moderately high temperature may show some advantage in particular situations. The projected short reaction time of about 15 min at 400°C is compatible with conditions in a fluid-bed roaster. Additional tests in a vendor's facility will be required in order to obtain design and scale-up information, confirm predicted yields and percent conversion, determine operating characteristics, etc.

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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task B.3

Liquid-Solid Separation Studies

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SUMMARY

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 with 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, percents decanted, and feed solids contents.

Batch centrifugation tests showed that the solids settled rapidly and to approximately 50% solids density at 1600g. Settling rates are not greatly affected by pH or temperature within the ranges tested.

At a commercial scale of operation, 50 MW or 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.

For regeneration by roasting, where much higher degrees of water removal are required, a centrifuge would be used.

Thickeners and continuous (vacuum) filters are alternatives in these two regeneration cases, respectively, but a batch filter would be significantly more costly and labor intensive.

BACKGROUND AND PURPOSE

The earliest liquid solid separation tests carried out on solids produced by removing hydrogen sulfide from simulated geothermal steam by scrubbing with copper sulfate showed that they settled rapidly and filtered easily. On this basis, it was proposed that a small, inexpensive batch filter could be used in the proposed 100,000 lb/hr field test facility, and a program of test work, Task A.3, was outlined to obtain the data required for the specification of such a unit. At the same time, it was realized that a batch filter might

not necessarily be the preferred type of device for use in a full scale, commercial environment. Accordingly, an additional series of tests, Task B.3, was outlined in order to obtain design data for alternate types of liquid solid separation devices, including continuous filters, centrifuges, and thickeners.

The results of the first series of tests to determine specifications for the device to be used in the 100,000 lb/hr field test facility, are described in detail in the Task A.3 Letter Report, issued March 8, 1977. Briefly, it was found that, while the solids indeed filtered very easily, the floccy nature of the aggregate restricted filter cake densities to rather low values. Thus, a very large filter would be required to simply provide adequate solids retention volume, and it was felt that this was not a viable approach even for the small demonstration facility.

Therefore, elements of the test work planned for the more general liquid-solid separation studies, Task B.3, were carried out in order to obtain design data for an alternative device for the 100,000 lb/hr facility. These results, focussing on the performance of continuous filters and thickeners - or decanter are also presented in the Task A.3 Letter Report.

Accordingly, the scope of work required to obtain design data for alternate types of liquid solid separation devices was reduced to those efforts needed for the design of centrifuges. However, since the use of a continuous decanter had been proposed for the demonstration facility, and since this type of device could be equally viable at full commercial scale, an additional series of continuous decantation tests was scheduled and executed.

TEST APPARATUS AND PROCEDURES

The apparatus and procedures used in filter leaf and liter cylinders test work have been described in detail in the Task A.3 Letter Report.

The apparatus used in the continuous decantation tests is shown in Fig. 1. The slurries being tested were held in a surge tank and suspended by a small, variable speed laboratory agitator. The flow rate of slurry to the decanter was controlled by adjusting the control valves on the circulating pump discharge to recycle varying amounts of slurry to the surge tank. A 2.5 liter conical laboratory separatory funnel 13 inches high with 2-1/2 and 4-1/2 inch

Fig. 1. Laboratory set-up, continuous decantation tests.

lower and upper diameters was used as a continuous decanter. Over- and underflow rates were controlled by adjusting pinch cocks on the flexible tubing used as drain lines.

Prior to initiating a test series, the contents of the surge tank were thoroughly agitated and a sample was taken to establish the initial or feed slurry density. If not in the desired range, additional acid copper sulfate - ammonium sulfate solution was added or agitation was stopped and excess solution decanted from the settled slurry. When the desired slurry had been obtained, flow was initiated to the decanter with no restriction on the underflow line. Then, flow was gradually restricted causing the level in the decanter to rise, and as it passed the feed point decantation began. After the clear liquid level passed the overflow tube, which projected about two inches down from the top of the decanter, overflow was initiated by establishing a syphon and its rate was controlled by adjusting the overflow pinch cock valve.

Steady state was considered achieved when, by balancing total input, underflow, and overflow rates both the settled pulp level and clear liquid level in the decanter had ceased changing. The total flow rate was obtained by collecting and measuring over- and underflow rates individually. Pulp and clear liquid levels (and volumes) were recorded and, occasionally, samples of these streams were taken for direct measurement of their solids contents. Solids contents were determined by filtering samples through a 10 micron filter element and weighing the dried cake and filtrate obtained.

Centrifugation tests were carried out in a small, variable speed laboratory batch centrifuge manufactured by Damon Corp. Speeds ranged from 150 to 3200 rpm, with forces applied from 3.5 to 1600 g's on samples contained in 15 cc tubes. Samples were prepared for testing by allowing the slurry of interest to settle in liter cylinders and decanting the clear liquid. The thickened pulp was then transferred to beakers and any additional clear liquid which formed as a result of further settling upon transfer was also decanted. Samples of the thickened pulp were taken for solids determination, and the balance transferred to the centrifuge's sample tubes as needed. The initial levels in the tubes were measured and they were then spun up at various speeds and for various times to determine the solids' settling characteristics.

Both the continuous decantation and batch centrifugation tests were carried out on a variety of slurries characterized as from "easy" to "difficult" to settle. In all cases, liter cylinder tests carried out on these materials served to quantify this characterization. In addition, a limited amount of work was done on heated slurries and on slurries which had been subjected to significant pH increases to determine the effects of these variables on settling rates.

TEST RESULTS

Settling rate curves for the various slurries subjected to continuous decantation and batch centrifuging tests are shown in Figure 2. The slurry used in Run 317 was a composite sample of solids produced during field trials in the 8" scrubber unit, Task C.2. This material had aged three months prior to testing, but had been kept cold and free from exposure to air. The settling curve is typical of those obtained from solids freshly produced in the 4" laboratory scrubber.

The slurry from Run 809 was produced in a small Venturi scrubber in the laboratory and was used in a series of decantation and centrifugation tests within a week of having been generated. While settling somewhat slower than the solids formed in the field trials, the settling rate is still rather fast, and does not differ greatly from other solids produced from time-to-time in laboratory trials.

The slurry labelled Run 817 was a composite of solids which had been produced in the laboratory scrubber in various runs and had aged for over a year. In addition, some of these solids had been subjected to a series of ambient air leaching tests and had been significantly altered chemically and physically. It was observed that this material seemed to contain both a higher than normal proportion of fines and of large, slowly settling floccy agglomerates. The majority of fresh, unoxidized solids produced in the course of the various scrubbing tests had settling rates between 50 and 100 ft/hr and can be characterized as lying between the curves for Runs 809 and 317. Solids such as those shown for Run 817, with settling rates of the

Fig. 2. Settling rate curves for various slurries tested.

order of 2 ft/hr, are atypical and are taken to represent worst case conditions.

Test results for a series of continuous decantation runs are summarized in Tables I and II. Since the amount of slurry available for these tests was generally limited, the level in the surge tank was usually low and difficulty was encountered from time to time in keeping a uniform suspension of solids. Thus, while it should be possible to calculate underflow densities from a known feed solids content and percent decanted, occasionally a direct measurement was made. In addition, the reactive solids leached somewhat during the course of these runs, thereby decreasing feed slurry densities. This was partially offset, however, by the loss of some water from the system due to evaporation. Thus, while the feed solids contents were continuously changing, this was not of great concern during this test since such changes will occur in an operating unit as a matter of course. The objective of these tests was to determine the operability of a continuous decanter under conditions which bracketed the expected extreme range of operating conditions.

The preliminary design criteria for the decanter for the field test facility, established in the Task A.3 study, provide for a 2 min solids detention time, 20 ft/hr nominal upflow velocity (30 ft/hr max) and 20% decantation to increase the streams solid content from 2.2 to 2.7%. The results of Run 317 show that this extent of decantation can easily be met at pulp detention times of less than a minute, at least for rapidly settling slurries. Although the poorly settling solids used for Run 817 were easily concentrated by high percents decantation, the underflow densities obtained were, in general, not in the range desired because of the low feed solids content. However, from an overall material balance point of view, a purge stream containing a low solids content need not be concentrated to as high as solids content at 2.7%, but only to the extent required to purge soluble reaction products from the system.

The results of Run 809 show that stable decanter operations is possible over a very wide range of flow rates, percents decanted, pulp residence times and upflow velocities for solids whose settling rates are within the range considered typical of normal operation. In general, the overflow clarity

Table I

Continuous Decantation of Fastest and Slowest Settling Solids

Solids Origin	Run 317	Run 317	Run 817	Run 817	Run 817	Run 817	Run 817	Run 817
Feed % Solids	4.1	4.1	2.6	1.3				1.2
Solution pH	1.16	1.16		1.83				
Solution g/l Cu	14.2	14.2		6.1				
Decanter Operating Conditions	Inter-mediate	Inter-mediate	Min total Flow	Max Total Flow	Max % Decanted	Inter-mediate	Inter-mediate	Inter-mediate
Overflow Rate, ml/min	550	320	135	360	400	400	240	230
Underflow Rate, ml/min	1800	1830	490	2040	680	1360	1040	440
% Decanted	23	15	22	15	37	23	19	34
Clear Liquid Rise Velocity, ft/hr	11	10	3	8	10	9	6	6
Clear Liquid Detention Time, min	1.18	4.38	2.59	2.08	2.88	2.13	4.58	4.74
Pulp Detention Time, min	0.97	0.36	3.35	0.81	1.84	1.14	1.25	2.95
Underflow Density, %	5.3	4.8	3.4	1.5	~2.0	~1.7	~1.6	1.8
Overflow Solids Content, PPM	34		8					35

Table II

Continuous Decantation of Intermediate Settling Solids

Solids Origin	Run 809	Run 809	Run 809	Run 809	Run 809	Run 809	Run 809
Feed % Solids	1.4						0.9
Solution pH	1.23						1.43
Solution g/l Cu	4.3						9.2
Decanter Operating Conditions	Max Total Flow		Intermediate Flow		Min Total Flow		Intermediate
	High % Decanted	Low % Decanted	High % Decanted	Low % Decanted	High % Decanted	Low % Decanted	Max % Decanted
Overflow Rate, ml/min	960	240	960	180	960	220	920
Underflow Rate, ml/min	3190	3910	1990	2770	690	1430	1080
% Decanted	23	6	33	6	58	13	46
Clear Liquid Rise Velocity, ft/hr	26	8	24	7	34	8	29
Clear Liquid Detention Time, min	1.35	6.88	1.25	8.61	1.61	7.73	1.30
Pulp Detention Time, min	0.34	0.19	0.6	0.24	1.02	0.34	0.93
Underflow Density, %	1.8	~1.5	~2.0	~1.5	~3.4	~1.6	1.7
Overflow Solids Content, PPM							90

obtained during these tests was excellent and, except during upset conditions, the decantate was sparkling clear. At low upflow velocities, measured overflow solids contents were in the 10-40 PPM range, while at the highest velocities tested the solids content approached 100 PPM. This occurred at the end of a long test series, however, and it was observed that the solids were beginning to be altered by leaching. The decantate had become turbid, whereas during earlier runs on the same material at higher velocities it has been clear. Therefore, it is anticipated that overflow solids contents of less than 50 PPM should be attainable on fresh solids under design conditions.

Settled density curves for enhanced gravity settling of solids from Runs 809 and 817 are shown in Figures 3 and 4. As expected, higher centrifugal forces and longer settling times promote higher settled densities. In addition, the rate of settling of the difficult to settle solids from Run 817 is improved relative to the more normal, Run 809 solids: at 1g the ratio of settling rates is 1/25 whereas at 1600g, the ratio is about 1/3. It is also of importance to note that, in spite of the widely differing settling rates and differing initial slurry densities, the final slurry density for both materials is approximately the same, 46-48% solids at 1600 g for the longest times tested.

In Figure 5 the effects of pH adjustment, operating temperature, and solids characteristics are compared for settling at 1600g. Except as noted, all test work was done at ambient temperature and in solutions as produced from the scrubber. For the high temperature runs, the samples were heated to 100°C before being placed in the centrifuge, where they cooled off to about 70°C during the course of testing. The pH adjusted samples had been titrated with strong ammonia solutions to increase their pH from 1.26 to 2.42 (in excess of 90% acid neutralization) and were tested at ambient temperature. Within the scatter of the data, there is little indication that either pH or temperature has a major effect on settling rate, although higher temperatures seem to promote higher final settled densities. Based on the data shown in Figures 3-5, it appears that commercially available centrifuges of the helical conveyor type would be well suited for service on this material, but that cake moisture contents would still be high, perhaps of the order of 50%.

Fig. 3. Rate of settling under centrifugal force, solids Run 809.

Fig. 4. Rate of settling under centrifugal force, solids Run 817.

Fig. 5. Effect of temperature and pH on settling rate.

ALTERNATIVES FOR A COMMERCIAL SCALE SYSTEM

The approximate sizes, costs, and operating characteristics of various types of liquid-solid separation devices for a commercial scale (50 MW) systems are summarized in Table III.

The type of liquid-solid separation device needed in a given application is fixed primarily by process considerations. Thus, if the solids are to be regenerated by roasting and it is desired to remove as much moisture as possible to permit an autogenous roast and/or minimize supplemental fuel requirements, use of a centrifuge would be recommended. If, on the other hand, regeneration is to be carried out by leaching and the process acid balance permits (or requires) relatively low slurry densities, then a continuous decanter would be preferred.

A thickener, though small by commercial standards, could be useful if somewhat higher underflow densities were required. Batch filters, whose sizes are controlled by solids holding requirements, do not appear to be cost effective devices for this service. The use of continuous filters would be possible and perhaps preferred vis-a-vis high maintenance requiring centrifuges, but the cake solids contents will be limited.

In summary, continuous decanters would be the preferred type of liquid solid separation device when regeneration is to be accomplished by leaching, and centrifuges would be preferred for use with roast regeneration systems.

Table III

Characteristics of Various Types of Liquid-Solid Separation Devices
at a Commercial Scale of Operation⁽¹⁾

Type of Device	Batch Filter	Continuous Filter	Continuous Decanter	Thickener	Centrifuge
Style	Horiz. Tank Press. Leaf	Rotary Vacuum			Helical Conveyor
Approx. Solids Attainable	25%	30%	10%	15%	50%
Solids Discharge	Batch	Continuous	Continuous	Continuous	Continuous
Size Unit Required	Three @ 530 ft ²	100 ft ²	2.5' dia x 5' high	4' dia ⁽³⁾	18" dia
Approximate Cost, \$M ⁽²⁾	150	50	10	~25 ⁽³⁾	75
Labor Requirements	2 men/shift	< 1/2 man/shift	Occasional Attention	< 1/2 man/shift	> 1/2 man/shift

(1) Nominal 50 MW; 10⁶ lb/hr steam @ 220 PPM H₂S. See also Task A.3 for sizing criteria.

(2) Installed, including drives and operating accessories, excluding solids transport system, piping, and foundations.

(3) Below smallest commercial size.

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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730,*000

Final Report on Task B.4

Scrubber Configuration Studies

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SUMMARY

The performance of shower type trayed columns, a spray column, and a venturi have 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 either high liquid scrubbing 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 scale of operation. Costs were estimated for both 80-90% and high degrees of H_2S removal. It was shown that a crossflow sieve tray type scrubber was cost effective for either degree of H_2S removal required, but the simpler types were 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 a significant 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 at low liquid scrubbing flow rates, such a configuration would represent a simple, compact, inexpensive scrubber system.

BACKGROUND AND PURPOSE

The earliest tests in a 2" diameter column showed that the kinetics of the removal of H_2S from steam under simulated geothermal conditions by scrubbing with copper sulfate were very rapid at pH's above 1.2. Near quantitative removal was obtained when proper liquid-vapor contacting was achieved, and removal rates appeared to be limited by vapor phase diffusion.

It was also determined in these preliminary tests that use of certain styles of internals could result in operability problems. Specifically, counterflow sieve trays could not be used because they tended to retain large agglomerates of solids which would ultimately foul the tray. Also, common styles of packing tended to flood at very low velocities, apparently because of the surface active nature of the froth formed during the scrubbing reaction.

Shower trays proved effective in removing H_2S and passed solids without difficulty, but also flooded at low velocities. It was finally determined that a crossflow sieve tray with a single downcomer was an effective device from both mass transfer and operability points of view. Test results for scrubbing experiments carried out in the 2" column are summarized in the Annual Status Report for the period 1 June 1975 to 31 May 1976.

In a companion study for the Pacific Gas and Electric Company, a series of scrubbing tests was carried out in a 4" diameter column fitted with a single crossflow sieve tray with downcomer. The scrubber was also equipped with a tray DP cell so that the effects of tray hydraulics on scrubbing efficiency could also be determined. These tests generally confirmed the results obtained in the 2" column, and suggested that this style of contactor would be suitable for use at a commercial scale. Test results are presented in the final report on the Control of Hydrogen Sulfide Emissions at the Geysers Geothermal Power Plant, September 10, 1976.

These results were, in turn, reconfirmed in tests on actual geothermal steam in an 8" scrubbing column at Unit No. 7 Geysers Power Plant. Test results are presented in the Task C.2 preliminary report on the design and operations of the 8" scrubber unit.

As a result of these three test series, on 2", 4", and 8" scrubbers, it was determined that:

- A single crossflow sieve tray is operationally stable and can give high removal efficiencies if pH and tray hydraulics are controlled.
- Counterflow sieve trays may present operational problems due to a propensity to retain solids agglomerates.
- More open tray styles, e.g., shower trays, may be operable although at rather low flow rates.
- Packed internals will flood at low flow rates, probably because of the surface active nature of the froth.
- Mass transfer rates are high, probably gas phase diffusion limited for pH's above 1.2, and tray hydraulics can be scaled at least to 8" diameter.

The last conclusions suggested that it would be worthwhile to determine the efficiency of venturi and spray type scrubbers in this service because of the possible cost advantages such systems would have at the commercial scale of operation. Also, since scale up had already been demonstrated to 8" diameter, the remaining solids production and scrubbing tests were carried out in the existing 4" column rather than constructing a new 6" unit. Finally, in view of the very poor hydraulics observed, further testing on packed internals were not warranted, but additional tests to rate shower or disk and donut trays were.

TEST APPARATUS AND PROCEDURES

The test apparatus and procedures used to evaluate alternative scrubber internals configurations are essentially the same as those used in previous tests on the 2", 4", and 8" scrubbers. Detailed descriptions have already been reported (op cit) and will not be repeated.

Two alternatives to the use of crossflow sieve trays were investigated: segmental or shower trays and disk and donut trays. The former consisted of a stack of six trays, with 20% segmental area removed from each, installed with the cut areas alternating by 180°. Tray spacing was 2". The disk and donut stack consisted of a series of 3" diameter disks centered in the column alter-

nating with a series of plates from which a 2-1/4" diameter centrally located holes had been cut. Six trays were provided with 2" spacing.

The set up used to determine scrubbing efficiency for a spray type column was essentially the same as that used for trayed column tests, except that the recirculated slurry was returned to the top of the scrubber through a Fulljet[®] spray nozzle with a 3/32" diameter orifice which would pass 1 GPM at 25 PSI ΔP with a 25-30° cone angle. No trays were used in these tests, and a pulsation damper was installed on the discharge line of the positive displacement pumps to smooth out fluctuations in the flow of recirculated slurry.

The test set up used to determine scrubbing efficiency in a venturi contactor also employed many components of the 4" column system, as shown in Fig. 1. Figure 2 is a section view of the venturi scrubber itself.

The minimum nozzle and throat area is approximately 0.001 ft², so that at nominal flow rates steam velocities were of the order of 150 ft/sec. Total vapor-liquid contact times in the venturi and piping were of the order of .01-.02 sec. The clearance between the nozzle outlet and diffuser throat could be varied by moving the spacer ring from the front shoulder to the back of the nozzle piece, which was removable. The nozzle was positioned by the steam inlet tube which was fixed to the assembly by a drilled-through 1" x 1" Swagelock connector. The venturi was close-connected to the scrubber sump at a point 6" above the maximum liquid level. The vapor-liquid mixture, after exiting the venturi, passed through a short length of 3/4" tube which had been sectioned and bent over to give the mixture a tangential flow as it entered the sump in order to promote disengagement.

All scrubbing tests in this task were carried out with steam containing H₂S/N₂ only, i.e., no NH₃ or CO₂ were injected. The pH of the scrub solution was controlled by adding (NH₄)₂SO₄ along with the makeup CuSO₄ fed to the system. The analytical method used to determine the H₂S content of inlet and outlet steam for these tests differed from that previously reported, and corresponded quite closely to techniques used at The Geysers. Samples of condensate were collected into strong ammonia solutions, and the sulfide content of the mixture was determined by potentiometric titration with standardized silver nitrate solutions.

FIGURE 1

TEST SETUP, VENTURI SCRUBBING EFFICIENCY TEST

FIGURE 2

SECTION VIEW OF LAB SCALE VENTURI SCRUBBER

TEST RESULTS

Test results showing H_2S removal efficiencies as a function of operating conditions for segmental and disk and donut trays, for a spray column, and for a venturi are summarized in Tables I-IV.

Trayed Internals

Both the segmental and disk and donut trays proved to be acceptable from an operational point of view in that they were self cleaning. Relatively small amounts of solids built up on the horizontal tray surfaces rather quickly, but soon reached steady state levels and were continuously flushed by the descending scrub solutions (slurry). The majority of the tests on these internals were run under hydraulic conditions (steam rates and liquid-to-vapor flow rate ratios) which resulted in pressure drops across the tray stacks in the range of 1-2 in. of water. Under these conditions, H_2S removal efficiencies ranged from 82-91% and averaged about 87%. Since six trays were used in each stack, average tray efficiencies were about 33%. By way of contrast, a single crossflow sieve tray operating under these conditions would be expected to show of the order of 85-90% removal efficiency, depending on the froth height actually obtained.

In one experiment, Run 714, Test No. 5, hydraulic conditions were set so that a pressure drop of about 5-1/2" was obtained and removal efficiency increased to 97% (comparable sieve tray operating conditions should give 95-98%). However, to achieve this pressure drop the tray stack had to be operated in the "loaded" condition, i.e., with a considerable amount of liquid held up on the trays by the rising vapors. The device was being changed from vapor-continuous operation, which is normal, to liquid-continuous operation at which point flooding is likely to occur. This is not a stable operating regime and is not desirable for trouble free operation.

It might appear that higher removal efficiencies could be obtained in the vapor-continuous mode of operation by the simple expedient of adding more trays. Within limits, this is true since at the least, longer contact times will be provided, although mass transfer driving forces will also be decreasing

Table I
Scrubbing Tests with Segmental Trays⁽¹⁾
Run 705

Test No.	2	3	4	5	6	7
Time into Run, min	25	50	60	140	180	230
Steam Flow, PPH	103	146	154	130	118	144
Scrubbing Liquid Flow, GPH	55	55	55	55	110	30
F Factor	0.54	0.76	0.81	0.68	0.62	0.75
L/V	4.4	3.1	3.0	3.5	7.8	1.7
Pressure Drop, in. H ₂ O	0.9	1.0	1.3	1.8	2.8	0.6
Scrubbing Solution						
g/l Cu	4.4	3.9	3.7	3.1	3.4	6.7
pH	1.82	1.56	1.52	1.43	1.37	-
Inlet Steam H ₂ S, PPM	179	127	200	233	204	184
Outlet Steam H ₂ S, PPM	29.7	19.1	18.1	20.2	26.7	26
% H ₂ S Removal	83.4	84.9	90.9	91.3	86.9	85.9
Number of Stages ⁽²⁾	1.80	1.89	2.40	2.45	2.03	1.96
Tray Efficiency, %	30	32	40	41	34	33

⁽¹⁾Six trays with 20% segmental area removed

⁽²⁾ $N = \ln (y_o/y_e)$

Table II
Scrubbing Tests with Disk and Donut Trays⁽¹⁾
Run 714

Test No.	2	3	4	5
Time into Run, min	30	90	120	145
Steam Flow, PPH	106	100	138	145
Scrubbing Liquid Flow, GPH	55	110	55	83
F Factor	0.56	0.53	0.73	0.77
L/V	4.3	9.2	3.3	4.8
Pressure Drop, in. H ₂ O	1.0	1.3	2.0	5.4
Scrubbing Solution				
g/l Cu	4.6	2.5	4.8	3.5
pH	1.59	1.45	1.36	1.23
Inlet Stream H ₂ S, PPM	245	255	278	266
Outlet Steam H ₂ S, PPM	43.8	27.5	29.3	8.0
% H ₂ S Removal	82.2	89.2	89.5	97.0
Number of Stages ⁽²⁾	1.72	2.33	2.25	3.50
Tray Efficiency, %	29	37	38	58

(1) Six trays with 56% area disks, 68% area donuts.

(2) $N = \ln (y_o/y_e)$.

Table III
Scrubbing Tests with a Spray Column
Run 0224

Test No.	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>
Time into Run, min.	15	35	50	65	80
Steam Flow, PPH	112	162	167	104	168
Scrubbing Liquid Flow, GPH	110	55	30	13	13
F Factor	0.65	0.94	0.97	0.61	0.98
L/V	8.2	2.8	1.5	1.0	0.65
Scrubbing Solution					
g/l Cu	4.4	6.8	8.1	7.2	8.4
pH	1.68	1.41	1.37	1.41	1.31
Inlet Steam H ₂ S, PPM	259	206	187	279	179
Cleaned Steam H ₂ S, PPM	8.4	47.2	63.7	91.7	79.3
% H ₂ S Removal	96.8	77.1	65.9	67.1	55.7
Number of Stages ⁽¹⁾	3.43	1.47	1.08	1.11	0.81
Contact Time, sec.	3.4	2.3	2.3	3.6	2.2

⁽¹⁾ $N = \ln (y_o/y_e)$.

Table IV

Scrubbing Tests with a Venturi

Run	803	803	808	808	808	808	808	808	808	808	808
Test No.	2	3	2	3	4	5	6	7	8	9	10
Time into run, min	25	55	15	40	75	100	120	140	195	225	245
Steam Flow, pph	104	105	101	102	136	130	130	132	170	120	79
Scrubbing Liquid Flow, GPH	110	55	110	55	110	55	30	15	55	55	55
L/V	8.8	4.4	9.0	4.5	6.7	3.5	3.5	3.5	2.7	3.8	5.8
Velocity Head, ⁽¹⁾ psi	0.28	0.28	0.26	0.27	0.47	0.43	0.43	0.44	0.74	0.36	0.16
Scrubbing Solution											
g/% Cu	1.9	9.8	1.0	8.3	3.1	5.0	2.6	2.8	9.4	5.9	4.2
pH			1.55	1.54	1.20	1.19	1.09	1.08	1.12	1.24	1.22
Inlet Steam H ₂ S, ppm	217	211	276	278	286	306	302	291	300	75.6	244
Outlet Steam H ₂ S, ppm	22.7	38.1	46.0	49.2	40.0	79.5	124	141	107	27.1	57.1
% H ₂ S Removal	89.5	81.9	83.3	82.3	86.0	74.0	59.1	51.6	64.3	64.2	76.6

(1)

$$\frac{\rho_g v_g^2}{2 g_c} \times \frac{1}{144}$$

as more H_2S is removed. With all else equal, it is to be expected that doubling the number of trays would increase removal efficiencies by only about 7% while substantially increasing scrubber column height. Although these tests were run at rather low vapor velocities ($F \sim 0.8$) due to boiler limitations, there is no reason why a commercial scale unit could not be designed to operate in the same range of vapor velocities as a sieve tray, although tray spacing might have to be increased.

In summary, these styles of trays would be effective and reasonably economic if removal efficiencies in the 80-90% range were acceptable. However, very high removal efficiencies will be difficult to obtain unless the system is operated in a loaded condition which would severely limit operational flexibility.

Spray Column and Venturi Scrubbers

Both spray columns and venturis are vapor phase continuous types of contactors whose efficiency depends on the specific surface area produced as the scrubbing liquid is atomized and on vapor-liquid contact time. Spray columns are well suited to applications where equilibrium considerations do not demand a high degree of staging, can operate in either co or counter-current flow arrangements, and have no internals which can foul although nozzle plugging always presents potential operating problems. Venturis are more compact devices, operate in cocurrent flow arrangements only and utilize relatively high gas velocities to promote vapor liquid contact; high shear rates further subdivide and mix the liquid droplets issuing from the nozzles. Since contact times are much shorter than are encountered in spray contactors, liquid specific surface areas must be much larger and/or contact more effective to obtain comparable efficiencies.

Test results in the laboratory spray column, summarized in Table III, illustrate the effects of contact time and liquid specific surface area. The latter is controlled by liquid flow rate through the spray nozzle, increasing with increasing flow rate, and the former is determined by the steam flow rate. The results are as expected; increasing liquid flow at a given steam rate and

decreasing steam rate at a fixed liquid flow both increase scrubbing efficiency. While quite high degrees of H_2S removal were obtained in Test No. 2, the high L/V and low steam velocity required would have serious economic consequences. Alternative nozzle styles, which give finer droplet sizes, and taller spray columns, to provide equal contact times of higher velocities, could be utilized to mitigate these disadvantages to a certain extent. However, inordinately high scrubbers are not desirable, and production of a very fine spray of liquid will cause difficulty in the design of a separator to control entrainment. As was the case with trayed internals, it appears that removal efficiencies in the 80-90% range can be obtained with little difficulty, but designs for achieving very high removal efficiencies will be more complex and costly.

Contact times in the venturi scrubber were two orders of magnitude less than in the spray column, yet reasonably high removal efficiencies were obtained as shown in Table IV. The results of Tests No. 2 and 3 (Run 803), 2 and 3, and 4 through 7 (Run 808) illustrate the beneficial effect of increasing liquid rate on scrubbing efficiency at a given steam flow rate. The results of Tests No. 3, Run 803, and 3, 5, 8, and 10 of Run 808 show the effect of increasing steam rate at a given liquid rate. Scrubbing efficiency passes through a maximum at 100-130 lb/hr steam flow for 55 gal/hr liquid flow for this venturi. This probably results from the method used to mix the liquid into the vapor (see Fig. 2); a liquid nozzle was not used and high vapor phase turbulence and shear are required to disperse the liquid adequately. At low steam flows, dispersion was apparently less than optimum, while at high steam rates short contact times apparently offset any advantage gained by decreased drop size or improved mixing.

Again, removal efficiencies in the 80-90% range proved to be relatively easy to obtain, although at pressure drops which are rather higher than are commercially desirable. Thus, industrial scale venturis have been shown to have pressure drops of about one velocity head at a liquid rate of four gallons per thousand cubic feet of gas, and pressure drops increase approximately linearly beyond that. Since the lowest L/V's run in these tests

exceed this liquid rate by a factor of 30, pressure drops of the order of 10 psi would be expected.

More efficient, lower pressure drop designs may be possible in industrial scale units, which would have throat diameters of the order of 3 feet, through the use of multiple liquid injection nozzles. Even though contact times in larger units would be of the order of 0.1 sec, 5-10 times higher than tested here, it is doubtful that substantially higher efficiencies can be obtained in a single unit, and two venturis in series would be required to obtain very high removal efficiencies. The results of Test No. 9, Run 808 show that lower efficiencies will be obtained in the second unit, as expected, because of the reduced mass transfer driving forces.

In summary, removal efficiencies in the 80-90% range would be possible with relatively simple spray columns or with a single venturi. High degrees of removal would require complex spray column designs or the use of at least two venturis in series.

ALTERNATIVES FOR A COMMERCIAL SCALE SYSTEM

The performance of laboratory scale sieve and shower tray and spray columns and venturi scrubbers was reviewed in order to establish preliminary criteria for the design of these types of devices at a commercial scale of operation.

The methodology for this involved determining the pertinent scale up laws for each type of scrubber when operating as a chemical reactor. Then, laboratory data were reduced to the form required for use in performance correlations. This approach was applied with varying degrees of effectiveness to each scrubber type since few data have been published on scale up principles for some, and the amount of laboratory data available was limited for all. Only the sieve tray data could be scaled up with a high degree of confidence, since this device has been tested extensively and on a larger scale. Critical assumptions had to be made with respect to the design criteria for all others.

Laboratory data on the scrubbing efficiency of segmental and disk and donut trays, while obtained at high L/V's, simulated operation at relatively

low weir overflow rates, e.g., 1-2 GPM/ft. For commercial scale operation at comparable vapor velocities, weir overflow rates would increase by an order of magnitude at $L/V \sim 1$. It was assumed that the increased overflow rate would permit efficient operation at this lower L/V , that tray efficiencies would remain unchanged, and that shower type trays with 70% free area with maximum F factors of about 3.5 (nominal $F \sim 2.5$) would be suitable for this service. It was assumed that both higher L/V 's and lower vapor velocities as well as an increased number of stages would be required to achieve high degrees of removal.

Scale up of a spray column at the same liquid flux used in most laboratory tests, about 10 GPM/ft², also permits operation at lower L/V 's at the commercial scale. It is assumed that multiple nozzles will be used to obtain the required droplet size distribution and uniform coverage, and that sufficient shell height will be provided to insure adequate contact time - nominally 2.5 sec. Doubling the liquid rate and increasing contact time to 3.5 sec, at the same vapor velocity, are assumed to provide at least the same (97%) removal efficiency found in laboratory tests.

Multiple nozzles would also be used in commercial scale venturries, and might be expected to provide better dispersions of liquid in vapor than was achieved in the simple laboratory venturi. A throat diameter of 3 ft would provide vapor velocities comparable to those tested, but liquid fluxes would be lower by a factor of about 5. However, the physically larger commercial scale venturi would also provide longer contact times, by about a factor of 5, than the laboratory device, and it is assumed that these would be offsetting effects. Since near quantitative removal was not shown in the laboratory venturi, even at the highest liquid rates, it was assumed that two venturis in series, with an intermediate vapor liquid disentrainer, would be required to achieve high degrees of removal.

The configurations these types of scrubbers would have at a commercial scale, the scrubbing liquid circulation rate required, scrubber pressure drop, and systems cost are summarized in Table V for low and high degrees of H₂S removal. All the tower configurations evaluated, and the venturis final

Table V
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
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.

separator have approximately the same diameter. A diameter of about 16 ft results in a vapor F of about 2.5 which is near the nominal design point for mesh pad type demisters. If more compact, efficient demisters could be used all tower sizes, and costs, could be decreased somewhat; decreasing diameters to 14' - $F \approx 3.3$ - would reduce system costs by about 10%. With the exception of the use of two venturis in series, pressure drops for all configurations are low enough to be acceptable.

The costs of the scrubber shells were estimated by weighing up the vessels once the configuration was established and applying a cost per pound for fabricated pressure vessels. The use of 20% clad construction was assumed with a 1/8" corrosion allowance and C20Cb3 used for all wetted parts. The venturi costs, estimated at \$50M per unit, were also determined by weighing the unit and using a cost per pound for the solid C20 construction assumed. Internals and auxiliaries costs include trays, demisters, spray nozzles, platforms and ladders, and miscellaneous equipment. Scrubbing liquid services include a circulating pump and spare, piping, and valves, all of Alloy 20. Pump capacity was restricted to 2000 GPM and the use of AVS standard designs was assumed so that multiple units would be required at high circulatory rates.

Total estimated costs show that it is not likely that shower tray type scrubbers would be cost effective in this service, particularly if high degrees of removal are required, because of the larger vessel sizes required. Spray columns, however, are smaller and cheaper. Simple in concept, they must be shown to be more effective than assumed here, however, to be attractive. A particularly simple configuration for a spray contactor, if effective, could be attractive, however. This would involve spraying the scrubbing liquid into a length of Alloy 20 steam pipe sufficiently long to provide the required contact time and providing disengagement at its end. This would require, however both effective liquid distribution and demisting to be more cost effective.

A sieve tray column with a single tray, the device to be tested at one tenth the scale assumed here, is clearly preferred if high degrees of removal are required, since this is achieved simply by using higher froth

heights. Only 5-10 ft of the shell is required for contacting and disengaging, another 4 ft are required for demisting, 6 ft for the steam inlet nozzle and steam distribution, and the balance is used as a sump to hold a 30 min inventory of copper in the system. If it can be shown that the make up CuSO_4 pump reliability and systems operability are such that this is excessive, systems cost would be reduced by about 10%.

This consideration, and demister design details, are especially important for the venturi systems, where the venturi proper is only a small part of the total costs. If these sump-demister costs could be reduced, and if a single venturi can be shown to be capable of achieving high removal efficiencies at reasonable liquid rates, this type of scrubber would be quite attractive. It would be simple, compact, relatively inexpensive, and probably readily accepted by plant operators who are already familiar with the venturi ejectors now used in the plants for noncondensibles removal.

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CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Task Report on Task C.2

Eight Inch Column Design and Operation

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SUMMARY

Nearly quantitative removal (cleaned steam < 0.7 ppm H_2S) of hydrogen sulfide from geothermal steam has been obtained, with no major operating problems, by scrubbing with copper sulfate solution in an 8" scrubbing column containing a single counter-flow sieve tray.

In a run of thirty hours duration, 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 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.

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. Approximately 80% of the ammonia and boron in the incoming steam were also removed under the process conditions tested.

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.

The main material of construction for the scrubber, C20Cb3, showed excellent service under operating conditions, being superior to types 304 and 316 stainless steel but not as passive as titanium or, apparently, EB26-1.

The test results obtained in the 8" scrubber are being incorporated into the updated design criteria for a 100,000 PPH field test facility.

TEST OBJECTIVES

The objectives of Task C.2 were to design, fabricate, install, and operate a small scrubbing column on geothermal steams to obtain data which would confirm laboratory results being used to establish criteria for the design of a 100M PPH field test facility.

Scrubbing was to be demonstrated in a continuous manner, but liquid/solid separation and regeneration operations would not be included. Samples from the column purge would be tested to determine settling and leaching rates and leach stoichiometries, while make-up scrub solution would be obtained by dissolving fresh copper sulfate for recycle.

It was anticipated that site-specific considerations, if any, would also be revealed during the design effort for the small system and during its operations. The system was to be designed, however, to be transportable and to have enough flexibility to permit its use at a variety of sites.

TEST PLAN

The expected onset of bad weather at The Geysers dictated that a very intensive test plan of short duration be developed. The test plan used, summarized in Table 1, contained the following elements:

- Mechanical integrity testing
- Clean steam calibration (water scrubbing)
- Open circuit operability testing
- Open circuit scrubbing efficiency testing
- Closed circuit scrubbing testing

In open circuit testing, the make-up scrub solution was to be made up fresh to simulate a recycle condition; in closed circuit testing, scrub solution was to be made up from recycled, decanted purge solution. Broadly, all elements of the test plan were executed as planned, except for closed circuit scrubbing testing.

TEST EQUIPMENT AND OPERATING PROCEDURES

The 8" scrubbing column system used in these tests is shown schematically in Dwg. 19320-1-1, and an assembly detail of the column proper is shown in Dwg. 19310-1-1.

Make-up scrub solution was prepared by dissolving the required amounts of CuSO_4 and $(\text{NH}_4)_2\text{SO}_4$ in 20-gal batches of warm tower water and transferring the solutions to the 200-gal holding tank. A metering pump transferred the solution at the desired rate through a double-pipe heater, heated with cleaned steam, into the scrub solution (slurry) recirculating line. Scrub solution was circulated through the 12" diameter column sump section by a centrifugal pump, and a portion was withdrawn, through a rotameter, and pumped to a sparge nozzle located at the top of the scrubbing column. A portion of this scrub solution was, in turn, withdrawn from the circulating line and passed through a double-pipe cooler and a purge flow control valve which responded to the sump level. The purge slurry was collected in a 200-gal surge tank.

The scrubbing column proper was 8" in diameter and 10 ft long and had a single sieve tray with 22% active area and a 2" diameter downcomer located at the bottom. There was also an 8"-deep Teflon mesh pad demister located at the top, above the scrub solution sparge nozzle. The column was fitted with two sight glasses, located approximately 6" and 6' above the tray, respectively, and nozzles for connection of a DP cell to measure the pressure drop across the tray. A spray nozzle was installed above the demister to permit it to be washed with heated tower water, if desired. Sample taps were provided to withdraw cleaned steam from the column above the demister and to sample scrub solution (slurry) from the recycle line.

Steam to be scrubbed passed through a rotameter/transmitter before entering the column in the sump section below the tray. Its flow rate was controlled by a valve on the exit steam line, which led cleaned steam to the PG & E turbine blade test stand and the cooling towers. Water for

pressurizing the centrifugal pump's mechanical seals, for demister wash, and for purge slurry cooling was drawn from the cooling tower sump and pressurized by a positive displacement pump.

At start-up, steam was passed through the scrubber at atmospheric pressure at about 500 PPH, and the scrub solution circulation pump was run at maximum flow until the system had come to steady state at 100°C. The pressure was then slowly increased to full line pressure by throttling the steam flow control valve, and condensate was purged from the system. When steady state was reached, usually within 1/2 hr of start up, the flow of scrub solution to the top of the scrubber was stopped, and make-up CuSO_4 solution was pumped into the sump at the maximum possible rate. It usually required less than 5 min to obtain the desired copper concentration, and scrubbing was then initiated at once by resuming flow of scrub solution.

The degree of scrubbing was controlled by varying the flow of scrub solution fed to the top of the column. Samples of cleaned steam were withdrawn periodically for pH measurement and determination of H_2S content by potentiometric titration with AgNO_3 . Samples of scrub solution were also withdrawn for pH measurement and determination of copper content by use of color comparators. Data logged routinely included steam flow rate, temperature and pressure, scrub solution flow rate, scrubber tray pressure drop (froth height), sump level, pump pressures and settings, and make-up and purge tank levels.

CHEMICAL ANALYTICAL TECHNIQUES

Analyses were performed in the field for process control purposes. Copper in solution was determined semiquantitatively by use of a color comparator (Nessler tubes). The hydrogen sulfide in steam was determined by the PG & E method of sparging the steam into concentrated ammonium hydroxide and titrating the absorbed soluble sulfide with standard silver nitrate solution to a silver ion-specific electrode end-point.

Samples returned to EIC were analyzed by the methods previously reported, except for details of the analytical procedure for the copper

sulfide solids. Copper in solution was determined by direct spectrophotometry (near-infrared wavelength); free sulfuric acid, by titration with standard sodium hydroxide to a pH end-point; total sulfate, after copper removal by cation exchange, by titration with lead perchlorate to a lead ion-specific electrode end-point; and ammonia, by use of an ammonia sensing electrode.

The copper sulfides, which are prone to oxidation in drying, were dried by a modified procedure which greatly reduced the oxidation. The dried solids were dissolved by prolonged digestion in concentrated nitric acid, with sodium chlorate-admixture to oxidize any elemental sulfur formed, and the final solution analyzed for copper spectrophotometrically. Comparison samples of the dried solids were analyzed for total sulfur by an outside laboratory, employing the combustion method. Values close to 100% for the sum of the copper and sulfur contents gave assurance of the reliability of the measured copper sulfide composition.

TEST RESULTS

Mechanical Integrity Testing and Clean System Calibration

Mechanical integrity testing utilizing incoming geothermal steam with cooling tower water as a scrubbing medium proceeded without incident. While all major components functioned as expected, several minor piping changes were made to improve operability, the most important of which was the installation of a cartridge filter to clean up cooling tower water prior to its use as a coolant for the circulating pump's seal cooling chamber. The only equipment failure experienced during these tests was of two (supposedly) Teflon-lined flexible connectors around the scrub solution circulating pump. The liners disintegrated after 7 hours operation, allowing acid copper sulfate to penetrate the bellows, causing failure at the connection to the flange. They were replaced with field-fabricated stainless steel spool pieces.

With a scrubbing solution flow of 7.5 GPM and a steam flow of 1200 PPH, a froth height of 6" was observed, while at 1000 PPH steam and 4 GPM

scrub flow (L/G ~ 2), the froth height dropped to 3-4" at a tray pressure drop of 2" H_2O . This behavior is consistent with that expected in the steam/water system for these hydraulic conditions and for the tray used (2" dia downcomer, 2" weir height, 22% active area).

Once the system had been run for some time to dry out the column and piping insulation, which had been wet with tower drift, a heat loss calibration was run by collecting condensate in the column sump overnight as steam was blown through at atmospheric pressure. The measured heat loss (3600 BTU/hr) and known ΔT (150°F) leads to a column UA of 24 BTU/hr/°F. This compares with a value of 22 BTU/hr/°F calculated from estimated areas and insulation U values.

Open Circuit Operability Testing

Scrubbing for hydrogen sulfide removal was initiated by simply injecting copper sulfate solution into the sump at a high rate to obtain the desired copper content. This was carried out with no circulation of scrub solution, after the system had been brought to thermal steady-state with steam and water. Once a flow of scrubbing solution was initiated, a low density froth was observed to form immediately on the scrubbing tray, with the concurrent formation of solids and removal of hydrogen sulfide. The time from initiation of copper sulfate addition to achievement of satisfactory operation (scrubbing efficiency >90%) was always less than 15 min.

Normal shutdown was also achieved in less than 15 minutes. The flow of scrub and make-up copper sulfate solutions were stopped and the sump level control bypassed to pump the contents of the sump into the purge tank at the maximum possible rate. The system could then be flushed by refilling the sump with tower water through the demister wash nozzle and circulating it through the system with the scrub solution pump. Essentially all of the solids produced during the run were usually flushed from the system after two or three sump displacement washes of the system.

Minor operating problems were encountered from time to time due to solids passing through the scrub solution rotameter and purge level control valve. The rotameter had to be cycled periodically from zero to maximum flow to prevent it from "sticking" at the nominal operating point, probably due to accumulation of solids around the float. Because of the low flow and high pressure drops involved, the level control valve's "trim" was quite small (required $C_v = 0.008$), and the valve was easily plugged. This plugging was at least partially overcome by cycling the valve, but a build up of packed solids in the valve seat prevented tight shut-off after long periods of time.

During the course of various scrubbing tests, it was found that froth height (actually, tray pressure drop was read directly; froth height is inferred) was not very sensitive to steam flow rate for step changes of about 10% from a nominal operating condition. Froth height and, therefore, scrubbing efficiency were, however, sensitive to changes in scrub solution flow rate, as had been observed in lab-scale tests. The variation was of sufficient magnitude to lend itself easily to automatic control of froth height by adjustment of scrub solution recirculation rate.

It was also found that the scrub solution flow rate required for a given froth height was a function of sump level, decreasing as sump level increased - and seal height decreased. A decreased seal height would have allowed less time for froth collapse and would, therefore, have limited downcomer capacity. At low sump levels, the downcomer size, 2" diameter, was too large to retain high froth heights at low scrub flow rates, ca. $L/G = 1$, and high rates ($L/G \sim 4$) or low seal heights (~ 1 ft) were required.

The downcomer was also fitted with a seal cup to permit operation at very low sump levels without bypassing steam up through the downcomer. This cup was ultimately fitted with a 2×1 concentric reducer which, while restraining liquid flow and improving tray hydraulics, also tended to act as a solids trap for the seal cup. There is evidence of a partial plug forming and clearing, presumably in the seal cup, at least twice during the 30-hour run.

At no time, however, was there any evidence of solids accumulation on or under the sieve tray, of hole constriction, or of downcomer blocking, except in the bottom of the seal cup. Neither were substantial amounts of solids found on the sump walls, in piping, or on the scrubber column walls below the normal froth level. Some solids had adhered to the column walls above the froth level in patches typically less than 1/16" thick, on the lower portion of nozzles, and in sight-glass necks. The loosely adhering solids were easily displaced by water washing.

A significant amount of solids was found to have accumulated within the bottom 1" of the 8" thick demister pad in the column top bonnet. The pad was only 5" from the scrub solution sparge nozzle, and solids were seen to have migrated along the outside of the sparge pipe from bottom to top. It is not known if the solids in the demister were 1) picked up directly from the sparge nozzle, 2) primed up on one of at least two occasions when froth heights exceeded at least 8' temporarily, or 3) were deposited during the "normal" demisting function of the pad. It should be noted that the top of the pad was clean and free of solids and that the demister wash was not normally used during the scrubbing tests, being on for only two hours out of a total of 50.

The make-up scrub solution contained nominally 30 g/l Cu and 100 g/l $(\text{NH}_4)_2\text{SO}_4$, with no free H_2SO_4 , and was heated with cleaned steam in a double-pipe heater. Laboratory solubility studies had shown that the formation of insoluble basic copper sulfate is possible at high temperatures and low acidities in solutions of this composition. Indeed, the heater was found to be badly fouled after 24 hrs operation under these conditions and was bypassed. This potential operating problem can be avoided by maintaining a concentration of free H_2SO_4 as indicated below.

Open Circuit Scrubbing Efficiency Testing

A series of four runs, including one of 30 hours duration, was carried out with open circuit scrubbing to gather design information on the effects of operating variables on scrubbing efficiency. These include:

- The effect of froth height on scrubbing efficiency, 100% purge case (no recycle of $(\text{NH}_4)_2\text{SO}_4$) - Run 1208.
- Scrubbing efficiency at high froth heights, simulated recycle from low- NH_3 steam scrubbing - Run 1209.
- The effect of contact time on scrubbing efficiency, maximum recycle of $(\text{NH}_4)_2\text{SO}_4$ - Run 1210.
- The effect of sump level (solids residence time) and scrub solution copper content on scrubbing efficiency and stoichiometry - Run 1214/1215.

The total stream time during these tests was approximately 50 hours, during which 50,000 lb of steam was treated with removal of approximately 12 lb of H_2S and the formation of 45 lb of solids.

The results for Run 1208 are summarized in Table 2. In the first test, 0850 hrs, the "scrubbing" solution was simply steam condensate, which was ineffective in removing H_2S from the incoming steam. If condensate were used and purged at rates comparable to those later used in scrubbing with CuSO_4 solution, it would be possible to remove only 5-10% of the H_2S from the incoming steam in this manner.

The scrubber was then run for about 4 hours to insure that steady state had been attained, but there appeared to be little change after the first hour. Approximately 90% removal was obtained at a froth height estimated to be about two feet. Then, as froth height was increased to an estimated 4-1/2 and 5-1/2 ft, recoveries increased to 95 and 98%, respectively. Further increasing the froth to 6-1/2 ft gave near-quantitative removal.

The results for Run 1209 are summarized in Table 3. Froth heights ranged from 3-1/2 to 6-1/2 ft, and removal efficiencies averaged almost 99.5% and were generally higher than for Run 1208 at a given froth height. This result is to be expected, since recycle $(\text{NH}_4)_2\text{SO}_4$ would buffer the scrub solution pH at a higher steady-state value, an action which has been shown to be beneficial in lab tests.

The results for Run 1210 are summarized in Table 4. The expected correlation between increased contact time and scrubbing efficiency is not

apparent in these data, due either to scatter in the data, analytical uncertainties, or the influence of other variables (copper concentration, pH, etc.) The correlation is apparent, however, in the data taken from Run 1214/1215, shown in Fig. 1. The trend line drawn through the data suggests a dependence of the number of transfer units obtained ($N = \ln(n_o/n_e)$) on the square root of contact time, as would be predicted from a penetration theory approach to the rate of mass transfer. Correlations for sieve tray efficiency based on penetration theory (First Annual Report, Appendix B) suggest that 99% removal would require a contact time of 1.8 - 1.9 seconds under these process conditions, while actually 1.5 seconds is sufficient, probably because of the increased surface area in the low density froth (~25%) obtained in this system. It is of interest to note that the two-film theory for bubble cap trays would predict sufficient contact in 0.6 - 1.2 seconds, which is clearly too short a time.

The log of operations for the 30 hours run of 1214/1215 is summarized graphically in Fig. 2. The first 5-1/2 hrs of the run were dedicated to operation at low sump levels and scrub solution copper contents, which conditions should produce the "freshest" solids, subject to the least alteration of CuS to sulfides of higher copper content. An unexpected result of this period was the demonstration that scrubbing efficiency falls off markedly at copper contents below about 1.5 g/l, even though the total flow of scrub solution carried a ten-fold excess of copper to the steam and contact times were sufficient to provide at least 97% removal at higher copper levels. At lower copper contents, liquid phase diffusion may be influencing kinetics. In other respects, the performance of the scrubber was as expected during the course of the run. The anticipated relations among contact time, froth height and pressure drop for various removal efficiencies derived from these data are summarized in Table 4. It can be concluded that high removal efficiencies are possible over wide ranges of operation, which will permit a highly flexible scrubber design to be developed.

During the first 5-1/2 hrs of the test, the average solids residence time in the system was 2-2/3 hrs at an average copper content of 1.9 g/l and a pH of 1.3. The solids produced had a composition of $\text{Cu}_{1.8}\text{S}$. During the next 5-1/2 hrs, the residence time was increased to 3-3/4 hrs at a copper content of 3.6 g/l and a pH of 1.4 and solids with a composition of $\text{Cu}_{1.95}\text{S}$ were produced. Over the entire run the averages were 3-1/4 hrs, 3.0 g/l, and pH 1.4 with solids produced of composition $\text{Cu}_{1.9}\text{S}$.

Analytical limitations do not permit the copper to sulfur ratio to be obtained to better than ± 0.05 units. Thus, while the indicated increase in copper to sulfur ratio with increased residence time is consistent with expectations, the absolute difference is not far beyond the limits of precision of analysis. It is clear, however, that for the solid residence times and solution composition of interest for commercial sized units, the covellite (CuS) formed in the initial precipitation reaction is nearly completely altered to approach chalcocite (Cu_2S) in composition.

Material Balance/Stoichiometry

The overall material balance for the 30 hrs run of 1214/1215 is summarized in Table 6.

The total volume of solution purged exceeded the calculated purge volume by 28 gallons. The source of the extra water is unknown (it would constitute 0.7% moisture in the inlet steam or a heat loss almost double that measured earlier), but it had the effect of diluting the concentrations in the purge stream by almost 20%.

The amounts of copper used and hydrogen sulfide scrubbed were measured fairly carefully, the main uncertainty arising from an allowance of ± 10 ppm in inlet H_2S compositions. This uncertainty, together with the analytical limit of ± 0.05 in solids copper to sulfide composition creates a significant range of possible error in the amount of sulfide oxidized to sulfur and sulfate, since it is found by difference.

The same consideration applies to the ammonia balance, where the amount scrubbed is found by taking the difference of large numbers, each

with its uncertainty. Thus, while the computed ammonia removal is only 70%, the range of uncertainty extends to as high as 95% removal.

This, in turn, contributes to the uncertainty in the acid balance since the total acidity formed in the scrubbing reaction appears in the purged scrub solution both as free acid and tied up, with the scrubbed ammonia, as ammonium sulfate. An independent check on the validity of the overall material balance may be made, however, by considering the requirements of the stoichiometry of the scrubbing reactions. The ratio of acidity produced to H_2S scrubbed and the extent of oxidation of sulfide sulfur to elemental sulfur are not independent of each other for a given solids composition.

For a ratio of copper consumed to H_2S scrubbed of 1.43 and a solids composition of $Cu_{1.9}S$, the stoichiometry demands that 10% of incoming sulfide be oxidized to elemental sulfur with an additional 14.5% oxidized to sulfate. However, the same stoichiometry requires a ratio of acidity produced to sulfide scrubbed of 2.96 while the directly calculated value is 2.79. Alternatively, an acidity to sulfide scrubbed ratio of 2.79 at a solids composition of $Cu_{1.9}S$ would require about 22% oxidation to S^0 with 10% oxidation to sulfate and a copper consumed to sulfide scrubbed ratio of 1.3. While the latter is outside the expected error in the observed consumption, $Cu/H_2S = 1.43 \pm 0.08$, the acidity ratio 2.96 is within the limits expected for the directly measured $H^+/H_2S = 2.79 \pm .6$.

Furthermore, direct measurements by PG & E of ammonia scrubbing efficiency made on condensate freshly produced during the test, indicated that at least 80% was removed. If this were so over the entire course of the test, an additional 14.1 moles (above the 70% removal case) should have been purged, and this amount is indeed well within the limits of possible uncertainty. If scrubbed, this ammonia would also consume an additional 14.1 moles of acidity, again well within expected uncertainties, and result in an acidity to sulfide scrubbed ratio of 2.94 which is in agreement with the value calculated directly from the measured copper consumption and solids composition.

It is likely, then, that the actual ammonia removal averaged about 80%, and 10% of the incoming sulfide was oxidized to elemental sulfur while 15% was oxidized to sulfate.

Ammonia Removal

The removal of ammonia obtained in these tests, ranging from at least 70% to a probable 80%, was rather lower than had been achieved in laboratory tests on simulated geothermal steam. However, the larger than expected dilution of the recirculating slurry and the absence of the 5-10 g/l level of free acid in the make-up scrub solution resulted in a scrub solution pH which was about 0.1 unit higher than anticipated. In an integrated process, this acid, recycled from the copper sulfate regeneration step, would not only alleviate the fouling problem in the make-up scrub solution preheater, but should increase the removal of ammonia to the 90% range demonstrated in laboratory tests by providing additional acidity to form ammonium sulfate and lower the scrub solution pH.

Boric Acid Removal

Samples of untreated steam condensate, scrub solution and cleaned steam condensate taken by PG & E on Dec. 15 were analyzed by them for boric acid. Results are shown in Table 7 together with boron analyses performed on selected samples shipped to EIC. As had been shown in laboratory tests, boric acid was removed from the steam accumulating in the recirculating scrub solution. Under the conditions of the 30-hr run, the boric acid removal efficiency was in the range 73.6-84.3%, or about 80% as stated above.

The overall boron balance can not be closed, however, for either set of analyses. The PG & E figures apparently understated the boron content of the purged scrub solution while the EIC value probably overstates it, and the errors are of the order of 50-100% in the overall balance. Nevertheless, the removal efficiency was high in both cases,

and the sump compositions are in the range of those expected in an integrated process.

Additional Analyses

Spectrographic analyses of one solid and four liquid field samples are given in Table 8, where all detected occurrences are included. Chemical species comprised only of nonmetallic elements, e.g., NH_3 , Cl^- , SO_2^{2-} , CO_3^{2-} , etc. are not detected by this technique. Thus, chemical analysis of the October 26 sample of Unit No. 7 cooling tower (coldwell) water gave $[\text{NH}_3]_{\text{total}} = 0.0062\text{M}$, $[\text{SO}_2^{2-}] = 0.002\text{M}$ and $\text{pH} = 7.8$, the major additional solute species being boric acid.

Of particular interest is the low impurity content of the cleaned steam. Except for boron and Na, Mg, Al, Si and Ca, which were probably from extraneous sources, no metallic impurities exceed 0.1 ppm in order of magnitude in the Dec. 14 condensate. The indicated low level of copper, about 1 ppb, confirms that the column demister was very effective in removing entrainment from the scrubbed steam.

There appears to be few, if any, metallic impurities in the scrub solution which could not have been derived from the make-up solution, which was prepared from commercial grade chemicals and cooling tower water. The same may be said with respect to the source of impurities, with the possible exception of cadmium, of the copper sulfide solids.

Overall, no direct evidence has surfaced for a measurable accumulation in the scrubber of the steam-borne particulates known as "rock dust". Scanning electron microscopy, with elemental detection, of the copper sulfide solids produced at 1400 and 2000 on Dec. 14 did reveal a very small concentration of extraneous microscopic particles, which were conspicuous in being smooth-surfaced as compared with the spongy microscopic texture of the sulfide. These extraneous particles appear to be silicates, but could well have been derived from the cooling tower water, which was atypically dirty during the period of the field test.

The presence of mercury is not indicated in Table 8. However, it is known to be present in the steam, but at an extremely low level, as the result of sensitive analyses at the site by Battelle Northwest. Their measurements of mercury were 3.7 $\mu\text{g/kg}$ (0.037 ppb!) in the condensable fraction of both incoming and scrubbed steam on Dec. 14 and 0.64 $\mu\text{g/kg}$ and 0.70 $\mu\text{g/kg}$, respectively, in the noncondensable portion. That is, there was no scrubbing of volatile mercury species under the condition of the test.

Condensate Properties

The cleaned steam condensate obtained in these tests was milky due to the presence of colloidal sulfur and had a lower pH than found in laboratory tests, although the pH data for the first three runs are suspect, apparently being low by 0.8 unit due to a faulty pH electrode. The measured condensate pH's were 5.5-5.6, somewhat lower than the value expected for steam condensate in equilibrium with 3000 ppm CO_2 , i.e., slightly lower than pH 6. A complete anion analysis would be required to determine the source of the acidity.

Checks for entrainment of copper and acid from the scrub solution always showed levels that were below the limit of detection (0.05 ppm). Since particles smaller than 100-500 μm will be entrained in the steam at the velocities used in these tests, and the expected level of entrainment was about 2×10^{-4} lb/lb of steam, the demister collection efficiency must have been of the order of 99.5%. This is consistent with the manufacturer's data for removal of particles with sizes above 5-10 μm .

Solids Properties

The macroscopic properties of the solids produced in the 8" scrubber from actual geothermal steam are quite similar to those produced from simulated geothermal steam in laboratory tests. Liter-cylinder settling tests at 50°C showed compression times of 30 seconds which are essentially the same as those found in laboratory tests. All materials produced in

laboratory runs, however, (and some samples from field runs) were flash-cooled from 175°C to 100°C, while the 8" column purge was "slow-cooled" in a heat exchanger. The "slow-cooled" material did show a slight tendency to settle more slowly and to a lower pulp density than flash-cooled material, but the difference is so small as to be unimportant for design purposes. A complete report on this behavior will be issued for Task A.3.

Materials Testing

A variety of corrosion test coupons was inserted in the column sump along with a Magna Corp. corrosometer probe with a C20Cb3 40-mil wire element. Post-run inspection of the coupons showed that all alloys tested as isolated specimens, including 304, 316, UHB 904L, EB26-1, and C20Cb3 stainless steels and Ti, gave excellent service, exhibiting corrosion rates from 0.2-4.8 MPY. However, a C20Cb3 crevice corrosion test showed severe attack, even though copper contents of the scrub solution were always kept high. Post-run inspection of the column and accessories, which were mostly C20Cb3, showed no evidence of attack of any pressure parts. Crevice corrosion was observed on a plug valve in the recirculation line. A complete report on this behavior will be issued for Task A.1.

IMPACT OF TEST RESULTS ON PRELIMINARY DESIGN CRITERIA

Observations made during the field testing of the 8" scrubber unit have led to the following conclusions, which will be incorporated into the final design criteria for the 100M PPH field test facility.

- The target H₂S removal efficiency will be 99%, rather than 90%, with a pressure drop less than 1 psi and a column F-factor greater than 1.5.
- A single sieve tray will be used, with an active area of about 20% and a downcomer capacity of about 500 GPM/ft². No seal cup will be used.

- A minimum of 6 ft disengagement space from maximum froth height to demister will be provided, with scrub solution returned at the normal maximum froth height level.
- A sump residence time of 4 hrs will be provided. The assumed scrubbing stoichiometry is the formation of Cu_2S with 10% oxidation of S^{--} to S^0 , 15% oxidation to SO_4^{--} .
- Rotameters will not be used to measure scrub solution (slurry) flow rates.
- Scrub solution purge will not be withdrawn from the recycle scrub solution line. Purge flow rate control will be cascaded from make-up scrub solution flow, rather than from sump level. The purge withdrawal rate will be isokinetic insofar as possible.
- Plug valves will not be used in piping loops at scrubber conditions of acidity and temperature.
- The pedigree of materials and methods of construction of trim components using composites and elastomers for liners will be carefully checked before their use is specified.
- The make-up scrub solution heater will be piped to allow bypassing, if fouled, and will be of a design which permits easy cleaning.
- The column proper and trim components will be designed and specified to minimize the occurrence of crevices.
- Make-up and seal-coolant water from tower sumps will be filtered prior to use.

Table 1
Test Plan Outline, 8" Column
Accelerated Program

	<u>Task</u>	<u>By</u>	<u>Days (x Shifts)</u> <u>Required</u>
I.	<u>INSTALLATION</u>	PG&E/EIC	
	i) Service Hook-Up		3
	ii) Intra Skid Hook-Up		1 x 2
		(t _o + 1 ⁻ wk)	
II.	<u>MECHANICAL INTEGRITY & STEAM/WATER TESTING</u>	PG&E/EIC	
	i) Electrical, H ₂ O, Steam, Air		2
	ii) Instrument, Auxiliary, Loop Piping		1 x 2
	iii) Limits of Operability & Clean Calibration		2 x 2
	iv) Start Up/Shut Down, Materials Handling, Emergency, Safety Review		1 x 2
		(t _o + 1 ⁺ wk)	
III.	<u>OPEN CIRCUIT SCOPING & DESIGN CONFIRMATION TESTS</u>	EIC	
	i) Open Circuit at Nominal Conditions for Operability		1 x 2
	ii) High & Low pH Scrubbing Tests		1 x 2
	iii) Effect of [Cu] and Holding Time on Solids		1 x 2
	iv) Hydraulics Testing		1 x 2
	v) Inspection, Revise/Repair		2 x 2
		(t _o + 2 ⁺ wk)	
IV.	<u>CLOSED CIRCUIT CONFIRMATION TEST & CLEAN STEAM PRODUCTION</u>	EIC	
	i) Closed Circuit at Nominal Conditions for Operability		1 x 2
	ii) Variation of Conditions as Required		1 x 2
	iii) Clean Steam Production		2 x 3
	iv) Inspection, Shut Down		2 x 2
		(t _o + 3 ⁺ wk)	

Table 2

Run 1208

Effect of Froth Height (Tray Pressure Drop) on Scrubbing Efficiency

Make-Up Scrub Solution: 40 g/l Cu, Zero $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4

Time	0850	1145	1300	1400	1430	1515	1600	1645
Time into Run, hrs	1/3	1-1/2	2-3/4	3-3/4	4-1/4	5	5-3/4	6-1/2
Steam Flow, PPH	1050	1000	1000	1050	1030	1020	1050	1030
Scrub Solution Flow, GPM	6.5 ⁽³⁾	7	7	7.2	7.3	> 8	> 8	> 8
Demister Wash Flow, GPH	0	0	0	0	0	0	5	4
Tray Pressure Drop, inches H_2O	1	6	6	5.6	8	14	16.5	19
Scrub Solution								
pH ⁽¹⁾	6.6	2.1		1.9	2.2	2.3	2.2	2.6 ⁽⁵⁾
g/l Cu	0	1.5	2	2	2	2.3	2.5	~ 6
Steam Condensate								
pH ⁽²⁾	6.6	3.1	3	3.7	3.9	4	4	4.8
ppm H_2S	243	21	33	30	25	12	5.4	0.7
% H_2S Removal ⁽⁴⁾	0	91.1	86.0	87.2	89.4	94.9	97.7	99.7

(1) Electrode probably reading high by 0.7 units.

(2) Electrode probably reading low by 0.8 units.

(3) Scrub solution is steam condensate.

(4) Inlet steam contains 235 ppm H_2S (5) Make-up scrub solution containing 50 g/l $(\text{NH}_4)_2\text{SO}_4$ fed for 1/2 hr prior to sampling.

Table 3

Run 1209

Scrubbing Efficiency at High Froth Heights (Tray Pressure Drops), Intermediate $(\text{NH}_4)_2\text{SO}_4$
 Make-Up Scrub Solution 40 g/l Cu, 50 g/l $(\text{NH}_4)_2\text{SO}_4$

Time	1130	1330	1430	1530	1630
Time into Run, hrs	1/2	2-1/2	3-1/2	4-1/2	5-1/2
Steam Flow, PPH	1050	1030	1050	1040	1050
Scrub Solution Flow, GPM	7.1	~ 8	7.5	> 8	> 8
Demister Wash Flow, GPH	0	0	0	4	0
Tray Pressure Drop, inches H_2O	16	10	11	20	17
Scrub Solution					
pH ⁽¹⁾	2.5	1.8	1.9	1.9	2.2
g/l Cu	4	3.5	3.5	2.5	2.5(4)
Steam Condensate					
pH ⁽²⁾	4.9	4.9	4.8	5.1	5.4
ppm H_2S	< 1.3	0.7	2.6	< 1.3	0.7
% H_2S Removal ⁽³⁾	> 99.4	99.7	98.9	> 99.4	99.7

(1) Electrode probably reading high by 0.7 units.

(2) Electrode probably reading low by 0.8 units.

(3) Inlet steam contains 230 ppm H_2S .

(4) Make up scrub solution containing 100 g/l $(\text{NH}_4)_2\text{SO}_4$ fed for 1 hr prior to sampling.

Table 4

Run 1210

Effect of Steam Contact Time on Scrubbing Efficiency, High $(\text{NH}_4)_2\text{SO}_4$
 Make-Up Scrub Solution 30 g/l Cu, 100 g/l $(\text{NH}_4)_2\text{SO}_4$

Time	1100	1200	1300	1400	1500
Time into Run, hrs	3/4	1-3/4	2-3/4	3-3/4	4-3/4
Steam Flow, PPH	1080	1080	1050	1250	770
Scrub Solution Flow, GPM	6.9	6.3	5.8	4.8	7.5
Demister Wash Flow, GPH	0	0	0	0	0
Tray Pressure Drop, inches H_2O	8	12	13	12	13
Steam Velocity, ft/sec	2.6	2.6	2.5	3.1	1.8
Contact Time, sec	1.0	1.5	1.7	1.3	2.4
Scrub Solution					
pH ⁽¹⁾	2.4	2.0	2.5	2.1	2.0
g/l Cu	4	3	2	1.8	2
Steam Condensate					
pH ⁽²⁾	5.2	5.2	5.2	5.4	5.5
ppm H_2S	2.8	< 1.3	2	6.5	2.6
% H_2S Removal ⁽³⁾	98.8	> 99.4	99.1	97.2	98.9

(1) Electrode probably reading high by 0.7 units.

(2) Electrode probably reading low by 0.8 units.

(3) Inlet steam contains 230 ppm H_2S .

Table 5

Influence of Tray Hydraulics on Scrubbing Efficiency
 Scrub Solutions: 3 g/l Cu, pH 1.4

Column F-Factor	1.5	2
Diameter at 10^5 PPH Steam	78"	68"
10^6 PPH Steam	18'	15.5'
Froth Height, ft, for		
90% Removal	1.1	1.4
95%	1.7	2.3
99%	4	5.4
99.7%	6.8	9
Tray Pressure Drop, psi, for		
90% Removal	0.15	0.2
95%	0.2	0.3
99%	0.4	0.6
99.7%	0.8	1.0

Table 6
Overall Material Balance
Run 1214/1215

Water Balance

Total make-up scrub solution fed	89 gal
Condensation due to heat loss ⁽¹⁾	31 gal
Condensation due to heating make-up solution	13 gal
Expected purge	133 gal
Actual volume of purged solution	161 gal

Copper Balance

Moles of copper fed with make-up scrub solution	168.6 ± 1.1
Moles of copper in purged scrub solution	31.2 ± 0.6
Moles of copper in sulfide solids	137.4 ± 1.7

Sulfur Balance

Moles of sulfide in incoming steam ⁽²⁾	97.4 ± 4.1
Moles of sulfide in cleaned steam ⁽³⁾	1.6 ± 0.1
Moles of sulfide removed	95.8 ± 4.2
Moles of sulfide associated with 137.4 ± 1.7 moles of copper in sulfide solids at Cu(1.9±.05)S	72.3 ± 2.8
Moles of sulfide oxidized to S° and SO ₄ ⁻⁻	23.5 ± 7
Percent of sulfide oxidized to S° and SO ₄ ⁻⁻	24.2

Ammonia Balance

Moles of ammonia fed with make-up scrub solution	414.3 ± 10.1
Moles of ammonia in purged scrub solution	514.0 ± 22
Moles of ammonia scrubbed from steam	99.7 ± 32.1
Moles of ammonia in incoming steam ⁽⁴⁾	141.3 ± 8.3
Percent ammonia scrubbed from incoming steam	70.5

Acid Balance

Moles of acid fed with make-up solution	0.9
Moles of acid in purged scrub solution	168.9 ± 11
Moles of acid used scrubbing ammonia	99.7 ± 32.1
Moles of acid formed in scrubbing H ₂ S	267.7 ± 43.1
Moles of acid formed per mole H ₂ S scrubbed	2.79

(1) For UA = 25 BTU/hr/°F, (2) at 235 ± 10 ppm H₂S, (3) at 98.4% removal,
(4) at 170 ± 10 ppm NH₃.

Table 7

Analyses for Boric Acid
(reported as boron)

<u>Sample</u>	<u>PG&E</u> <u>ppm</u>	<u>EIC</u> <u>ppm</u>
Untreated steam condensate (12/15/76)	14	
Cleaned steam condensate (12/14, 1700 hrs.)		3.7
Cleaned steam condensate (12/15, 1200 hrs.)	2.2	
Make-up CuSO_4 feed solution (12/13)		179
CuSO_4 scrub solution purge (12/15)	190	
CuSO_4 scrub solution purge (12/16)		691

Table 8

Semiquantitative* Spectrographic Analyses of Field Samples

Element	10/26 Coldwell Water ppm	12/13 Make-up Solution ppm	12/16 Scrub Solution ppm	12/16 Final Purge Solids, ppm	12/14 Cleaned Steam Condensate, ppm
B	0.1%	150 /	700	0.5	5
Na	5	5	1	N.D.	1
Mg	0.5	20	10	3	1
Al	0.01	5	0.2	0.5	0.5
Si	1	20	0.2	50	0.5
Ca	0.1	5	1	N.D.	0.5
Cr	N.D.	5	4	1	N.D.
Mn	0.001	0.02	0.2	0.1	0.001
Fe	N.D.	50	20	1	0.1
Cu	0.005	3%	0.3%	>10%	0.001
Mo	N.D.	N.D.	0.2	N.D.	N.D.
Ag	N.D.	1	N.D.	N.D.	N.D.
Cd	N.D.	N.D.	N.D.	5	N.D.
Sn	N.D.	N.D.	0.2	N.D.	N.D.
Pb	N.D.	10	1	2	N.D.

* Within one order of magnitude, i.e., 10 ppm could be as high as 30 ppm or as low as 3 ppm.

Fig. 2.

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GENERAL NOTES

- 1) PROCEED TO STEP 2, IN PARAGRAPH 2, LINE 10 OF THE ATTACHED FORM
- 2) IF THE ANSWER IS "UNKNOWN" OR "NO" BY CH-135
- 3) THE ANSWER IS "A" FOR "UNKNOWN" AND "B" FOR "NO" BY CH-135

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FOR INFO

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EIC Corporation
55 Chapel Street
Newton, Massachusetts 02158

CONTROL OF HYDROGEN SULFIDE EMISSION FROM
GEOTHERMAL POWER PLANTS

Contract No. EY-76-C-02-2730.*000

Final Report on Task C.6

Optimization and Economics Studies

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SUMMARY

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

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 system. Because solids disposal costs are high, purge stream neutralization with ammonia is preferred at The Geysers. 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 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, 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 to 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 are 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 estimated 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 Stratford plants supplemented by a standby upstream vent gas cleaning system and the use of H_2O_2 to oxidize residual H_2S in the plant condensate is capable of highly effective abatement but is likely to be very costly.

BACKGROUND AND BASES FOR DEMONSTRATION AND COMMERCIAL PLANT DESIGNS

A series of laboratory studies, Tasks A.1-A.4, process engineering studies, Tasks B.1-B.4 and process and project engineering work, Tasks C.1-C.5, has been carried out which has led to the detailed design of a demonstration plant for the copper sulfate process for removing hydrogen sulfide from geothermal steam at upstream conditions.

The laboratory work and process engineering studies were carried out in order to obtain the data necessary to support the design criteria needed for the demonstration plant. In the first engineering task, C.1, demonstration plant objectives, operating, and performance criteria were fixed and site specific factors were determined. Then, with performance criteria and design criteria fixed, and the site specific material balance and operating requirements known, it was possible to develop a detailed design for the demonstration plant. The plant, designed to treat 100,000 lb/hr of steam, would be of sufficient size that all operations would be carried out in equipment of scaleable design. However, for operating convenience, and because of site specific and material balance considerations, it was recognized that the demonstration plant would not necessarily reflect the most appropriate configurations for a commercial process.

Thus, the costs for the demonstration plant can not be scaled up directly to obtain the costs of a commercial facility. While the demonstration plant design must be flexible enough to permit operation over a wide variety of conditions, the design of a commercial facility would be "optimized" for conditions at a particular site and, of course, economies of scale would be possible. System "optimization" in this context has two components:

Given data on the kinetics and equilibria of scrubbing and regeneration, for instance, it might be determined that a venturi scrubber is cost effective only if low degrees of H_2S removal are required or that pressure leaching with oxygen is preferred to air leaching at current oxygen and power costs. These considerations would be quite general and apply to operations of any site. Site specific considerations, on the other hand, might dictate that the sulfide solids produced in several small, scattered scrubbers be collected for regeneration in a large, central regeneration facility to minimize operator attention and take advantages of the economies of scale.

In the absence of a great deal of specific information as to the characteristics of a given site, the latter type of "optimization" can be addressed only qualitatively. However, if the criteria used for the design of the demonstration plant are accepted as valid bases (and the objective of the demonstration plant operation is to show that they are), and the effects of alternative steam compositions on the system material and energy balances are comprehended, it is possible to "optimize" the system from a process point of view, at least for defined ranges of capacities and steam compositions.

This task, C.6, consists of a process engineering and economic evaluation of the copper sulfate process to determine its "optimum" configuration for a range of steam compositions and treatment capacities likely to be encountered at a commercial scale. To this end, it is necessary to fix "base case" conditions as a point of departure for material and energy balance calculations and equipment sizing and costing. Therefore, an evaluation of system configurations and costs has been carried out for the

treatment of two million pounds per hour of steam, corresponding to a nominal 110 MW power generating capacity, under conditions similar to those encountered at The Geysers. System performance criteria are summarized in Table I along with those used in the design of the demonstration plant. Equipment design criteria for the major items of equipment are summarized in the cost estimate, Table VIII.

Optimization studies have already been carried out for the scrubbing and liquid-solid separation steps. The results are reported in the preliminary task reports for Tasks B.4 and B.3 and will not be repeated here. In this report, detailed analyses of purge treatment and regeneration alternatives are presented, and the results of the previous work are integrated into a complete system description.

OPTIMIZATION OF A COMMERCIAL SYSTEM FOR BASE CASE CONDITIONS

It is convenient for purposes of this evaluation to break down a commercial system into major components or operations, and examine the characteristics of each. Then, the interaction among components and the impact of alternative material balances may be examined separately.

The system components or operations which have been examined in this study include:

- Scrubbing
- Purge slurry liquid-solid separation
- Regeneration, including preleach and residue releaching.
- Solubles purge stream treatment, including neutralizations and decopperization.
- Other process steps, including polish filtration, heat exchange, and support services.

Table I

**Design Bases for Demonstration and Commercial Plants for the Copper Sulfate
Process for the Removal of Hydrogen Sulfide from Geothermal Steam**

	<u>Demonstration Plant</u>	<u>Commercial Facility</u>
Plant Size, MW	5	110 ⁽¹⁾
Steam Treated, 10 ⁶ lb/hr	0.1	2 ⁽¹⁾
H ₂ S Inlet Concentration, PPM	220	220
% removal	99	99
Solids composition	Cu _{1.9} S	Cu _{1.9} S
% S ²⁻ oxidized to S ⁰	10	10
NH ₃ Inlet Concentration, PPM	170	170
% removal	90	90
Solubles Purge Neutralization	Batchwise, NH ₃	Continuous, NH ₃
Solubles Purge Decopperization	Occasionally, with H ₂ S or Fe	Continuous, solid ion exchange
Preregeneration Treatment	Occasional ambient leach	Continuous ambient leach
Regeneration Technique	Oxygen or air pressure leach	Oxygen pressure leach
Post Regeneration Treatment	None	Oxygen pressure leach of residues
Disposal of Soluble Impurities	Reinjected with condensate	Reinjected with con- densate
Operator Attention Required	Intensive	To be minimized.

(1) Two 55 MW generators each requiring 1 × 10⁶ lb/hr steam.

Scrubbing and Purge Slurry Liquid-Solid Separation

Evaluations of alternative styles of scrubbing and liquid solids separation devices have been presented in preliminary reports for Task B.4 and B.3 respectively.

It was shown that the degree of H_2S removal required influenced the type of scrubbing device chosen and its costs. For the high degree of removal required here (see Table I), a trayed column with a single crossflow sieve tray is the least expensive device. If, however, adequate removal efficiencies could be obtained in a single venturi stage, this would be a cost effective device if pressure drops approaching 5 psi are acceptable.

It was also shown that a continuous decanter is the preferred type of device for obtaining the desired degree of liquid-solid separation of the purge slurry if regeneration is to be carried out by pressure leaching. The costs for this device are so low, and its operation is so simple, that this conclusion would be valid over the entire expected range of purge stream flow rates, inlet slurry densities, and outlet slurry densities up to 10%. If the roast regeneration alternative is contemplated, however, use of a centrifuge would be required to obtain a slurry density high enough to permit autogenous roasting. A centrifuge, however, would be more labor intensive and require far more maintenance than a decanter.

Regeneration Options

The two major options for regeneration of copper sulfate from copper sulfides precipitated from geothermal steam involve pressure leaching with air or oxygen and roasting. The former approach would be carried out in agitated pressure vessel(s), the latter in fluid bed roasters with a supporting bed of

inert material. Kinetic data on regeneration of scrubber solids are presented in the preliminary reports for Tasks A.2 and B.2 for leach and roast regeneration respectively.

A commercial scale operation must regenerate somewhat less than 20 tons per day of sulfide solids for the conditions specified in Table I. By way of contrast, a commercial scale roaster for treating concentrates of natural copper sulfide minerals would typically handle about 500 tons per day of solids.

The components of a fluid bed roaster system for this application would include: (wet) solids storage, solids feeding, the roaster proper, makeup inert bed material storage and feeding, primary and secondary dust removal from roaster offgas, waste heat recovery (or gas cooling), offgas scrubbing for SO_2 control, disposal of SO_2 scrubbing sludge, redissolution of the basic copper sulfate salts formed in the roasting reaction, and polish filtration for removal of insoluble residues. The roaster itself would be about 5 ft in diameter and would require, with its auxiliaries, more or less constant operator attention.

The components of a pressure leach reactor system for this application would include: slurry storage and feeding, energy recovery (feed preheating, effluent cooling), the regeneration reactor proper, (cooled) effluent liquid separation, leach residues storage, leach residues re-leaching, and re-leached effluent polish filtration for removal of insoluble residues. A source of oxygen or air under pressure would also be required. A commercial scale regeneration reactor would have a volume of the order of 10,000 gal and would be designed for 150 psig operation.

At this scale of operation, the equipment required for regeneration by pressure leaching is near normal commercial size and relatively simple.

Except for releaching of residues, no solids handling operations are involved and a minimum of operator attention would be required. Here, and at lower production rates, regeneration by pressure leaching is clearly the preferred alternative. If a central facility for regeneration of solids from a 500 MW operation were contemplated, however, this would not necessarily be the case. For this production level, the roaster would be 10-11 ft in diameter, which is quite reasonable, while a large, 50,000 gallon regeneration reactor would be required. For this evaluation, however, we will consider only the configuration of a pressure leach regeneration system in detail.

Preleaching, Leaching, and Polish Leaching

It is necessary to develop a general rate expression, to predict the effects of oxygen partial pressure and temperature on regeneration kinetics, for system optimization studies. The data presented in the preliminary results for Task A.2 and of a subsequent ambient leach tests were reduced to obtain the predictive equation shown in Table II. The pressure leach data are reasonably consistent with a variation of one standard deviation of ± 1.0 in the time constant, 6% of the average value. The ambient leach data fall well outside this range, however, appearing to be over seven times as rapid as pressure leach results when normalized to oxygen partial pressure. It is probable that this results from the method of gas-liquid contacting used in the ambient leach tests which promoted formation of a froth in the surge tank. Liquid diffusional resistances would be expected to be low, and leach rates rapid in this circumstance.

Preliminary energy balances suggest that the cooled purge slurry from the scrubber will be at 95°C, and if leached at "ambient" conditions will

Table II
Evaluation of Leach Regeneration Data

<u>Run No.</u>	<u>Leach Temperature °C</u>	<u>Oxygen Pressure psia</u>	<u>Time to 99% Leaching min</u>	<u>Time Constant (l. min/psia)</u>
<u>Pressure Leach</u>				
3	115	94	130	19.5
4	115	94	140	21.0
6	130	25	360	18.2
7	135	31	200	13.5
9	130	30	260	15.8
10	96	75	170	14.6
11	144	76	70	13.3
12	116	65	160	16.8
13	135	50	205	22.4
15	140	100	90	21.1
17(2)	135	16	380	13.3
18(2)	135	19	330	13.7
				Avg. 16.9
<u>Ambient Leach</u>				
	45	2.5	2400 ⁽³⁾	2.3

- (1) Time for 99% Leaching = constant $\times \exp (2500/T^{\circ}K)/\text{oxygen pressure.}$
 (2) Air pressure leach.
 (3) Extrapolated from data for times less than 8 hours.

cool to about 80°C as a consequence of the evaporation of water carried off with the inerts. With 400% excess of air at slightly above atmospheric pressure, approximately 32 hours would be required for 99% leaching. This would require a tank with a holding capacity approaching 250,000 gallons, and a design which would insure adequate gas-liquid contact, effective solids suspension, and retention of solids to prevent by-passing.

An alternative to attempting complete regeneration under ambient conditions is to "preleach", taking advantage of the fact that initial leach rates are significantly faster than average rates. Since the pressure leach data show that, within the scatter of the data, the slope of plots of $1-(1-\text{fraction reacted})^{1/3}$ vs. time are linear, the relationship between percent regenerated as a function of the fraction of time to 99% regeneration shown in Table III is obtained. Thus, over 20% of the solids are leached in 10% of the total time, and almost half are leached in 25% of the total time. Beyond 50% of the total time leach rates drop sharply. The consequences of "preleaching" solids for, say, 20% of the total time required for 99% regeneration is to leach 40% of the material initially present. Then, required holding times in a subsequent pressure leach would be reduced to 80% of that required for "fresh" solids, and oxygen consumption would be reduced to 60%.

A minimum surge capacity of about 8 hours would be provided to isolate the scrubber from a regeneration reactor for operating flexibility, so that only the incremental costs of the increased tank size to provide additional free board need be considered. The savings from decreased oxygen consumption would exceed air compressor power costs by about \$50,000/year, and the net purchased equipment costs of the larger air compressor and surge (preleach) tank and decreased pressure leach reactor are about \$30,000. Since capital

Table III

Extent of Regeneration as a Function of the
Fraction of Time to 99% Regeneration

<u>Leaching Time/ Time for 99% Regeneration</u>	<u>Fraction Solids Reacted</u>	<u>Leach Rate, $\Delta F/\Delta (t/t_{99})$</u>
0.05	0.11	2.2
0.1	0.22	2.2
0.17	0.34	1.8
0.2	0.40	1.8
0.25	0.48	1.6
0.33	0.60	1.5
0.5	0.78	1.1
0.67	0.89	0.6
1	0.99	0.3

charges on the increased total investment will be less than \$25,000/year, the incremental investment would have a pay back time of about 5 years and the use of a preleaching step is justified.

The empirical relation between leaching temperature, oxygen pressure, and time required for 99% regeneration was used to predict required holding times over a wide range of operating conditions. A leach temperature was chosen, which fixed the solution's vapor pressure, and a range of oxygen pressures fixed so that the total pressure equaled a desired value. The results, shown in Fig. 1, show that an optimum temperature exists for each pressure: below the optimum, kinetic factors limit and above the optimum the increased vapor pressure decreases oxygen pressure at a rate which more than offsets the kinetic gain. The residence times, reactor volumes, and vessel configurations required at optimum temperature for a range of pressures are summarized in Table IV.

To a first approximation, vessel costs will decrease with vessel weight, although construction for service above 150 psi will be more expensive because of the need for special fittings. And while smaller agitators will be required as the vessel size decreases, larger feed pumps will be needed to work against the higher pressures, and energy recovery exchangers will be required to raise the feed to the desired optimum temperature. The exchanger and agitator sizes and regeneration equipment capital and operating costs are summarized in Table V as a function of total pressure. This analysis shows a broad optimum in the pressure range between 100 and 150 psig. Below 50 psig, large vessel costs dominate, and above 150 psig high pressure construction and power costs offset savings from the use of smaller vessels. A prudent design strategy would be to specify operating conditions corresponding to

Fig. 1. Effect of leach temperature and total pressure on the time to obtain 99% regeneration with oxygen.

Table IV

Effect of Total Pressure on Residence Time and
Reactor Configuration Required for 99% Regeneration

<u>Operating Pressure psig</u>	<u>Optimum Temp. °C</u>	<u>Residence Time min (1)</u>	<u>Design Volume M gal (2)</u>	<u>Vessel Diameter ft (3)</u>	<u>Wall Thickness in. (3)</u>	<u>Vessel Weight M lb</u>
10	90	860	120	17.5	1/4	68
15	90	660	93	16.0	1/4	57
25	100	420	60	13.5	1/4	40
50	110	200	29	10.5	1/4	24
75	120	130	18	9.25	5/16	24
100	130	86	12	8.0	5/16	18
125	135	63	9	7.25	3/8	18
150	140	50	7	6.75	7/16	18
200	155	34	5	6.0	1/2	16
250	160	24.	3.5	5.25	9/16	14

(1)

With 40% regeneration accomplished by preleaching.

(2)

With 25% freeboard allowed.

(3)

Horizontal vessel with four stages of length equal to diameter.

Table V

Effect of Total Pressure on Regeneration Equipment Size and Cost

<u>Operating Pressure psig</u>	<u>Exchanger Area ft²</u>	<u>Agitator Power HP</u>	<u>Feed Pump Power HP</u>	<u>Total (1) Equipment Cost, \$M</u>	<u>Annual (2) Operating Cost, \$M/yr</u>
10	100	25	2.5	221	192
15	100	20	2.5	189	162
25	50	10	2.5	136	116
50	-	5	5	91	80
75	75	3.5	7.5	88	77
100	125	2.5	7.5	70	63
125	150	2	10	71	64
150	200	1.5	15	74	66
200	275	1	20	82	72
250	300	1	25	90	78

(1)
Reactor, agitators, exchangers, and incremental pump purchased equipment costs.

(2)
Cost of pump plus agitator power plus capital charges on equipment.

100 psig operations, but to rate all items for use at 150 psig conditions. This would provide a safety factor which would permit normal operations even if the preleach step were not used.

Even with an effective leach, however, kinetic and hydraulic limitations, due to by-passing for example, will cause some solids to pass through unleached along with insoluble materials such as "rock dust". This material must be purged from the system, and a continuously back washed polish filter would be well suited to removing them from the regenerated leach solutions. The amount of unregenerated solids to be retreated is so small, however, that a continuous leaching operation may not be convenient. Rather, it is likely that a day's worth would be worked off in the leaching of a single batch on one shift per day. Finally, the truly insoluble residues would be separated from the regenerated sulfides and purged from the system following this "polish" leach step. Since none of this type of residue has as yet been generated however, the design criteria for this operation can not be fixed with a high degree of confidence.

Solubles Purge Stream Neutralization and Decopperization

The solubles purge stream flow rate is fixed by the requirement to remove soluble impurities, e.g., $(\text{NH}_4)_2\text{SO}_4$, H_2SO_4 , and H_3BO_3 , from the system at a "reasonable" concentration and to preserve the system's water balance. Since an excess of cupric ion must be present in the scrubbing solution to prevent corrosion and insure high degrees of removal of H_2S , it will be present in the solubles purge stream and must be removed and recycled for economic and environmental reasons. Since for all geothermal steams of interest the ratio of $\text{NH}_3:\text{H}_2\text{S} \leq 2$, the solubles purge stream will also contain excess H_2SO_4 formed in the scrubbing-regeneration reactions. This

acid must be neutralized for environmental and operational reasons, e.g., to prevent corrosion in the reinjection wells.

Possible neutralizing agents, in order of increasing cost, are limestone, anhydrous ammonia, and caustic soda. The use of caustic is convenient from an operational point of view, but its cost is more than double that of ammonia per pound of acid neutralized, and the product of the neutralization reaction is a non-volatile salt which might, over time, cause problems when reinjected into the formation. The cost of limestone, if locally available, is only one tenth that of ammonia, but there are material handling problems associated with its use. Solids must be stored and fed, and the product of the neutralization reaction, gypsum, must be removed from the neutralized purge stream by filtration, stored temporarily, and disposed of. At The Geysers, disposal would require drumming the wet gypsum cake and trucking it out of the area to a landfill at a cost of about \$5/bbl. Capital and operating costs for neutralization of the purge stream from a 110 MW process plant are summarized in Table VI. The costs of waste gypsum disposal essentially offset the higher cost of ammonia, and the ammonia neutralization route would be preferred unless waste disposal costs decreased or ammonia costs increased by more than 50% from the values assumed here.

At least five major processes routes are known to have been practiced commercially for the removal of copper from solution. These processes, shown diagrammatically in Figs. 2-7 in configurations appropriate for use in this application, include:

- Precipitation with H_2S scrubbed from ejector vents.
- Displacement with Fe, reoxidation and dissolution in acid.
- Precipitation with $CaCO_3$ and redissolution in strong acid.
- Electrowinning to extraction in liberator cells.
- Removal by solid or liquid ion exchange reagents.

Table VI

Capital and Operating Costs for Purge Stream Neutralization

Using Either Limestone or Anhydrous Ammonia

<u>Capital Costs, \$M</u>	<u>Limestone</u>	<u>Ammonia</u>
Purchased Equipment Costs	53.0	17.5
Piping, Foundations, Instrumentation, Electrical, etc.	79.5	26.5
Engineering and Construction, Fees and Contingencies	<u>67.5</u>	<u>21</u>
Total Installed Cost, \$M	200	65
<u>Operating Costs, \$M/yr</u>		
Materials: CaCO_3 @ \$5/T, NH_3 @ \$200/T	8	100
Power @ 3¢/kWh	2	2
Labor @ \$20,000/MY	20	5
Capital Charges @ 20% TIC	40	13
Waste Disposal Costs @ \$5/BBL	<u>110</u>	<u>-</u>
Total Operating Cost, \$M/yr.	180	120

Fig. 2. Copper removal by precipitation with H_2S .

Fig. 3. Copper removal by displacement on iron.

Fig. 4. Copper removal by precipitation with limestone.

Fig. 5. Copper removal by electrowinning to extinction.

Fig. 6. Copper removal by solid ion exchange.

Fig. 7. Copper removal by liquid ion exchange.

Copper removal by precipitation with hydrogen sulfide is the same process as used on the H_2S containing steam used for power generation. An uncontrolled source of steam containing H_2S can be scrubbed in a column containing the purge stream from the primary scrubbing system. The steam, scrubbed clean of hydrogen sulfide, could be exhausted to the atmosphere. The decopperized purge solution would contain the by-products of scrubbing, mainly sulfuric acid and copper sulfide. The copper sulfide precipitate is filtered and the solids returned to the main scrub process regeneration reactor while the acid containing filtrate is neutralized with ammonia prior to disposal.

Figure 3 presents a scheme for removal of copper by displacement on iron. A portion of the solubles purge stream is held in contact with scrap iron in so called cementation cones. Copper metal is formed and precipitated while the iron scrap goes into solution as a sulfate. The cones are periodically emptied of the copper, which is placed in a redissolve tank containing acid supplied by the other portion of the split purge stream. The copper reacts with air and acid to form the sulfate for recycle to the scrubbing process. The soluble iron sulfate from the cones is reacted with limestone and air to form iron precipitates, and gypsum is also formed from the limestone reacting with residual acid. The solid-liquid mixture is separated by filtration. The solids, containing iron, gypsum and unreacted limestone, are disposed of and liquid wastes are reinjected.

Copper might also be removed by precipitation with limestone. Precipitates of basic copper salts and gypsum are formed from reaction of the copper and sulfuric acid of the purge stream. The solids are separated by

filtration with the liquid filtrate containing solubles of ammonium sulfate, boric acid, and manganese sulfate going to disposal. The filtered solids are placed in a redissolve tank where a portion of the scrubber purge stream containing sulfuric acid reacts with the solid copper precipitates to form soluble copper sulfate which is separated from the non-reacting solid gypsum by filtration. The filtrate containing soluble copper sulfate is recycled to the scrubbing system while the gypsum residue is sent to disposal.

Electrowinning to extinction requires that the copper sulfate purge stream be treated electrochemically in liberator cells of commercial design to plate copper out of solution and produce sulfuric acid. The copper is removed in a batch operation and placed in redissolve tank containing sulfuric acid, supplied from a portion of the electrochemical cell effluent containing the enriched concentration of generated acid. The tank is sparged with air to dissolve the copper as copper sulfate to be used in the process. The remainder of plating cell acid effluent is neutralized with ammonia prior to disposal.

The solid ion exchange process uses polymeric beads containing functional groups that selectively complex positively charged ions such as copper. The entering purge stream is polish filtered to remove trace amounts of finely suspended solids from the decanter to prevent contamination and plugging of the ion exchange beds. The sulfuric acid containing purge stream is unequally split with the largest fraction being pH adjusted in the neutralization/surge tank with ammonia for optimal removal of copper. The stream passes through the ion exchange column which removes the copper and generates sulfuric acid. The copper is retained with the column while the acid laden effluent is neutralized with ammonia and sent to the tower sumps

for disposal. A copper sorbing column is cyclically replaced with a regenerated copper free column. The spent column is stripped of copper with the smaller fraction of the split purge stream that contains sulfuric acid. The regeneration produces both an effluent of recovered copper in sulfate form that is returned to the process and a column free of copper for reuse in copper sorption.

An alternative ion exchange scheme involves the use of a liquid organic exchange media. The solubles purge stream from the decanter is filtered of fines then unequally split to retain an acid containing portion of the purge stream. The larger stream is pH adjusted with ammonia to a value most favorable for copper removal, then sent to extraction. The extraction stage counter currently contacts the aqueous copper containing stream with the copper removing organic ion exchange stream in mixer-settler vessels. The copper depleted aqueous stream passes to air floatation cells for removal of entrained organic liquid and additional neutralization, with ammonia, of sulfuric acid generated in the ion-exchange step. The recovered organic ion exchange liquid is returned to the process while the neutralized solubles purge goes to disposal. Following the extraction step, the copper enriched ion exchange fluid goes to the stripping step where contact in a mixer settler is made with the split portion of the original aqueous solubles purge stream containing sulfuric acid. The acid removes the copper from the ion exchange liquid to form strong copper sulfate for recycle and regenerated ion exchange liquid. The ion exchange liquid is filtered and recycled to the extraction step. The aqueous stream containing copper sulfate is treated by air floatation to remove entrained ion exchange liquid which is then filtered and returned to extraction. The copper sulfate is recycled to the scrubbing process.

Capital and operating costs estimated for each of these process routes are summarized in Table VII. These costs include the costs associated with neutralizing the decopperized purge stream by whichever technique, e.g., limestone or ammonia, is most suited to the decopperization operation. Thus, the precipitation techniques (excluding H_2S) are at a substantial disadvantage due to the costs of waste disposal at The Geysers. The electrowinning route would require two commercially full sized liberator cells and a low voltage rectifier which are relatively expensive, and a significant labor input to remove the copper sludge from the cells. Use of the purge stream's copper content to remove H_2S from vent gases presents the opportunity to achieve two objectives in one operation. However, the equipment is not inexpensive, and the process conditions must be carefully chosen: too much H_2S in relation to the amount of copper available will result in continued emissions while too little H_2S will leave the purge stream only partially decopperized.

Decopperization by either solid or liquid ion exchange is relatively low in both capital and operating cost. In this instance, the relatively low flow rates would permit use of dual bed solid ion exchange units of essentially standard design which are automated and require little operator attention. Weak cation exchange resins are available that have reasonable loading capacities and stabilities in a liquid of neutralized purge stream composition. Questions remain only as to the kinetics of sorption and regeneration kinetics and equilibria in a liquid with the composition of the unneutralized purge stream.

All of the neutralization-decopperization techniques evaluated above would result in the generation of a soluble purge stream for reinjection which would contain of the order of 10-15% $(NH_4)_2SO_4$. It has been presumed that

Table VII

Capital and Operating Cost Estimates for Various Purge DecopperizationTechniques for Operation at a Commercial Scale⁽¹⁾

<u>Copper Removal Technique</u>	<u>Precipitation with Vent H₂S</u>	<u>Precipitation on Iron</u>	<u>Precipitation with Limestone</u>	<u>Electrowin to Extinction</u>	<u>Solid Ion Exchange</u>	<u>Liquid Ion Exchange</u>
<u>Capital Costs, \$M</u>						
Purchased Equipment Cost	66	62	53	66	52	48
Equipment Installation, Piping Electricals, Controls, etc.	99	93	82	124	63	67
Services Costs	5	5	5	10	5	5
Engineering and Construction, Fees and Contingency	80	80	70	100	60	60
Total Investment, \$M	250	240	210	300	180	180
<u>Operating Costs, \$M/yr</u>						
Materials and Supplies	96	28	8	96	102	102
Utilities	4	4	2	14	2	2
Labor @ \$20M/MY	20	30	30	20	10	20
Capital Charges @ 20% TI	50	48	42	60	36	36
Other Costs ⁽²⁾	-	130	128	-	-	-
Total Operating Cost, \$M/yr	170	240	210	190	150	160

(1)

Recovery of 100 tons/yr copper. Includes cost of purge stream neutralization.

(2)

Solid waste disposal.

reinjection of this solution, which also contains smaller amounts H_3BO_3 and other, undefined soluble impurities, would be allowed. If these materials, and particularly the $(NH_4)_2SO_4$, must be removed prior to reinjection another process step would be required. Preliminary evaluations of the costs of its removal by lime boil or evaporation/crystallization indicate that capital costs would be comparable, and of the order of \$300,000. While direct operating costs are also comparable, the possible by-product credits available from the scale of $(NH_4)_2SO_4$ and the costs of waste disposal for gypsum sludge from the lime boil operation make it likely that evaporation would be the preferred route.

Other Process Steps

Few data are available to support design criteria for other process steps. In the absence of data, "typical" values have been assumed for design criteria such as service heat transfer coefficients and filtration rates and cycles. Costs have been based on the use of standard designs, with standby capacity provided only for pumps in critical service.

PROCESS CONFIGURATIONS FOR ALTERNATE STEAM COMPOSITIONS

The optimization developed in the preceeding section was based on a system configuration which was fixed in large part by the process material balance. This, in turn, evolved from the assumptions made as to the amount of steam to be treated, its composition, and the chemistry involved in the scrubbing and regeneration reactions. The question naturally arises as to the impact of alternative steam flow rates and compositions on the system configuration. To answer this in general, it is necessary to define the key variables which effect equipment size and cost and the influence of steam composition on the required flow rates of the various streams in the process.

To a first approximation, the size and cost of the scrubber is fixed by the flow rate of the steam to be treated and its pressure, and is independent of the composition of the steam. The flow rate of makeup CuSO_4 solution and the slurry purge rate, however, are fixed by the amounts of H_2S and NH_3 to be removed: a lower limit is set by the requirement to maintain the scrub solution $\text{pH} > 1.1$ and to limit the concentrations of CuSO_4 in the makeup stream to prevent precipitation of basic copper salts. Obviously, the size of the energy recovery exchanger and decanter are directly related to these flow rates.

The percent decantation necessary in the liquid-solid separation steps is fixed by material balance considerations for both the process as a whole and for the requirements of the leach regeneration step. The soluble purge stream's flow rate-times-compositions must be sufficient to remove soluble impurities from the system at reasonable concentrations, given solubility and pH restrictions. Since the copper concentrations in the scrub solution must be maintained above 1 g/l, the size of the decopperization equipment is directly related to the volume of the purge stream. Neutralization requirements, of course, depend on the overall process acid balance which is a function of steam compositions and scrubbing and regeneration reaction stoichiometry.

Operation of the decanter must also satisfy the requirements of the preleach-leach regeneration system, however. The desire to limit the copper content of the makeup CuSO_4 solution can, of course, always be met by diluting a more concentrated stream. But it would be desirable from a process point of view to supply the acid required for regeneration of Cu_nS ($n > 1$) from the acid produced in the scrubbing reaction itself rather than having to "import" acid which will ultimately be neutralized anyway. Since the acid concentration is,

in turn, held within limits to maintain the desired pH, the ratio of solid to liquid - the decanter underflow density - must be controlled. Since solids residence time is the dependent variable for a fixed temperature and pressure, a low slurry density requires large reactor volume and heat exchanger and agitator sizes. Air or oxygen consumptions are determined by the amount of sulfide to be regenerated and not by the slurry density.

The relation between the amounts of NH_3 and H_2S removed from the steam, the extent of oxidation of S^{2-} to S^0 , and the purge stream composition (assuming complete regeneration and recycle of Cu_nS with no use of external acid) is shown in Fig. 8. Thus, if 155 PPM NH_3 and 228 PPM H_2S are scrubbed from the steam, the mole ratio removed is 1.36. If 10% of the sulfide which is removed, 23 PPM, is oxidized to elemental sulfur and steam stripped out of the scrubber, the ratio of $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4$ in the purge stream is 3.25 mole/mole or 4.38 lb/lb. If the total ammonia removed is 310 lb/hr, 1204 lb/hr $(\text{NH}_4)_2\text{SO}_4$ and 275 lb/hr H_2SO_4 are purged, and if it is desired to maintain the acid concentration at about 25 g/l, the purge stream flow rate must be about 22 GPM. This amount of water must be made up to the process by the net flow of demister wash plus steam condensation plus evaporation from leach and preleach steps.

This balance does not address the issue of how much acid containing liquid must be allowed to pass to the regeneration step to eliminate the requirement for addition of "imported" acid. This amount is a function of the scrub (or purge) stream composition - in turn a function of the variables shown in Fig. 8, the solids composition, and the amount of excess acid it is desirable to pass through the regeneration step to prevent the precipitation of basic copper salts. These relations are summarized graphically in Figs. 9-13 for the range of variables of interest in scrubbing geothermal steam.

Fig. 8. Relation between ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed from steam and purge stream composition.

Fig. 9. Effect of ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed and scrubbing reaction stoichiometry on purge requirements.

Solids composition Cu_2S .

----- Stoichiometric acid requirements in regeneration

—— 25% excess acid provided.

Fig. 10. Effect of ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed and scrubbing reaction stoichiometry on purge requirements.

Solids composition $\text{Cu}_{1.9}\text{S}$

--- Stoichiometric acid requirements in regeneration

— 25% excess acid provided

Fig. 11. Effect of ratio of $\text{NH}_3/\text{H}_2\text{S}$ removed and scrubbing reaction stoichiometry on purge requirements.

Solids composition $\text{Cu}_{1.8}\text{S}$

----- Stoichiometric acid requirements in regeneration

—— 25% excess acid provided

Fig. 12. Effect of ratio of NH_3/H_2S removed and scrubbing reaction stoichiometry on purge requirements.

Solids composition $Cu_{1.6}S$

- - - Stoichiometric acid requirements in regeneration

— 25% excess acid provided.

PERCENT OF TOTAL FLOW FROM SCRUBBER
PURGED FOR SOLUBLES REMOVAL

For the case of removal of 155 PPM NH_3 and 228 PPM H_2S at 10% oxidation of S^{2-} to S^0 , the purge stream flow rate is about 22 GPM at an acid concentration of 25 g/l. If the precipitated solids have the composition $\text{Cu}_{1.9}\text{S}$, and it is desired to maintain a 25% excess of acid in the leach, only 20% of the purge slurry from the scrubber may be purged for solubles removal. In this case, then, the total purge from the scrubber would be 110 GPM, and 88 GPM would pass via the decanter under flow to regeneration. By material balance on the scrubbed, unoxidized sulfide, the solids ($\text{Cu}_{1.9}\text{S}$) flow rate would be about 1650 lb/hr, a slurry density of 3.7%. By the same balance the oxygen (plus air) requirements in regeneration are 9.4 tons/day.

Thus, with a definition of the rate and composition of the stream to be treated and a knowledge of the effect of scrubber operating conditions on scrubbing efficiency and reaction stoichiometry, it is possible to calculate flow rates at key points in the process. This information, together with design criteria for the process equipment permits a rapid evaluation to be made of the effect of differing material balances on process configurations. This will permit optimization studies to be carried out for a wide range of variables with relative ease.

COMMERCIAL PLANT DESIGNS AND COST ESTIMATE

System Description

The process flow diagram and material and energy balance for a commercial scale plant for treating steam of The Geysers composition are shown in Fig. 14. Key process design criteria are summarized in Table I, and the item list and equipment design criteria are summarized in Table VIII.

The process and equipment design criteria are based on:

- Steam flow rates, compositions, and conditions corresponding to those at Units No. 7 and 8 at The Geysers.
- Scrubbing efficiencies and stoichiometries for H_2S and NH_3 removal at process conditions and in equipment types demonstrated in field tests at The Geysers.
- Liquid solid separation and leach regeneration rates demonstrated in laboratory tests on solids produced from field tests on geothermal steam.
- Standard and conservative design criteria for heat transfer, polish filtration, neutralization with NH_3 , and decopperization by ion exchange steps.

Referring to Fig. 14 and Table VIII, each turbine's steam is introduced to the scrubber after passing through the Centrex units for removal of large particulates as is now done. At least 99% of the H_2S plus lesser amounts of NH_3 , H_3BO_3 , "rock dust" and other materials are removed from the steam as it is contacted, on a single crossflow sieve tray, with a scrub solution containing mainly $CuSO_4$, H_2SO_4 , $(NH_4)_2SO_4$ and precipitated sulfide solids. Process conditions are carefully controlled to maintain the scrub solution pH in the desired range and to insure that the copper concentration is sufficient to promote high removal efficiency. The scrubbed steam passes through a water washed demister for removal of entrained scrub solution and then to the turbine for power extraction.

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	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175
PRESSURE ATM	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
TOTAL FLOW GPM			24	18	57	151	264	110	10	108																		
LB/HR																												
SCFM																												
SOLIDS FLOW LB/HR	20	10	21	1	775			225	40																			

Fig. 14.

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FIGURE 14
PROCESS FLOW DIAGRAM
COPPER SULFATE FERTILIZER
PROCESS

REMOVAL OF H₂S FROM
GEOTHERMAL STEAM AT
THE GEY. CONDITIONS

05-10-77

Table VIII

Item List and Design Criteria

110 MW Prototype Plant - Geysers Conditions

Item No.	Item	Design Criteria	Equipment Description
C101, 102	Scrubbing Towers	Reduce H ₂ S from 220 to 2 ppm, NH ₃ from 170 to 15 ppm from 1×10^6 pph steam saturated at 120 psig. Froth height 7 ft, pressure drop 1.5 psi. Vapor F = 2.5, L/G = 1.	Sixteen ft dia C20Cb3 clad tower, 30 ft high. Internals consists of 1 tray of 20% area, 6" thick washed wire mesh demister.
P101-104	Circulating and Transfer Pumps	Circulate 2000 GPM slurry at 350°F through tower for scrubbing of steam, 75 ft TDH required.	Centrifugal pump with Alloy-20 casing and impeller, mechanical seal. 50 HP motor.
X101, 102	Energy Recovery Exchangers	Recover energy/heat makeup to within 10° of column temperature. Service U = 300, allow fouling factor 0.002.	750 sq. ft all T304 stainless steel plate type heat exchanger.
C103, 104	Decanters	Provide two minute solids detention time, 20 ft/hr nominal upflow velocity.	2.5 ft dia, 5 ft high, stainless steel.
T101	Return Copper Sulfate Surge Tank	Provide 5 hr surge for makeup scrub solution @ 160°F.	Two 15,000 gal closed top tank fiberglass reinforced plastic (FRP), atmospheric pressure.
T102	Reserve Copper Sulfate Storage Tank	Provide 12 hr of concentrated, reserve scrub solution @ 60°F.	Two 20,000 gal closed top fiberglass reinforced plastic (FRP), atmospheric pressure.
P105-108	Makeup Copper Sulfate Feed Pumps	Feed 60 GPM makeup scrub solution to towers 350 ft TDH required.	Centrifugal pump with stainless steel casing and impeller, mechanical seal. 15 HP motor.
P109-110	Reserve Copper Sulfate Transfer Pumps	Transfer 50 GPM reserve solution to copper sulfate surge tank as required.	Centrifugal pump with stainless steel casing and impeller, mechanical seal. 1 HP motor.

Table VIII
(continued)

Item No.	Item	Design Criteria	Equipment Description
T201	Ambient Leach Tank	Provide 12 hrs of surge capacity prior to regeneration, minimum 6 hrs solids residence time for 40% leach regeneration with compressed air at near atmospheric pressure, 80°C.	75,000 gal, stainless steel, covered vessel with agitator mounting facilities.
A201	Ambient Leach Agitator	Provide adequate solids suspension and aid gas dispersion power input 1 HP/1000 gal.	Turbine type stainless steel, 50 HP, packed stuffing box.
P201, 202	Leach Reactor Feed Pumps	Feed 110 GPM leach slurry to regeneration reactor, 350 ft TDH required.	Centrifugal pump with hardened stainless steel casing and impeller, mechanical seal. 15 HP motor.
X201	Leach Preheater	Recover energy from leach effluent, pre-heat leach solution to within 50°F of leach temperature. Service U = 300, allow fouling factor 0.002.	125 sq. ft all T304 stainless steel plate type heat exchangers.
R201	Regeneration Reactor	Regenerate 99% of entering solids in 1-1/2 hr retention time at 130°C, 100 psig total pressure, with high purity O ₂ . Provide 20% free board and design to allow operation at 150 psi for 1 hr retention.	12,000 gal T316 stainless steel horizontal reactor with 4 gas dispersion agitators. Vessel 7.5 ft dia, 30 ft long, 150 psi design.
A202-205	Regeneration Reactor Agitators	Provide solids suspension and gas dispersion to achieve k _g ^a of 0.5 SCFH/gal atm. Allow 1.5 HP/1000 gal.	Turbine type, stainless steel, 5 HP, mechanical seal.
P203-204	Leach Effluent Transfer Pumps	Transfer leached slurry to leach effluent filters. Deliver 110 gpm at 100 ft TDH.	Centrifugal pump with hardened stainless steel casing and impeller, mechanical seal. 5 HP motor.
X202	Auxiliary Cooler	Cool regenerated slurry to 160°F with tower water. Service U = 150, allow fouling factor 0.002.	300 sq. ft 2 × 4 fixed tube sheet L/L exchanger. Stainless steel tube side, C/S shell.

Table VIII
(continued)

Item No.	Item	Design Criteria	Equipment Description
F201	Leach Effluent Filters	Filter 110 GPM regenerate stream containing 0.1% solids, filtrate solids <5 ppm. Backwash with feed stream to 5% slurry density.	Automatic multiplex backwashing filters, stainless steel construction, 700 mesh screen.
R202	Polish Leach Reactor	Provide capacity for one day's backwashing from the leach effluent filter. Provide capacity to regenerate leach residues in one shift, 6 hrs.	3,000 gallons, stainless steel, 150 psi design single stage, unjacketed, agitated.
A206	Polish Leach Reactor Agitator	Provide for suspension of solids and gas-solid contacting to obtain k_{ga} of 1.0 SCFH/gal atm. Allow 2 HP/1000 gal.	Turbine type, mechanical seal, SHP, T316 stainless steel.
P205	Polish Leach Effluent Transfer Pump	Transfer 10 GPM leached slurry to filters and ultimately to the return copper sulfate purge tank.	Centrifugal pump with hardened stainless steel casing and impeller, mechanical seal, .5 PH
F202	Polish Leach Effluent Filter	Filter 10 GPM regenerate stream to remove unreacted materials and rock dust. Filtrate solids <5 PPM, backwash with cooling tower water.	Automatic multiplex backwashing filters of stainless steel construction, 700 mesh screen.

Table VIII
(continued)

Item No.	Item	Design Criteria	Equipment Description
F301	Solubles Purge Filter	Filtration of purge stream of 26 GPM prior to copper recovery by ion exchange. Reduce solids from 100 PPM to <10 PPM, backwash with feed to ambient leach tank.	Automatic multiplex backwashing filters of stainless steel construction, 700 mesh screen.
T301	Solid Ion Exchange Neutralization/ Surge Tank	Provide 10 hr surge for process purge stream. Provide pH adjustment prior to ion exchange.	15,000 gal closed top fiberglass reinforced plastic (FRP), at atmospheric pressure.
T302	Acid Purge Surge Tank	Provide 16 hr surge for acid containing purge stream used for copper recovery from ion exchange.	5000 gal closed top fiberglass reinforced plastic, atmospheric pressure.
P301, 302	Ion Exchange Sorption Feed Pumps.	Feed copper containing purge stream through ion exchange column @ 25 GPM, 50 ft TDH.	Centrifugal pump, stainless steel casing and impeller, mechanical seal, .5 HP.
P303, 304	Ion Exchange Regeneration Feed Pumps	Feed acid containing purge solution through loaded resin bed to recover copper @ 26 GPM, 50 ft TDH.	Centrifugal pump, stainless steel casing and impeller, mechanical seal, .5 HP.
C301, 302	Cation Exchange Columns	Remove 2 g/L Cu from neutralized surge stream, regenerate resin with unneutralized purge. Resin capacity 0.8 equivalent Cu ⁺⁺ /L @ 1 GPM/ft ³ flow rate. Use 3 ft deep bed, allow 100% excess capacity.	Dual bed ion exchange package unit complete with tankage, piping, valves and controls. Each bed to contain 60 ft ³ of resin.
X301	Purge Stream Cooler	Cool 26 GPM filtered purge stream from 95° to 50°C. Service U = 300, allow fouling factor 0.001.	50 ft ² shell and tube heat exchanger, T316 stainless steel tubeside, C steel shell.

Table VIII
(continued)

Item No.	Item	Design Criteria	Equipment Description
T303	Decopperized Purge Neutrali- zation Tank	Provide 4 hr surge capacity to allow for neutralization of the acid containing effluent of the ion exchanger and recycle if decopperization is incomplete.	7000 gal, open top fiberglass rein- forced plastic (FRP), atmospheric pressure.
P305, 306	Neutralization Purge Transfer Pumps	Transfer 25 GPM of neutralized decopperized effluent to the tower sumps. TDH 50 ft.	Centrifugal pumps, stainless steel casing and impeller, mechanical seal. .5 HP.
T401	Process Water Surge	Provide 2 hr surge for process water.	4000 gal, open top fiberglass rein- forced plastic (FRP), atmospheric pressure.
F401	Process Water Filter	Filter 30 GPM of water for process use, backwash to tower sumps.	Automatic multiplex backwashing filters stainless steel construction. 400 mesh screen.
P401-404	Process Water Transfer Pumps	Transfer 30 GPM of water to process for use in tower demister wash and mechan- ical seals, 350 TDH.	Turbine pump with C/S casing and impeller, mechanical seal, 15 HP motor.
V401	Leach Reactor Vent Scrubber	Provide for removal of entrained liquid from pressure leach reactor vent streams. Treat up to 10 CFM vent gases, design $F = 0.5$ wash with tower water if required.	Six inch diameter, stainless steel with 4 high free area trays.

Table VIII
(continued)

Item No.	Item	Design Criteria	Equipment Description
P405	Ambient Leach Air Blower	Spurge 1.5 MSCFM of air to ambient leach tank.	Rotary blower, 10-15 psi, 100 HP.
V402	Liquid Ammonia Storage	Provide 30 days storage for ammonia for purge stream pH adjustment prior to ion exchange and subsequent neutralization.	Four standard design, 10 ton liquid ammonia storage cyclinder with automatic controlled/heater vaporizer.
V403	Sulfuric Acid Storage Vessel	Provide 30 days storage of acid to be used in polish leach regeneration.	500 gal closed top C/S storage tank.
P406	Sulfuric Acid Transfer Pump	Transfer up to 1 GPM of acid to the leach and polish leach reactors, 350 ft TDH.	Positive displacement stainless steel metering pump, .5 HP motor with vary-speed drive.
V404	LOX Storage	Fourteen day storage for process use.	Two standard design, 55 ton liquid oxygen storage vessels.

A portion of the recirculating scrub solution is purged from the scrubber and passes through an energy recovery exchanger where makeup CuSO_4 solution is heated prior to being introduced to the scrubber. The cooled purge solution - actually a slurry containing precipitated sulfide solids - is introduced to a continuous decanter which separates it into a clarified stream for solubles removal and a more concentrated slurry for regeneration of CuSO_4 . The clarified purge streams, containing soluble impurities and reaction products, pass through polish filters for the removal of fines which passed through the decanter. They are continuously backwashed to the regeneration section while the solids free purges are treated for copper removal by solid ion exchange. The majority of the stream is partially neutralized to permit its copper content to be exchanged by the acid form of a cation exchanger. The balance, unneutralized, is used to strip the copper from loaded resin and regenerate it. The decopperized purge is then neutralized to remove residual acidity and reinjected along with condensate from the cooling towers, while the solution containing regenerated copper is recycled to the process.

The decanter underflow and backwashed polish filter solids are held in a large, agitated, covered storage tank which serves both to provide surge capacity to isolate scrubbing and regeneration operations and as a preleach reactor. The slurry is contacted with air at near ambient conditions and a significant portion of the sulfide fines are leached in this step. The preleached slurry is then transferred to the pressure leach reactor, being preheated by countercurrent exchange with leached reactor effluent. Regeneration takes place in a staged vessel at high temperature and under

oxygen pressure so that a high degree of leaching is obtained. The leached effluent passes through a continuously backwashed polish filter which removes "rock dust" and unleached sulfide solids from the leach effluent.

• The cleaned effluent is cooled and transferred to storage for recycle, and the solids are collected for releaching. Releaching, with additional acid if required and under high oxygen pressure, serves to regenerate refractory sulfide solids for recycle and separate them from "rock dust" and other insoluble impurities which are backwashed to the tower sumps and purged from the system.

Makeup CuSO_4 is added to the system to offset losses in the solubles and insolubles purge streams and entrainment losses in the scrubbed steam. Water is added, primarily in the demister wash step, at a rate sufficient to balance water requirements of the solubles purge stream. Oxygen, and some H_2SO_4 if required, is consumed in regeneration, ammonia is used to neutralize net acid produced in the scrubbing - regeneration reactions, and makeup ion exchanger solids are supplied to offset decrepitation losses. Nominal amount of power and cooling water are required continuously, but the system will be automated and alarmed to permit unattended operation. Some operator attention will be required on one shift per day to check the inventories of solutions and slurries and to operate the polish leach reactor, if required.

Capital and Operating Cost Estimates

Purchased equipment costs are summarized in Table IX, by category, for the equipment described in Table VIII. Each of the scrubbers represents approximately one third of the total cost, and all other items account for the remaining third. Vendor estimates or quotes were obtained for most of the

Table IX

Purchased Equipment Cost Estimate 110 MW Prototype Plant

<u>Equipment Type</u>	<u>Estimated Cost</u> <u>1977 \$ × 103</u>
Scrubbers(1)	950
Reactors(2)	105
Tankage(3)	155
Pumps and Agitators	125
Heat Exchangers	35
Liquid-Solid Separation	45
Miscellaneous	<u>35</u>
TOTAL	1,450

- (1) Two scrubbers, including internals, platforms and ladders.
(2) Pressure leach reactors (two).
(3) Surge tankage, preleach reactor, and ammonia storage.

items described in Table VIII, amounting to approximately half of the total estimated costs of all equipment other than the scrubber. Three quarters of the remaining non scrubber costs are associated with the preleach and regeneration reactors, items T201 and R201. The cost of the preleach reactor was estimated from published costs for atmospheric pressure storage tanks with an additional allowance made for the extra costs of additional nozzles, baffles, man ways, etc. The cost of the regeneration reactor was estimated by determining the approximate weight of the vessel plus fittings and using an estimated cost per pound for the fabricated reactor. This unit cost was obtained from quotations and estimates for pressure vessels of somewhat smaller size.

Total costs, however, are dominated by the cost of the scrubbers, large vessels for which some field fabrication will be required. The cost of the scrubbers was also estimated by carrying out a preliminary mechanical design to determine the vessels wall thicknesses and weights. Since alloy clad construction would be used, material and estimated fabrication costs were solicited from vendors who had cladding capabilities. The costs of internals and other trim were estimated from costs quoted for comparable items for the six foot scrubber in the demonstration plant. In practice, it is difficult to categorize these costs as "purchased equipment costs", since the vessel will be erected and installed as final fabrication and assembly takes place. However, the scrubber costs estimated in this way are an accurate representation of material and base labor costs and are necessary as a base cost for estimating physical plant costs by a factoring technique.

Total costs for a commercial installation were estimated by using the appropriate factors for the costs of installation, piping and instruments,

auxiliaries and services, and indirect costs such as engineering and construction expenses, fees and an appropriate contingency. The factors, taken as percentages of the purchased equipment costs, are based on "typical" historical costs for various types of plants and judgment must be used in applying them to an installation such as The Geysers at which no similar type of construction has been carried out. The rationale for selecting factors appropriate for use in this case is summarized in Table X. It is known that construction and civil cost are high at The Geysers because the site is remote, soil conditions are poor, and seismic and wind loads are severe. While instrumentation and control costs will be higher than normal to permit unattended operation in a remote, severe environment, the requirements for additional services and site work will not be great since only a small amount of additional power (400 kW connected) and water (150 GPM) are needed and only a relatively few, large items of equipment need be installed.

The total fixed capital cost estimate for a 110 MW commercial plant at The Geysers is summarized in Table XI. In developing this estimate, an adjustment has been made to the installation factors to be applied to the scrubbers. It is not obvious how, even under the worst conditions, it would be possible to account for \$2 millions worth of installation, services and piping work around two such vessels which is what direct use of the factors of Table X would indicate. Since to a first approximation, civil, instrumentation, and service factors are independent of the material of construction of the process equipment, these components of the installation costs for the scrubbers have been based on the costs of an equivalent steel vessel. Only piping and control cost factors, which will involve use of alloy materials,

Table X

Ratio Factors for Estimating Total Capital Investment

Based on Delivered Equipment Costs

<u>Component of Total Cost</u>	<u>Percentage Used for Typical Plant (1)</u>	<u>This Estimate</u>	<u>Rational for Use of Percentages in this Estimate</u>
Purchased Equipment	100	100	
Equipment Installation	47	70	Remote site, poor conditions.
Instrumentation and Controls	18	25	Unattended operation required.
Piping	66	55	Simple piping, few services.
Electrical	11	5	Low power requirement.
Buildings, including Services	18	15	No new buildings needed.
Yard Improvements and Land	16	15	Extensive improvement not needed.
Service Facilities	70	35	Only incremental power required.
Physical Plant Costs	346	320	
Engineering and Construction, % of Physical Plant Costs	21	25	Higher construction costs.
Fees and Contingency, % of Direct & Indirect Costs	15	15	Normal fee and contingency.

(1)

Fluid processing plant, from "Plant Design and Economics for Chemical Engineers".

Table XI

Total Fixed Capital Investment Cost Estimate

110 MW Commercial Plant

Purchased Equipment Costs	Installation, Piping, Controls, Electricals, Services, Etc.	Physical Plant Costs
\$ × 10 ³	\$ × 10 ³	\$ × 10 ³
Scrubbers, 950	1180 ⁽¹⁾	2130
All Others, ⁽²⁾ 500	1100	<u>1600</u>
Total Physical Plant Costs		3730
Engineering and Construction @ 25% TTPC		930
Fees and Contingency @ 15% Direct & Indirect		700
Total Fixed Capital Investment		5360
		\$48.7/kw

(1) Factors based on erection of steel vessel of same configuration for mechanical factors, alloy construction for piping and instruments.

(2) See Table IX.

have been applied to the full cost of the scrubbers, although all other items of equipment were assumed to bear the percentage factors indicated in Table X. Within the accuracy of this estimate, the total fixed capital investment required for a 110 MW plant at The Geysers will be of the order of \$50/kW. The total costs are strongly dependent on the erection and installation costs of the scrubbers which are likely to be fairly site specific, and a more detailed analysis of these costs would be warranted as soon as preliminary process design criteria can be confirmed.

Total operating costs for a 110 MW plant are summarized in Table XII. Materials, supplies and utilities consumptions are based on operation of the process for 8000 hr/yr (90% stream factors) while unit costs are based on 7500 hr/yr of turbine operation (85% on line factor). The rationale for the use of different stream factors is that the upstream scrubbing process could be used to clean steam vented during periods when the turbines had been tripped out for temporary repair. Oxygen and ammonia consumptions are fixed by the steam composition and total flow rate and are not likely to vary considerably. The majority of the copper loss, however, has been assumed to be unleached solids purged from the system along with "rock dust". More efficient polish leaching and careful control of entrainment and purge stream decopperization could reduce these costs by two thirds. While little if any steam is required for process use, an allowance has been made for the cost, at power generation rates, of steam lost due to condensation in the scrubbers. The labor costs estimated here represent the commitment of the equivalent of the attention of 3-1/2 men. Only casual attention will be required on off shifts, but some allowance must be made for maintenance and

Table XII

Operating Cost Estimate 110 MW Commercial Plant

(1) <u>Materials and Supplies</u>	<u>Operating Cost</u> <u>\$ × 10³/yr</u>
Oxygen @ \$50/ton	99
Ammonia @ \$200/ton	96
Copper Sulfate @ \$2.5/lb	77
Sulfuric Acid @ \$50/ton	3
Ion Exchange Resin @ \$100/ft ³	12
Miscellaneous, allow	5
Total Material and Supplies	292
 <u>Utilities and Fuel</u> (1)	
Power @ 2.5¢/kWh	53
Water	-
Steam @ \$0.8/1000 lb	11
Fuel	-
Total Utilities and Fuel	64
 <u>Labor</u>	
Operating Labor @ \$20,000/MY	40
Maintenance Labor @ \$22,000/MY	22
Supervision @ \$25,000/MY	12
Plant G & A @ 40% Total Labor	30
Total Labor	104
 <u>Capital Charges</u>	
Taxes, Insurance, Depreciation, and other Charges @ 18.5% TFI	990
Total Operating Cost	1,450
	0.18¢/kWh ⁽²⁾

(1)
Based on 8000 hr/yr process operation.

(2)
Based on 7500 hr/yr turbine operation.

supervision requirements and the possibility that the polish regeneration step will require regular operator attention.

While decreased copper consumption and labor requirements might reduce operating costs by up to 0.2 mills/kWh, the total costs are dominated by capital charges which are unlikely to decrease by more than 0.1 mill/kWh under even the most favorable circumstances. Since total investment is so strongly dependent on the installed costs of the scrubbers, an increase in these costs significantly increases operating costs as well; a twenty five percent increase in scrubber system physical plant costs will increase operating costs by about ten percent, almost 0.2 mills/kWh. Unexpected maintenance material and supply costs would also increase operating costs by as much as 0.1-0.2 mills/kWh. In the absence of operating data and a more detailed capital cost estimate, it is possible to say with certainty only that the operating costs are likely to be less than 2 mills/kWh.

ALTERNATIVES FOR CONTROL OF H₂S EMISSIONS

While it is not the purpose of this study to carry out a comprehensive evaluation of the technical and economic characteristics of alternative H₂S control technologies, a brief review of possible abatement strategies brings useful perspective to this work.

We know of no other upstream H₂S control technology under consideration for use at The Geysers, although two downstream control processes are considered viable. One approach, currently being utilized at Unit 11, involves addition of iron salts to the circulating cooling water to promote oxidation of the H₂S dissolved in the water and scrubbed from the ejector vents to elemental sulfur. The sulfur, insoluble inerts from the steam, and iron hydroxide precipitates would be removed from the circulating water by filtration. It is known that, for kinetic and hydraulic reasons, it will be difficult to get very high degrees of H₂S abatement by this technique, and 90% removal is a reasonable expectation under optimum operating conditions. It is also known that the addition of iron salts at the operating pH of the system could cause significant corrosion problems to arise in the cooling system and that the liquid-solid separation step is very troublesome because of the slimy nature of the solids formed. Because of these difficulties, and the limited degree of H₂S removal possible, this approach will not be used on newly constructed plants.

All units following No. 13 will employ surface condensers, which replace the direct contact condensers now in use, to keep condensate volumes to a minimum and small, modular Stretford units to remove H₂S from the ejector vents and oxidize it to elemental sulfur. This approach is, theoretically,

capable of attaining very high degrees of H_2S removal. An attempt will be made to run the surface condensers "hot", i.e., to avoid subcooling the condensate to maximize the partition of H_2S to the vapor phase in the condensers. If, however, the condensers prove to be as prone to fouling as the turbines themselves are now, this may cause substantial operating difficulties or an increased backpressure with a corresponding loss of efficiency. In any case, to be effective the condenser must also promote mass transfer of sufficient CO_2 to the condensate to neutralize the NH_3 present in order to maintain the pH low enough to prevent retention of significant amounts of bisulfide. It is by no means certain that this can be done since the kinetics of CO_2 sorption are known to be slow. A conservative estimate of the amount of H_2S which might remain in the condensate is 10% of that entering, and to prevent its being released to the atmosphere as condensate passes through the cooling towers, it will be necessary to destroy the dissolved sulfide, probably through the use of a strong oxidant such as O_3 or H_2O_2 .

Neither of these post plant abatement techniques addresses the problem of emissions from steam which is vented when the turbines are tripped out for mechanical reasons. While such events are infrequent and of relatively short duration, it has been estimated⁽¹⁾ that they contribute an additional 4% to the emissions in the vicinity of the power plant. Emissions of equal magnitude occur in the steam field operations, but their control is beyond the scope of this work. No other process is currently under development for the abatement of these emissions, but it has been suggested that an "iron oxide box" could be used.⁽²⁾ This approach is based on technology which has been abandoned in the treatment of other H_2S laden gases, but could be considered

(1) "Resource, Technology, and Environment at The Geysers", Weres et al., 1977.

(2) Environmental Analysis for Geothermal Development in The Geysers Region, SRI, Contract No. 4-0132, 1977.

here on the basis that it would be used only occasionally and would constitute standby control. It would not be inexpensive, however, since the system would have to be designed to treat the entire steam flow for some period of time although the regeneration cycle might be relaxed somewhat.

It is difficult to carry out a realistic economic evaluation of alternative technologies because few data have been published for some of the alternatives, they are in various stages of development from conceptual to operational, and there is uncertainty as to the bases which have been used for those cost figures which have been published. Nevertheless, an order-of-magnitude comparison can certainly be made which will be useful for scoping purposes.

The Pacific Gas and Electric Company, in a report to the California Public Utilities Commission, estimated the cost of downstream H_2S abatement using surface condensers and Stretford plants at \$6.2 millions for a 55 MW station. However, since some type of condenser is required in any case, it is appropriate to base abatement costs on only the incremental costs of the surface condensers, which are of the order of \$3 million more than surface condensers of the same capacity. Furthermore, a very conservative modular design strategy has been assumed for the Stretford plants, and it is not likely that this component of the cost would double in a 110 MW station. A fifty percent increase is more likely, so that total capital costs would be of the order of \$8 million. The capital charges associated with the operation of this process amount of approximately 1.8 mills/kWh, and will dominate operating costs since direct costs for labor and materials will add only about 0.2 mills/kWh. If add on treatment for removal of H_2S from the plant con-

densate is required, it has been estimated⁽²⁾ that capital costs will increase by at least \$.25 million. Operating costs depend on the amount of excess H_2O_2 required, on the amount of sulfate formed in the reaction, and the amount of residual H_2S ; removal of 10% of the incoming H_2S with 200% excess H_2O_2 would increase costs by about 1.2 mills/kWh.

The costs of an iron catalyst abatement system are apt to be highly site specific since the process would have to be retrofitted with existing plants and a substantial disposal problem exists for removal of the hydrous, sulfurous sludge formed when colloidal sulfur - iron mixtures precipitate. However, it is to be expected that capital costs for the treatment system will be relatively low since the process is straightforward and operates at ambient conditions. Total costs would escalate greatly, of course, if existing cooling systems had to be replaced with equipment constructed of more corrosion resistant alloys than are now in use. The direct components of operating costs are expected to be higher than for the surface condenser - Stretford approach since operations are more labor intensive, particularly the liquid-solid separation step, significant quantities of iron salts are consumed, and solid waste disposal costs are high at The Geysers. The information available suggests that capital costs for the iron catalyzed abatement system in a 110 MW plant would be about \$2.5 million, and total operating costs would be about 1.4 mills/kWh, with 85% of the total being waste disposal and capital costs.

No data are available to support a cost estimate for an abatement system for treating steam vented during turbine outages. However, it has been reported⁽²⁾ that a "predesign" cost estimate for an "iron oxide box" projects capital costs of about \$2.2 million. On the assumption that capital charges

will be the dominant component in operating costs, total operating costs would be expected to be in the range of 0.6-0.7 mills/kWh.

Capital and operating costs for the various alternatives considered here are summarized in Table XIII as a function of the degree of H_2S abatement obtained for both normal plant operation and during steam venting. The iron catalyzed oxidation system is least costly if relatively low degrees of removal are acceptable but is probably incapable of obtaining in excess of 90% abatement. The use of surface condensers and Stretford plants represents a more costly approach but is capable of achieving high removal efficiencies is supplemented by a standby vent scrubbing system and the use of H_2O_2 to remove residual H_2S from the plant condensate. The copper sulfate system appears to present the possibility of both high removal efficiency and acceptable capital and operating costs. The design criteria and cost estimates used in this estimate must be verified, however, in long term, closed cycle operation of a demonstration plant of scaleable size.

Table XIII
Capital and Operating Cost Estimates for H₂S Abatement Processes

110 MW Capacity, 220 PPM H₂S in Steam

Process	Upstream Scrubbing with Copper Sulfate		Iron Catalyzed Air Oxidation Downstream		Surface Condensers- Stretford Plants	
	Fixed Capital Investment \$/kW	Operating Cost ⁽¹⁾ mill/kWh	Fixed Capital Investment \$/kW	Operating Cost ⁽¹⁾ mill/kWh	Fixed Capital Investment \$/kW	Operating Cost ⁽¹⁾ mill/kWh
Approximate % H ₂ S Removal Obtained ⁽²⁾						
85 ⁽³⁾			25	1.4	70	2.0
90 ⁽⁴⁾			45	2.0	90	2.6
95 ⁽⁵⁾					75	3.2
99	50	1.8			95	3.8

- (1) Includes direct costs plus capital charges. Based on 7500 hr operation.
- (2) From steam to plants plus 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.