PILOT TESTING OF A NOVEL HYDROGEN SULFIDE ABATEMENT PROCESS-MAK-BAN UNIT 3, BULALO, PHILIPPINES GEOTHERMAL FIELD

D. L. Gallup
Unocal Corp., Brea, CA, USA

T. H. Viloria
Philippine Geothermal Inc., Manila, Philippines

SUMMARY - A new liquid phase oxidation process for abatement of hydrogen sulfide emissions from geothermal power plants was tested in 1991 at Mak-Ban Unit 3, Bulalo, Philippines geothermal field. The process comprises contacting neutralized cooling tower circulating water with a small, substantially less-than-stoichiometric amount of an oxidizing biocide required to oxidize sulfide to sulfate. Determining precise abatement efficiencies in the Unit 3 direct contact condenser proved extremely difficult. Process monitoring suggested that the oxidation reaction in the direct contact condenser resulted in up to 50 - 77% abatement of H_2S emissions from both the vent gas ejectors and degassing at the cooling tower. Microbiological growth in the circulating water was controlled by periodically adding a second (non-oxidizing) biocide. The oxidizing biocide treatment had little, if any, effect on circulating water corrosivity.

1. INTRODUCTION

The emission of hydrogen sulfide into the atmosphere is strictly regulated in many locations where geothermal fields are situated. Several years ago, Unocal Corp. entered the electric power production business at the Salton Sea field in southern California (USA). Unocal's geothermal electric generating facilities are required by law to abate hydrogen sulfide emissions as part of operational permits. Therefore, processes to abate these emissions were investigated.

Significant progress has been made in the past decade to control toxic hydrogen sulfide emissions to the atmosphere at geothermal fields located in the United States and other countries (Weres, 1984). Hydrogen sulfide abatement systems developed at these geothermal fields, and especially at the steam-dominated Geysers, California field, generally consist of incineration or liquid redox sulfur recovery processes (Dalrymple, et al., 1989). Hydrogen sulfide-laden gas streams (hereafter referred to as primary emissions) can be incinerated, oxidized over catalysts or absorbed in solutions that are eventually oxidized to yield elemental sulfur and water (Kenny, et al., 1988). Steam condensates (hereafter referred to as secondary emissions) are also oxidized to convert hydrogen sulfide to elemental sulfur. Abatement technologies used at the Geysers and other field have included Stretford, Lo-Cat, and SulFerox. A recent technology developed at the Geysers, known as RT-2, has resulted in a combination primary-secondary process that produces thiosulfate as the reaction by-product (Bedell and Hammond, 1987). Various metal catalysts have also been tested for application in geothermal systems (Weres, et al., 1985).

In most brine-dominated geothermal resources, such as those encountered at the Salton Sea field, abatement of hydrogen sulfide is preferably practiced in power generation facilities where we focused our abatement process development efforts. Not unexpectedly, attempts to scavenge, scrub or oxidize hydrogen sulfide in the brine have only been partially successful. Oxidation of brine at Salton Sea to convert H_2S to sulfur or higher oxidation state products can result in the formation of ferric iron that is extremely corrosive to piping and deposits as scale with silica (Jost, 1980).

2. DEVELOPMENT OF THE BIOX ABATEMENT PROCESS

When Unocal Corp. entered the power generation

business at the Salton Sea field, hydrogen sulfide abatement technologies were investigated for the installed surface condenser systems. Processes utilized at the Geysers field were found to be extremely expensive. Most of the processes produced solid sulfur waste contaminated with traces of heavy metals, especially arsenic. As a result, we investigated novel, alternative abatement methods for application at the Salton Sea field.

During the course of these investigations, it was discovered that addition of only a few kg per day of chlorine and bromine-stabilized biocide tablets to countercurrent cooling tower circulating water, in ratios hundreds of times less than stoichiometric amounts required to oxidize hydrogen sulfide, completely abated secondary emissions by converting dissolved sulfides to soluble sulfate salt (no elemental sulfur solids were observed). Subsequent jar and pilot cooling tower testing of various oxidizing biocide additions to sulfide-contaminated cooling waters yielded wide ranging results. Oxidizing biocides, such as chlorine gas, sodium and calcium hypochlorites, and chlorine dioxide added to water at up to stoichiometric amounts sufficient to oxidize all sulfides, were only partially successful in converting these sulfides primarily to elemental sulfur. By contrast, compounds such as bromo-chlorohydantoin and trichloroisocyanuric acid added in much less-than-stoichiometric amounts, proved to cause sulfides to rapidly disappear and to produce sulfate ion without precipitating elemental sulfur (Gallup, 1991a). This newly-discovered abatement process was named BIOX (biocide-assisted oxidation).

Based on the success of the process to control secondary emissions by adding much less-than-stoichiometric amounts of the "halogen-stabilized" biocidal agents in tablet form to oxidize all sulfides to sulfate, we investigated the concept of contacting turbine offgas laden with hydrogen sulfide (from the surface condensers) against the oxidizing biocide-treated water to control primary emissions. Sparging offgas into circulating return water or cooling tower basin water scrubbed the hydrogen sulfide, provided the water pH was maintained in the slightly basic range (pH 7 - 9):

$$H_2S_{(g)} = H_2S_{(aq)} \text{ or}$$
$$H_2S + OH = HS^- + H_2O \qquad (1)$$

Scrubbed hydrogen sulfide in the offgas was found to be rapidly oxidized by the biocides in an apparent "catalytic" reaction to soluble sulfate without formation of elemental sulfur solids (Gallup, 1991b). By-product sulfate in cooling tower blowdown from the BIOX process was re-injected into the geothermal reservoir for disposal (see Figure 1) (Hoyer, et al., 1991).

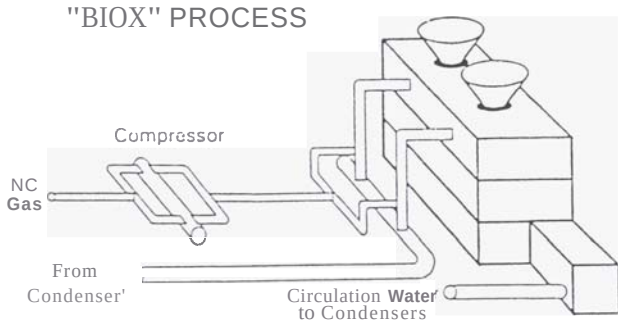


Figure 1 - BIOX Process installed at Salton Sea field

3. PILOT TESTING OF THE BIOX PROCESS AT THE BULALO GEOTHERMAL FIELD

In 1989, a one-month pilot test of the BIOX process was successfully conducted at the Bulalo, Philippines geothermal field. This testing was designed to determine if the BIOX process could be applied in a direct contact condenser system utilizing motive steam gas ejectors and a cross-current flow cooling tower installed at Mak-Ban Unit 3. Unocal and Philippine Geothermal Inc. (PGI) personnel conducted the test at the 55 MW power generation facility operated by NAPOCOR (National Power Corporation of the Philippines). Test results showed that some primary and secondary abatement was achieved by adding much less-than-stoichiometric amounts of a BIOX agent, trichloroisocyanuric acid, to the cooling tower circulating water. Due to the promising results of this test, a longer-term test was proposed to improve abatement efficiency and to better understand the unusual chemistry of the process.

The longer-term pilot test of the BIOX process was conducted at Mak-Ban Unit 3 from January to July

1991. The pilot test was designed to abate primary emissions from the gas ejectors as well as secondary emissions from the cooling tower as a result of offgassing of circulating return water containing steam condensate. Figure 2 shows a schematic diagram of the Unit 3 power plant test. BIOX agent in tablet form was added to the cooling tower circulation water at the coldwell. From the coldwell, the BIOX-treated water is sent to the direct contact condenser where it mixes with condensed steam. Scrubbing and oxidation of hydrogen sulfide occurs in the condenser. From the condenser, the reaction water flows to the hotwell and then returns to the cooling tower. Non-condensible gases from the condenser are released to the atmosphere through the gas ejectors.

MAK-BAN UNIT 3 FLOW DIAGRAM

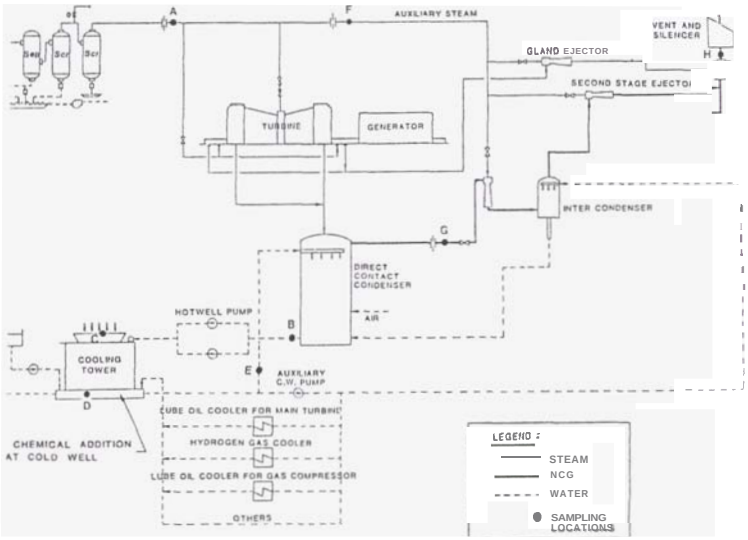


Figure 2 - Mak-Ban Unit 3 BIOX pilot test flow diagram

In addition to daily additions of the BIOX agent, primarily for hydrogen sulfide abatement, a non-oxidizing biocide (isothiazalone) was added to the circulating water bi-weekly to ensure complete control of microbial activity. The BIOX process is most effective at pH 7 - 9. Steam condensate at Bulalo is acidic, so the circulating water also had to be treated for pH control. Caustic soda was primarily employed to maintain the pH of the cooling water in the neutral range for both corrosion control and hydrogen sulfide scrubbing (Reaction 1). Attempts to control the pH with lime were unsuccessful due to hydrogen gas cooler fouling.

Chemical monitoring was conducted throughout the test to determine abatement efficiencies, corrosion rates and microbial activity. Hydrogen sulfide and dissolved sulfides were analyzed by common titrimetric and air sampling techniques. Corrosion was monitored by standard coupon methods; microbial activity was monitored by culture slides. Sulfide mass balances and abatement efficiencies were quite difficult to monitor since partitioning ratios of hydrogen sulfide across direct contact condensers is confused by condensed steam mixing with circulating water before flow rates and analyses are obtained. Analysis of gas ejector streams proved troublesome and blowdown rates at Unit 3 that could aid in calculation of concentration cycles are not metered. Thus, accurately determining abatement efficiencies throughout the test was much more difficult than expected and experienced in surface condenser systems at the Salton Sea field.

4. PILOT TEST RESULTS

Pilot testing of the BIOX process at Mak-Ban Unit 3 consisted of five phases. Table 1 presents the results of the abatement monitoring. In the first phase, no BIOX agent was added to the cooling water to obtain "baseline" (no abatement) conditions. In Phases 2 - 4, various dosages of BIOX agent were added to the coldwell to oxidize hydrogen sulfide to soluble sulfate salt. The last phase examined the effect of eliminating the oxidizing agent.

In Phase 1, an average of 1750 kg/day of hydrogen sulfide was sent to the turbine - 1270 kg/day appeared to partition to the gas phase (primary emission) and 480 kg/hr to the liquid phase. Secondary emissions degassing from the liquid phase at the cooling tower were estimated to be 220 kg/day. Total H_2S emissions were 1490 kg/day; natural abatement due to sulfide oxidation by dissolved oxygen in the coldwell water was —260 kg/day or 15%. Natural abatement by air-wet conditions produced elemental sulfur sludge in the tower catch basin and distribution trays, together with —50 ppm dissolved sulfate in the circulating water.

Table 1 - BIOX pilot test results

	Phase				
	1	2	3	4	5
Days	30	28	28	48	28
BIOX, kg/day	0	8	16	50	0
H2S, kg/day:					
Inlet Steam	1750	1920	1820	1900	1950
Gas Ejector	1270	1200	1240	750	1210
Cool. Tower	220	160	180	120	210
Abatement:					
Primary*	0	6	3	41	5
Secondary*	54	67	63	75	56
TOTAL**	15	29	22	54	27

* Compared to Phase 1
** Based on inlet steam from given Phase

Cooling tower water was treated with 8 kglday of BIOX agent in Phase 2. Over the 28-day test, hydrogen sulfide entering the plant increased to 1920 kg/day. Primary and secondary emissions were reduced to 1200 and 160 kglday, respectively, an abatement efficiency of 29%. Meanwhile, sulfate concentrations in the cooling water increased by 11%.

In Phase 3, a 28-day test, 16/kg day of BIOX agent was added to the tower water. Inlet H_2S to the plant averaged 1820 kg/day, primary emissions were estimated to be 1240kg/day and secondary emissions, 180 kg/day. Although the abatement efficiency was calculated to only be 22%, sulfate concentrations in the cooling tower increased by 86% compared to Phase 1 (blowdown rates appeared to be constant between phases).

For 48 days, Phase 4 testing consisted of treating cooling tower water with an initial shock feed of 100 kg of BIOX agent followed by a 50 kg/day maintenance dosage. An average of 1900 kg/day of H_2S entered the plant. Primary and secondary emissions were reduced to 750 and 120 kg/day, respectively. That greater than 50% of total H_2S emissions that could have been released to the atmosphere were abated was confirmed by a 270% increase in sulfate concentration (over 200 ppm was often observed) in the cooling tower circulation water. Based on estimated cycles of concentration in the water (~6), obtained from both cation and anion analyses, this increase in production of sulfate translates to oxidation of 1460 kg/day of H_2S or an abatement efficiency approaching 77%. No additional elemental sulfur solids were observed in the tower water compared to the baseline case (Phase 1).

In the final phase of testing, no abatement chemicals were added to the water for a one month period. Hydrogen sulfide sent to the plant in steam averaged 1950 kg/day, with primary and secondary emissions averaging 1210 and 210 kg/day, respectively. This test showed that natural abatement due to dissolved oxygen and slow purging of the abatement chemical converting sulfides to sulfur and sulfate was about 27%.

Throughout the pilot testing phases, cooling tower circulation water pH at the hotwell was maintained in the 6.3 - 7.2 range with caustic soda addition to the coldwell. Caustic dosages ranged from –150 - 1000 kg/day. Abatement appeared to improve at higher pH due to enhanced scrubbing of H_2S in the steam by the circulating water. Low dosages of lime were also added to the cooling water in Phases 2 and 3 in an effort to decrease pH control costs (Datuin and Gazo, 1989). During testing with lime, calcium hardness levels ranged from 5 - 10 ppm (as $CaCO_3$). Apparently these dosages of lime caused scaling of hydrogen gas coolers, so lime addition was terminated after completion of Phase 3. Corrosion data from the BIOX pilot testing is given in Table 2.

Table 2 - Pilot test corrosion results

	Phase				
	1	2	3	4	5
Days	30	28	28	48	28
BIOX, kg/day	0	8	16	50	0
pH (ave.):					
Coldwell	7.4	7.6	7.7	7.9	7.9
Hotwell	6.6	6.3	6.7	7.2	7.1
NaOH, kg/day	144	136	644	1156	934
CaO, kg/day	0	10	22	0	0
Corros. Rate, mils/yr:					
Coldwell	40	41	27	26	29
Hotwell	38	33	34	18	16

Although BIOX agent (oxidizer) is a corrosive agent, the corrosivity of the cooling water system did not change appreciably during the pilot test. That the coldwell corrosion rate is higher than the hotwell rate is likely due to the presence of dissolved oxygen, and possibly unreacted BIOX agent.

No significant microbiological activity was detected in the cooling water system before, during or after treatment with the BIOX agent. Analyses of total bacteria, fungus, algae and sulfate-reducing bacteria consistently showed no infection. Initially, in Phase 1, cooling water was treated with isothiazalone biocide at a dosage of 100 kg/month added once every two weeks. However, due to low microbiological activity, the dosage was later reduced by half in subsequent test phases.

5. DISCUSSION OF ABATEMENT CHEMISTRY

Chlorinated waters or chlorine solutions are used extensively to oxidize hydrogen sulfide in wastewater treatment processes. Hypochlorite generated from applying chlorine to water easily converts sulfides to elemental sulfur:

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl + H_2S = S + HCl + H_2O \quad (3)$$

The above chemical reactions have a theoretical requirement of 210 kg of chlorine per 100 kg of hydrogen sulfide. Often, due to the presence of other oxidizable species in wastewater, typical dosage rates range from 500 - 800 kg of chlorine per 100 kg of hydrogen sulfide. Sodium hypochlorite is used to scrub and oxidize hydrogen sulfide to sulfate in many industrial applications. In such a reaction, 1750 kg of sodium hypochlorite (bleach) are theoretically required to completely oxidize 100 kg of hydrogen sulfide. Actual bleach requirements can often exceed 2000 kg (Pope and Federici, 1989). Obviously, the use of these oxidants in a typical, geothermal, hydrogen sulfide abatement application would be prohibitively expensive.

Pilot testing of the BIOX process at the Bulalo geothermal field in a direct contact condenser has shown that dissolved oxygen in circulating water is partially responsible for sulfide oxidation. Typically, several ppm dissolved oxygen are consumed during the abatement process in each circulation cycle of the cooling tower. The results of pilot testing indicate that oxygen converts about 20% of sulfides to sulfur and sulfate by the following reactions:

$$H_2S + 1/2\ O_2 = S + H_2O \quad (4)$$

$$H_2S + 2\ O_2 = H_2SO_4 \quad (5)$$

In the BIOX process, additional sulfides in the water are oxidized to sulfate employing much less-than-stoichiometric amounts of oxidizing biocides, implying that these agents react "catalytically".

Due to complexities of the BIOX process in cooling towers, it is difficult to explain why certain oxidizing biocides react in a catalytic fashion at much less than theoretical stoichiometric dosages required to convert sulfides to sulfate. One explanation for the unusual reactivity of agents, such as trichloroisocyanuric acid, is that this compound is more stable in water against decomposition than other, more common chlorine-containing oxidants. In this regard, chlorine gas stability in water is improved when added together with cyanuric acid (White, 1972). In the BIOX process developed here, the oxidants are also added as tablets that allow for slow dissolution and "time-release" action.

The oxidizing biocides that have proven most useful in the BIOX process, to date, are bromo-chlorohydantoin and trichloroisocyanuric acid. The reactions of these oxidizing agents with hydrogen sulfide to yield sulfate are, respectively:

$$2\ C_5H_6N_2O_2BrCl + 4\ H_2O + H_2S = 2\ C_5H_8N_2O_2 + H_2SO_4 + 2\ HBr + 2\ HCl \quad (6)$$

$$4/3\ C_3N_3O_3Cl_3 + 4\ H_2O + H_2S = 4/3\ C_3H_3N_3O_3 + H_2SO_4 + 4\ HCl \quad (7)$$

To abate 2000 kg per day of hydrogen sulfide equivalent sent to a cooling tower at a power plant, such as Mak-Ban Unit 3, with some of the oxidation occurring as a result of reaction with dissolved oxygen, is predicted from Reactions 6 and 7 stoichiometries to require 14,200 and 9110 kg per day of these oxidizing biocides, respectively. A process to oxidize dissolved sulfides to sulfate in oilfield produced waters with these types of compounds at stoichiometric dosages was

previously developed (Allison and Wimberley, 1987).

That 50 kg per day of these oxidizing biocides is required to effectively convert 50 - 77% of hydrogen sulfide to sulfate suggests that the above reactions are somehow catalytic. Recent kinetic and mechanistic studies have shown that compounds similar in nature to the BIOX agents react rapidly with sulfites to yield sulfates (Yiin, et al., 1987; Yiin and Margerum, 1990). Oxidation reactions of chloramines with sulfites are general-acid-catalyzed over the pH range, 5 - 9, involving H(+) and Cl(+) transfer mechanisms. Further, acid-catalyzed oxidation reactions of organochloramine with organic sulfides to yield organic sulfoxides are well-known (Rees and Sugden, 1973). Thus, it is believed that the oxidizing biocides used in the BIOX process react in a similar, acid-catalyzed manner. The presence of traces of dissolved transition metals in cooling water also appears to enhance the BIOX abatement reaction. However, regardless of the specific nature of the abatement reaction involved, it has nevertheless been demonstrated that the "BIOX" process developed here is effective in controlling hydrogen sulfide emissions from geothermal power generation facilities.

6. BENEFITS OF THE BIOX PROCESS

The BIOX process developed for hydrogen sulfide abatement at geothermal power plants is relatively cheap to operate due to low addition rates of abatement chemicals. Oxidizing biocides and pH control additives, such as caustic soda and lime, added to circulating water, can cost much less than other chemicals used in abatement processes. For example, the total cost of Phase 4-type treatment at Mak-Ban Unit 3 (1500 kg/month BIOX agent, 50 kg/month non-oxidizing biocide and 36,000 kg/month caustic soda) is c US$ 22,000 per month. We believe that increasing the BIOX agent dosage to 100 kg/day to improve abatement to > 90% efficiency and replacement of caustic with lime and a scale dispersant could reduce the cost to < US$ 12,000 per month. Furthermore, the BIOX process utilizes no special equipment requiring capital costs. By contrast, operating expenses (primarily chemical costs) of other, currently-available abatement technologies for Mak-Ban Unit 3 are expected to cost > US$ 45,000 per month. Capital costs for other abatement technologies that require incinerators or sulfur waste disposal systems can exceed US$ 1,000,000. BIOX technology is available for license from Picheney World Trade, Inc., Brandeis Division, Greenwich, CT (USA).

7. CONCLUSIONS

The BIOX process pilot tested at Mak-Ban Unit 3 shows promise for cheaply abating hydrogen sulfide emissions to the atmosphere. BIOX agent dosages of up to 100 kg/day will likely be required to abate over 90% of the H_2S sent to the Bulalo geothermal field power plants in steam. Scrubbing and oxidation of sulfides to soluble sulfate salts occurs within the direct contact condenser and circulating water return piping. Due to production of acidic steam condensate at the field, cooling water pH must be controlled to enhance abatement and mitigate corrosion. BIOX abatement efficiency will be maximized when the hotwell pH is maintained in the 7 - 7.5 range. Treatment of cooling water with BIOX oxidizing biocide agent and a supplemental non-oxidizing biocide appears to control microbiological activity. The process tested here appears to offer a cheap and simple alternative to other commercially-available hydrogen sulfide abatement processes.

BIOX is also an attractive abatement technology with respect to waste generation. No elemental sulfur is produced in the process that would need to be disposed of or sold for relatively low value. Additionally, there are no metal wastes generated by the process. The by-product of the process is soluble sulfate that can be simply disposed in cooling tower blowdown.

8. ACKNOWLEDGEMENT

We thank Unocal Corporation management for permission to publish this paper. Thanks also to Philippine Geothermal Inc. and National Power Corp. personnel for assistance and cooperation in the pilot test.

9. REFERENCES

Allison, J. D. and Wimberley, J. W. (1987) Processes and oxidizing agents for oxidizing sulfide ion to innocuous, soluble sulfur species. US Patent 4,710,305.

Bedell, S. A. and Hammond, C. A. **(1987)** Chelation chemistry in geothermal H_2S abatement. ***Geo. Res. Council, Bull., 3-6.***

Dalrymple, D. A., Trofe, T. W., and Evans, J. M. **(1989)** Liquid redox sulfur recovery options, costs, and environmental considerations. ***Env. Prog.,*** 8, **217-222.**

Datuin, R. and Gazo, F. M. **(1989)** Material problems of geothermal power plants: a Philippine experience. ***Proc. 11th New Zealand Geothermal Workshop,*** 275-281.

Gallup, D. L. **(1991a)** Process for treating sulfide-containing water to reduce sulfide emissions therefrom. ***US Patent*** **5,028,340.**

Gallup, D. L. **(1991b)** Process for treating condensate of steam derived from geothermal brine. ***US Patent*** **5,061,373.**

Hoyer, D., Kitz, K., and Gallup, D. **(1991)** Salton Sea **Unit 2 -** Innovation and successes. ***Geo. Res. Council, Trans.,*** **15,** 355-361.

Jost, J. W. **(1980)** Preventing scale deposition from geothermal fluids. ***US Patent*** **4,224,151.**

Kenny, K. A., Bacon, T. R., and Kirby, L. H. **(1988)** Site specific needs affect process choices for H_2S abatement in geothermal power plants. Geo. ***Res. Council, Trans.,*** **12, 411.**

Pope, R. J. and Federici, N. J. **(1989)** Effective odor control technology at wastewater treatment plants. ***Waterworld News,*** **12-13.**

Rees, G. D. and Sugden, J. K. **(1973)** Oxidation of sulfides with chloramines. ***Amer. Lab.,*** **48-56.**

Weres, ***O.*** **(1984)** Environmental protection and the chemistry of geothermal fluids. ***LBL Report*** **14403.**

Weres, O., Tsao, L., and Chhatre, R. M. **(1985)** Catalytic oxidation of aqueous hydrogen sulfide in the presence of sulfite. ***Corrosion,*** **41, 307-316.**

White, G. C. **(1972)** Handbook of chlorination. Van Nostrand Reinhold Co., New York, Chapter 8.

Yiin, B. S., Walker, D. M., and Margerum, D. W. **(1987)** Non-metal redox kinetics: General-acid-assisted reactions of chloramine with sulfite and hydrogen sulfite. ***Inorg. Chem.,*** **26, 3435-3441.**

Yiin, B. S. and Margerum, D. W. **(1990)** Non-metal redox kinetics: Reactions of trichloramine with ammonia and with dichloramine. ***Inorg. Chem.,*** **29, 2135-2141.**