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OPEN FILE REPORT

Quality Improvement and Conservation of Copper Mill Waste Water

By R. O. Dannenberg and P. C. Gardner

BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

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16. Abstract (Limit: 200 words)

This report describes a series of laboratory and full-scale tests to develop a process for improving the flotation characteristics of lime-treated wastewater. Unknown substances in the wastewater reduced the flotation efficiency of the metal sulfides. An estimated annual loss of 795,000 lb Cu, 232,000 lb Mo, 5,625 tr oz Ag, and 617 tr oz Au would result from recycling the total flow from the lime treatment plant to the flotation mill in an effort to conserve water and reduce associated expense. The tests indicated that aeration or treatment with activated carbon significantly improved the water quality. The improvements in molybdenum recovery averaged 8 pct for aeration, 11 pct for activated carbon, and 16 pct for combined aeration and activated carbon. The combination of the two processes produced water quality as good as or better than normal feed water.

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FOREWORD

This report was prepared by the U.S. Department of the Interior, Bureau of Mines, Salt Lake City Research Center. It was administered under the technical direction of the Salt Lake City Research Center, with Parkman T. Brooks acting as Technical Project Officer. This report was submitted by the authors on February 25, 1987.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT
With Factors for Conversion to Units of the International System of Units (SI)

Abbreviation	Unit of measure	To convert to--	Multiply by--
emf	electromotive force		
gal	gallon	liters	3.785
gpm	gallon per minute		
lb	pound	kilogram	.4535
lb/yr	pound per year		
min	minute		
oz	ounce		
pct	percent		
ppm	part per million		
tr oz	troy ounce		

QUALITY IMPROVEMENT AND CONSERVATION OF COPPER MILL WASTE WATER

By R. O. Dannenberg[1] and P. C. Gardner[2]

ABSTRACT

The Bureau of Mines conducted laboratory and full-scale tests to develop a process for improving the flotation characteristics of lime-treated waste water produced by the Kennecott Copper Corp., Magna, UT. Unknown substances in the waste water reduced the flotation efficiency of the metal sulfides. An estimated annual loss of 795,000 lb Cu, 232,000 lb Mo, 5,625 tr oz Ag, and 617 tr oz Au would result from recycling the total flow from the lime treatment plant to the flotation mill in an effort to conserve water and reduce associated expense.

The tests indicated that aeration or treatment with activated carbon significantly improved the water quality. The improvements in molybdenum recovery averaged 8 pct for aeration, 11 pct for activated carbon, and 16 pct for combined aeration and activated carbon. The combination of the two processes produced water quality as good as or better than normal feed water.

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Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

INTRODUCTION

Kennecott Copper Corp., Magna, UT, operated a lime treatment plant for neutralizing and reducing the metallic contamination in approximately 10,000 gpm of the combined waste water from various processing facilities.[3] In the past, approximately 20 pct of the treated waste water was recycled to the flotation mill; the remainder was discharged to the Great Salt Lake. Total recycle of the treatment plant effluent would be desirable because (a) it is difficult to reduce the metallic contamination, particularly arsenic, to an acceptable level for discharge to the Great Salt Lake, and (b) it would reduce the fresh mill water requirements and the associated cost. However, the presence of unidentified contaminants in the effluent depressed copper, and to a greater extent, molybdenum flotation. The contaminants were thought to be primarily dextrin, an organic used in the plant flotation process.

[3]Since this research was performed, Kennecott ceased operations at the smelter and at the refinery which produced most of the acid in the waste water. The waste water treatment plant continued processing water until the final close-down operation of the concentrator which did not require neutralization. In July of 1985, Kennecott changed from lime treatment to biological treatment of waste water. In 1986, Kennecott announced plans to resume plant operations.

Based on laboratory flotation tests, it was estimated that total recycle of the treatment plant effluent would reduce copper and molybdenum recovery by 795,000 and 232,000 lb/yr, respectively. Research to improve the flotation characteristics of the treatment plant effluent was performed as part of the Bureau's program to minimize undesirable environmental impacts associated with mineral processing operations and to maximize productivity.

This report describes the treatment processes that were successful in improving the quality of the waste water treatment plant (WWTP) effluent for recycle. Since the nature or identity of the flotation depressant was unknown, treatment effectiveness was defined by copper and molybdenum recoveries achieved using standard laboratory flotation tests; results using tested water were compared to results using WWTP effluent. In many instances, variations in metal recovery results were small and could be masked by small differences in flotation test results or water supply. Therefore, after early testing phases, the flotation tests were performed in triplicate to provide an estimate of error using statistical analyses of the results. Other copper producers experiencing similar problems could benefit from the studies of Kennecott waste water. Other industries using flotation processing may also find the results beneficial.

ACKNOWLEDGMENTS

The cooperation of Kennecott Copper Corp., Utah Mining Division staff who provided plant site structures and facilities and performed all of the flotation test work is appreciated. Gas and liquid chromatographic studies and total organic carbon analyses performed by Kennecott Research Center personnel is also acknowledged.

DESCRIPTION OF KENNECOTT WATER SYSTEM

The Kennecott operation is comprised of three main sections; flotation concentrators, smelter, and refinery. The flotation concentrators consumed 60,000 gpm of water. Lesser amounts of water were used by the smelter and refinery for cooling and other functions. The water source was recycled tailings pond overflow and fresh water makeup from various other areas. Waste water from the three sources was combined for treatment in the WWTP.

WASTE WATER TREATMENT PLANT

The combined waste water flow to the treatment plant was approximately 10,000 gpm; it was composed typically of 8,000 gpm from the concentrators, 1,600 gpm from the smelter, and 400 gpm from the refinery. A typical analysis of treatment plant influent and effluent is shown in table 1. A diagram of the WWTP provided by Kennecott Copper Corp. is shown in figure 1; figure 2 is a photograph of the plant. Waste water from the various sources was combined in a junction box and passed through a metering box where ferric chloride was added, when necessary, to improve arsenic precipitation. The resulting mixture then passed into a fast mixer where lime and recirculated sludge were added. This limed slurry flowed into a series of four slow mixers where precipitation was completed and a synthetic organic flocculant was added. The flocculated slurry flowed to two clarifiers where the sludge settled. Overflow from the clarifiers was either recycled to the concentrator or mixed with excess tailings pond overflow for discharge to the Great Salt Lake. Sludge was pumped to a nearby sludge pond.

EFFECT OF RECYCLING TREATMENT PLANT EFFLUENT

Average flotation results for samples taken in each of 47 consecutive weeks from four individual water sources are shown in table 2. Samples were taken from July 1978 to February 1980. The water tested was from (1) pump station No. 1, which supplied two-thirds of the normal process feed water; (2) pump station No. 4,

TABLE 1. - Typical analysis of waste water treatment plant influent and effluent

Parameter	Analysis, ppm			
	Influent		Effluent	
	Soluble	Total	Soluble	Total
Ag.....	ND	0.01	ND	0.01
Al.....	ND	4.1	ND	.23
As.....	2.2	2.32	0.57	.63
Bi.....	ND	.01	ND	.02
Ca.....	213	ND	524	ND
Cd.....	.025	.033	.010	.018
Cl.....	1,500	ND	1,825	ND
Cu.....	2.02	7.77	.052	.245
CN.....	ND	ND	.026	ND
Cr.....	ND	.10	ND	.07
Fe.....	13.5	23.3	.102	.76
K......	62	ND	59	ND
Mg.....	95	ND	79	ND
Mn.....	.51	.55	.31	.36
Mo.....	2.10	2.53	1.97	2.03
Na.....	1,350	ND	1,313	ND
Ni.....	ND	.20	ND	.12
Pb.....	.71	1.14	.07	.15
Sb.....	ND	.11	ND	.11
Se.....	.22	.27	.22	.24
SO_4....	1,000	ND	1,009	ND
Zn.....	.79	.92	.06	.20
BOD....	ND	ND	ND	6.4
Phenol.	ND	ND	.077	ND
TDS....	ND	ND	5,640	ND
TOC....	ND	ND	ND	1.75
TSS....	ND	162.9	ND	7.8
pH.....	2.9	ND	8.3	ND

ND Not determined.
BOD Biochemical oxygen demand.
TDS Total dissolved solids.
TOC Total organic carbon
TSS Total suspended solids.

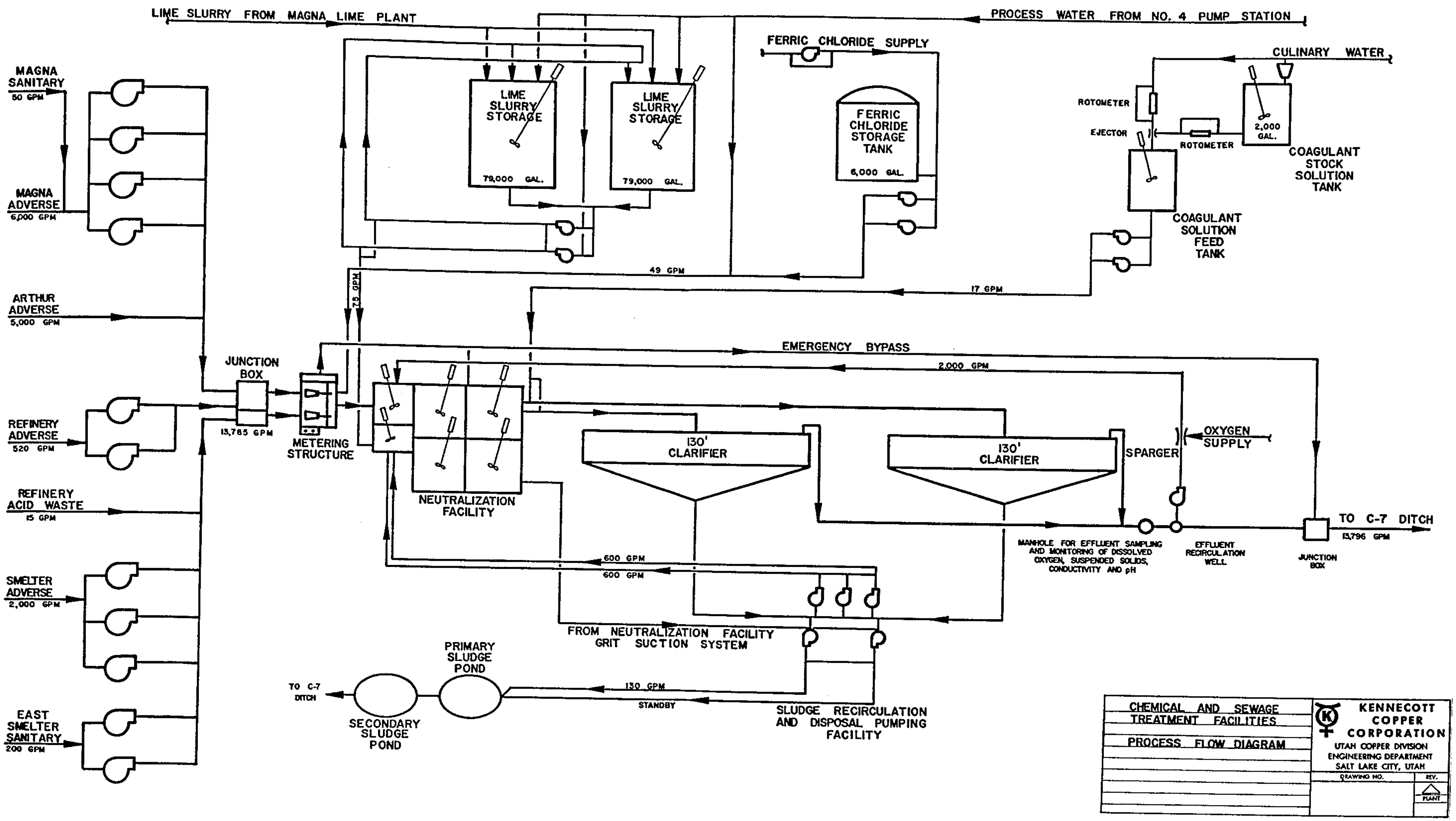
LIME SLURRY FROM MAGNA LIME PLANT
PROCESS WATER FROM NO. 4 PUMP STATION
FERRIC CHLORIDE SUPPLY
CULINARY WATER
MAGNA SANITARY
50 GPM
MAGNA ADVERSE
6,000 GPM
ARTHUR ADVERSE
5,000 GPM
REFINERY ADVERSE
520 GPM
REFINERY ACID WASTE
15 GPM
SMELTER ADVERSE
2,000 GPM
EAST SMELTER SANITARY
200 GPM
LIME SLURRY STORAGE
79,000 GAL.
LIME SLURRY STORAGE
79,000 GAL.
FERRIC CHLORIDE STORAGE TANK
6,000 GAL.
ROTOMETER
EJECTOR
ROTOMETER
2,000 GAL.
COAGULANT STOCK SOLUTION TANK
COAGULANT SOLUTION FEED TANK
49 GPM
75 GPM
17 GPM
EMERGENCY BYPASS
2,000 GPM
JUNCTION BOX
13,765 GPM
METERING STRUCTURE
NEUTRALIZATION FACILITY
130' CLARIFIER
130' CLARIFIER
SPARGER
OXYGEN SUPPLY
TO C-7 DITCH
13,796 GPM
MANHOLE FOR EFFLUENT SAMPLING AND MONITORING OF DISSOLVED OXYGEN, SUSPENDED SOLIDS, CONDUCTIVITY AND pH
EFFLUENT RECIRCULATION WELL
JUNCTION BOX
600 GPM
600 GPM
FROM NEUTRALIZATION FACILITY GRIT SUCTION SYSTEM
PRIMARY SLUDGE POND
TO C-7 DITCH
SECONDARY SLUDGE POND
130 GPM
STANDBY
SLUDGE RECIRCULATION AND DISPOSAL PUMPING FACILITY
CHEMICAL AND SEWAGE TREATMENT FACILITIES
PROCESS FLOW DIAGRAM
KENNECOTT COPPER CORPORATION
UTAH COPPER DIVISION
ENGINEERING DEPARTMENT
SALT LAKE CITY, UTAH
DRAWING NO.
REV.

FIGURE 1. - Kennecott waste water treatment plant process flow diagram.

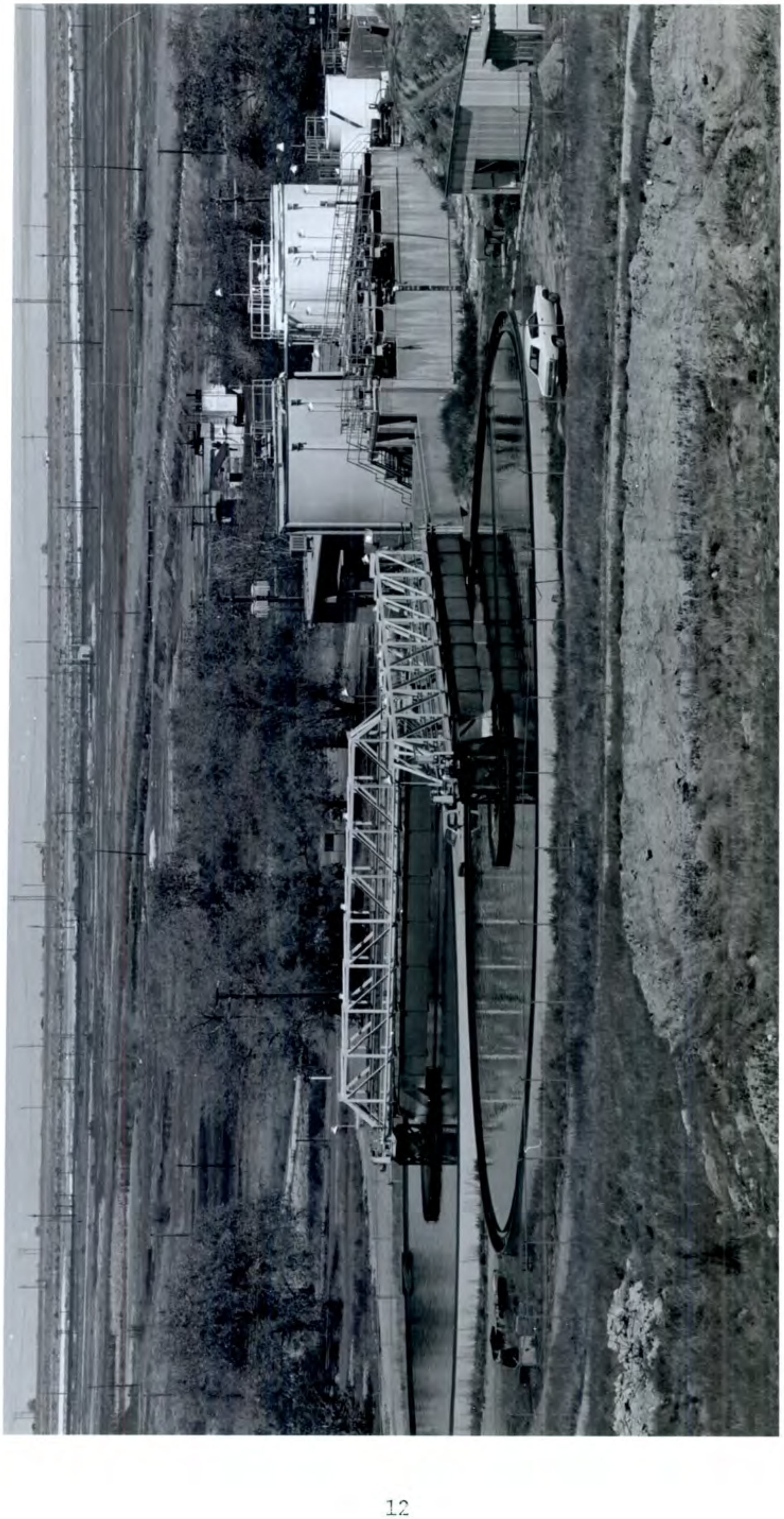

FIGURE 2. - Kennecott waste water treatment plant.

FIG 2

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which supplied one-third of the normal process feed water; (3) pump station No. S-21, which supplied culinary water; and (4) WWTP effluent. These test results indicate that the use of WWTP effluent would reduce copper recovery by 0.5 to 1 pct and molybdenum recovery by approximately 10 pct. Under normal operation, assuming that the average water flows were 40,000 gpm from pump station No. 1 and 20,000 gpm from pump station No. 4, average copper and molybdenum recoveries would be 93.91 and 83.62 pct, respectively. If 10,000 gpm of the flow from pump station No. 4 were replaced with 10,000 gpm of WWTP effluent, average copper and molybdenum recoveries would drop to 93.72 and 81.70 pct, respectively.

TABLE 2. - Weekly water quality flotation comparison tests

Parameter, pct	Water source			
	Pump		Culinary	WWTP effluent
	No. 1	No. 4		
Tailing:				
Wt pct	96.02	96.09	96.04	96.00
Cu analysis	.041	.037	.037	.044
Cu distribution	6.31	5.65	5.58	6.77
MoS_2 analysis	.006	.006	.005	.010
MoS_2 distribution	17.06	15.01	13.41	26.58
Concentrate:				
Wt pct	3.98	3.91	3.96	4
Cu analysis	15.62	15.64	15.76	15.61
Cu distribution	93.69	94.35	94.42	93.23
MoS_2 analysis	.81	.84	.86	.78
MoS_2 distribution	82.94	84.99	86.59	73.42

EXPERIMENTAL PROCEDURE

Preliminary testing was performed in the Bureau's Salt Lake City Research Center using water which was transported about 20 miles from the Kennecott plant site to the laboratory. Later, work was conducted at the plant site (fig. 3) to eliminate any errors or changes which might have occurred during transportation and storage of water. Treatment processes were evaluated by comparing standard copper flotation test results for treated and untreated waste water to results using culinary water and normal process feed water. Flotation using culinary water provided baseline data and represented the best flotation attainable. Flotation using normal process feed water equaled the mill potential. The flotation tests were performed by experienced Kennecott personnel. Specific test procedures are described in the sections discussing each treatment process. In addition, when tests of WWTP influent and effluent showed the presence of measurable amounts of SO_2, additional testing was conducted to explore the possibility of eliminating the SO_2 through air sparging or temperature variations. Those results are shown in Appendix A.

FIGURE 3. - On-site testing facility.

FIG 3

D-4726-5L

EVALUATION AND PRESENTATION OF RESULTS

The effect of the treatment process variations was analyzed statistically using either the Analysis of Variance or the Student's "t" test. Generally, metal recoveries from tests using water treated with aeration and/or activated carbon processes were compared to recoveries using normal process feed water. Replicate samples were also tested, and day-to-day condition variations were recorded to determine factors which might have had a high probability of influence. The test of significance was employed to provide a measure of the probability that any variation in the results could be attributed to changes in the treatment method. Statistical calculations, showing a variance ratio corresponding to a probability level of 5 pct, indicated a probability of only 5 in 100 that a variation in results was due to chance errors, rather than any treatment change. For the work described in this report, a level of 5 pct (0.05) was selected. Any response that did not reach this level of probability was not considered free enough from chance error to exist and was not tabulated.

Average molybdenum recoveries are either tabulated or presented as bar graphs. Copper recoveries generally followed the same trends as molybdenum recoveries, but variations for copper were of less magnitude. Consequently, only molybdenum recoveries have been shown on the bar graphs. Data shown in the "laboratory screening" test section are averaged results. Other data were derived from tests which were run in triplicate to provide an error term so that the data could be analyzed using statistical methods.

LABORATORY SCREENING TESTS

A variety of possible treatment processes were investigated on a bench scale using WWTP effluent to determine which processes effectively removed the contaminant and should be investigated further, and which could be eliminated from further consideration. Most testing involved either oxidation- or adsorption-type processes and were conducted with water transported to the Bureau laboratory. Evaluation of the preliminary test results considered both water quality improvement and process costs.

Treatment processes adopted for field tests were aeration and activated carbon. In laboratory tests, both processes produced measurable improvements in the WWTP effluent quality and would involve relatively low added costs.

During batch aeration tests, air was sparged into WWTP effluent for 1/2-, 1-, 3-, and 24-h periods. Water quality improved with increased time; however, most of the improvement occurred during the first 1/2 h. Agitation increased the effectiveness of aeration.

During batch activated carbon tests, both powdered and granular lignite-based carbons were tested. Lignite-based carbon was selected because it is readily available and has average characteristics for carbon. Also, in an initial batch comparison test, a lignite-based carbon produced significantly more improvement in WWTP effluent quality than did a coconut shell-based carbon. For the laboratory batch tests, various amounts of carbon were added to WWTP effluent and stirred for 30 min. Samples were filtered before flotation testing. As results show in table 3, filtering the carbon-treated samples improved subsequent flotation of molybdenum in each instance and copper in over one-half the instances. Unused carbon suspended in unfiltered water very likely adsorbed organic flotation reagents, thereby adversely affecting flotation results. Results in table 4 show that both powdered and granular carbon treatments significantly improved molybdenum flotation.

Results shown in tables 3 and 4 were produced from tests conducted on different dates. Differences in results for apparently like waters, i.e., culinary, WWTP effluent, and carbon treated waters, reflect variations in water quality and flotation operator performance from day to day.

TABLE 3. - Effect of filtration of activated powdered carbon treated water on water quality

Type of water or treatment	Metal floated, pct			
	Effluent			
	Not filtered		Filtered	
	Cu	Mo	Cu	Mo
Culinary	95.1	75.1	88.7	84.6
WWTP untreated effluent	92.5	59.6	87.7	66.9
0.5 lb C/1,000 gal	90.3	55.4	90.9	80.5
1 lb C/1,000 gal	92.1	63.3	88.4	76.2
2 lb C/1,000 gal	81	48.6	89.5	79.4
5 lb C/1,000 gal	63.4	60	87.4	74.6
10 lb C/1,000 gal	49.1	54.4	88.2	79.1

TABLE 4. - Effect of activated carbon on water quality

Type of water or treatment	Metal floated, pct			
	Carbon			
	Powdered		Granular	
	Cu	Mo	Cu	Mo
Culinary	94.4	86.14	94.84	83.4
WWTP untreated effluent	94.6	59.9	94.6	59.9
0.2 lb C/1,000 gal	94.1	81.35	94.88	81.26
0.5 lb C/1,000 gal	93.8	77.8	94.52	76.25
2 lb C/1,000 gal	94.6	84.6	93.92	80.89
5 lb C/1,000 gal	95.4	85.57	94.69	83.92

Other treatment processes tested on WWTP effluent, but eliminated from further consideration included:

- Hydrogen peroxide - Treating WWTP effluent with 0.13 and 1.3 lb hydrogen peroxide (H_2O_2) per 1,000 gal followed by a 30-min agitation produced little improvement in molybdenum recovery. A significant decrease in copper recovery could result if accidental overtreatment occurred.

- Calcium hypochlorite - Treating WWTP effluent with dry calcium hypochlorite [$Ca(ClO)_2$] at 0.0003 lb per 1,000 gal (equivalent to 37 ppm available chlorine) improved molybdenum and copper flotation, but less so than did aeration or activated carbon. Close control with sodium sulfite (Na_2SO_3) was necessary to avoid excess hypochlorite from entering the flotation circuit; this could be detrimental to flotation reagents.

- Chlorine gas - Chlorinating to 800 emf had an effect similar to that produced by adding calcium hypochlorite; again, excess chlorine must be avoided.

- Ozone - Treating WWTP effluent with 0.025, 0.1, 0.25, and 1.0 lb ozone (O_3) per 1,000 gal improved molybdenum and copper recoveries; however, such a process would entail significantly higher costs.

- Ion exchange - Treating WWTP effluent with the sodium form of the strong cationic resin Duolite C-25D,[4] or the hydroxyl form of the strong anionic resin Amberlite IRA 410 improved molybdenum and copper recoveries, but again, the process would be costly.

- Synthetic organic adsorbents - Treating WWTP effluent with non-polar resins, Amberlite XAD-2 and XAD-4, improved molybdenum and copper recoveries, but not sufficiently to warrant the higher cost of such a process.

ON-SITE TESTS

After completing the preliminary screening tests in the laboratory, testing was conducted at the plant site; this eliminated the delay caused by delivering samples from the plant site to the laboratory, and thereby removed a source of possible errors. In most on-site tests, triplicate samples were submitted for flotation tests to provide a basis for estimating the testing error. The flotation responses after various combinations of water treatments were examined by statistical methods to determine which factors had a high probability of affecting the response. Water samples were also submitted for analysis by gas and liquid chromatography as discussed in Appendix B.

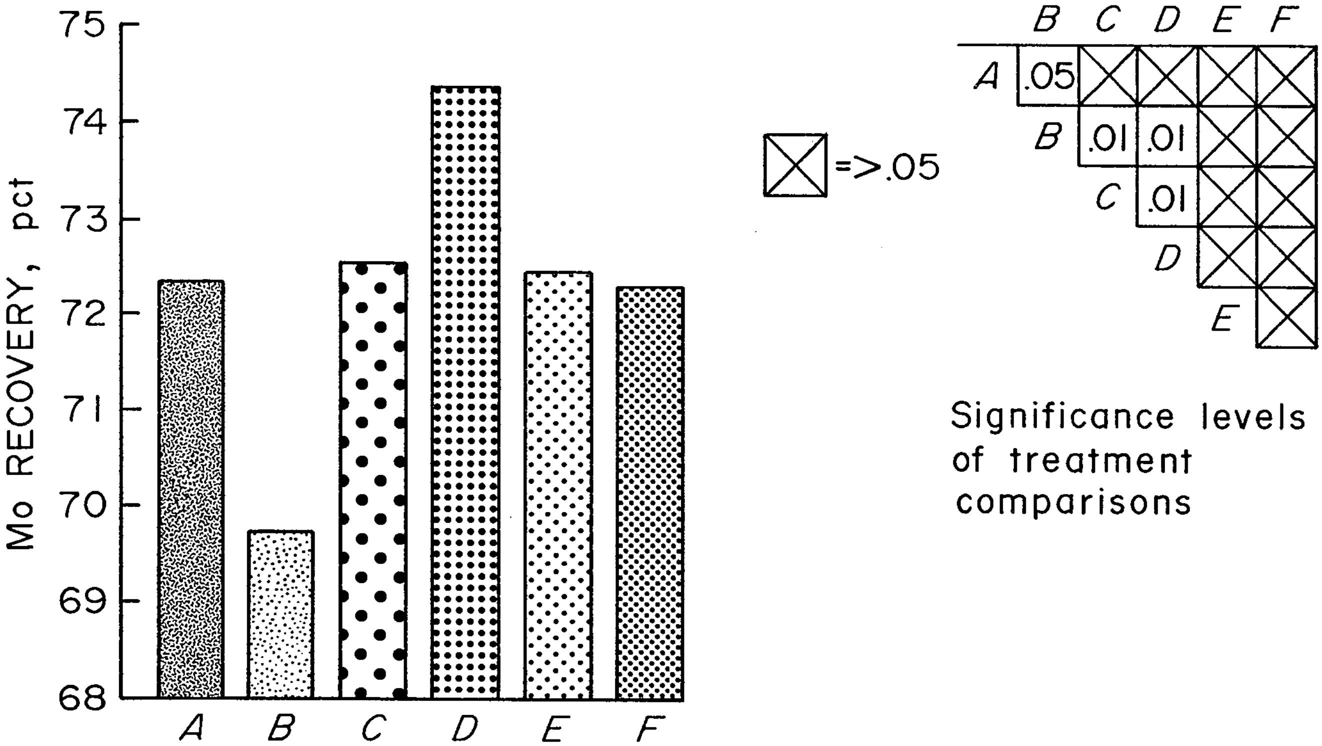
[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

COMPARISON OF EFFLUENTS FROM CONCENTRATORS AND WWTP

The WWTP treats the combined streams of waste water from all parts of the operation. To find out whether the major source of contamination causing the depression in flotation was in the waste water from the flotation concentrator, as suspected, or in one of the other streams, tests were conducted to compare concentrator effluent with WWTP effluent. The WWTP feed comprised 80 pct concentrator water; if both waters depressed flotation, it would indicate that the contamination was in the concentrator water, not in the other feed streams. Two series of tests were performed: one in the late autumn and the other in the winter. These tests showed the effect of the ambient temperature on water quality. Results (fig. 4) indicate that during the winter, the quality of the concentrator effluent is better than that of the WWTP effluent. However, results from autumn tests show the comparative quality reversed. Combining the winter and autumn results, there was no significant difference in the overall quality of the concentrator and WWTP effluents; this lends credence to the belief that the troublesome contaminant was present in the waste water from the concentrator and not necessarily in other WWTP feed streams. This indicated that either the concentrator effluent or the WWTP effluent could be treated in processes for improved water quality.

EFFECT OF FILTRATION, AERATION, AND ACTIVATED POWDERED CARBON TREATMENT ON QUALITY OF CONCENTRATOR EFFLUENT

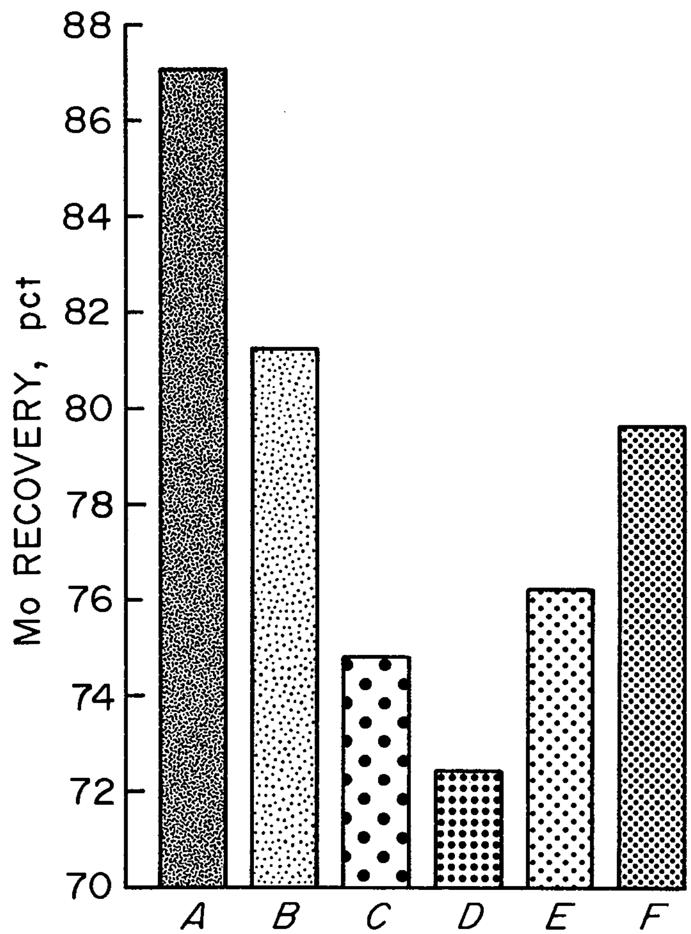
Since the quality of the concentrator effluent was nearly the same as the quality of the WWTP effluent, initial tests were conducted to determine whether treatment of the concentrator effluent would be a suitable alternative to treatment of the WWTP effluent. The effect of filtration, aeration, or treatment with 0.5 lb of activated powdered carbon per 1,000 gal was determined. Comparative results of flotation tests, using the treated water (fig. 5), indicates that the following results were statistically significant: (1) Filtering the water reduced molybdenum recovery slightly, indicating that the troublesome contaminant was soluble. (2) Aeration improved the quality of the water. (3) Carbon treatment produced an even greater improvement in water quality; this treatment produced a water quality nearly as good as that of normal process water. Therefore, treatment of the concentrator effluent was shown to be effective; results were comparable to those achieved earlier during treatment of WWTP effluent on a bench scale.



KEY

A Concentrator effluent-winter
B WWTP effluent-winter
C Concentrator effluent-autumn
D WWTP effluent-autumn
E Concentrator effluent-overall
F WWTP effluent-overall

FIGURE 4. - Comparison of concentrator and WWTP effluents and season of year effect on water quality.



	B	C	D	E	F
A	.01	.01	.01	.01	.01
B		.01	.01	.01	.05
C			.05	.05	.01
D				.01	.01
E					.01

Significance levels of treatment comparisons

KEY

A Culinary water
B Normal process feed water to concentrator
C Concentrator effluent
D Concentrator effluent filtered
E Concentrator effluent aerated
F Concentrator effluent treated with 0.5 lb C/1,000 gal

1.20

FIGURE 5. - Effect of filtration, aeration, and carbon treatment on quality of concentrator effluent.

D-7435-SL

EFFECT OF POWDERED CARBON TREATMENT ON QUALITY OF WWTP EFFLUENT

Batch tests showed that treating the WWTP effluent with powdered carbon followed by disposal of the carbon in the treatment plant sludge, was as effective as column treatment with granular carbon. Powdered carbon was advantageous because equipment requirements would be less, and carbon regeneration would be eliminated. Investigations determined the effect of carbon dosages ranging from 0.1 to 0.5 lb per 1,000 gal. In all tests, the appropriate amount of powdered lignite-based carbon was added to the water, and the mixture was stirred for 30 min. The carbon was filtered off before submitting the water samples for flotation tests. Figure 6 shows the flotation test results using the treated water. Increasing the amount of carbon from 0.1 to 0.5 lb per 1,000 gal of WWTP effluent significantly increased the water quality so that it was nearly as good as that of normal process feed water.

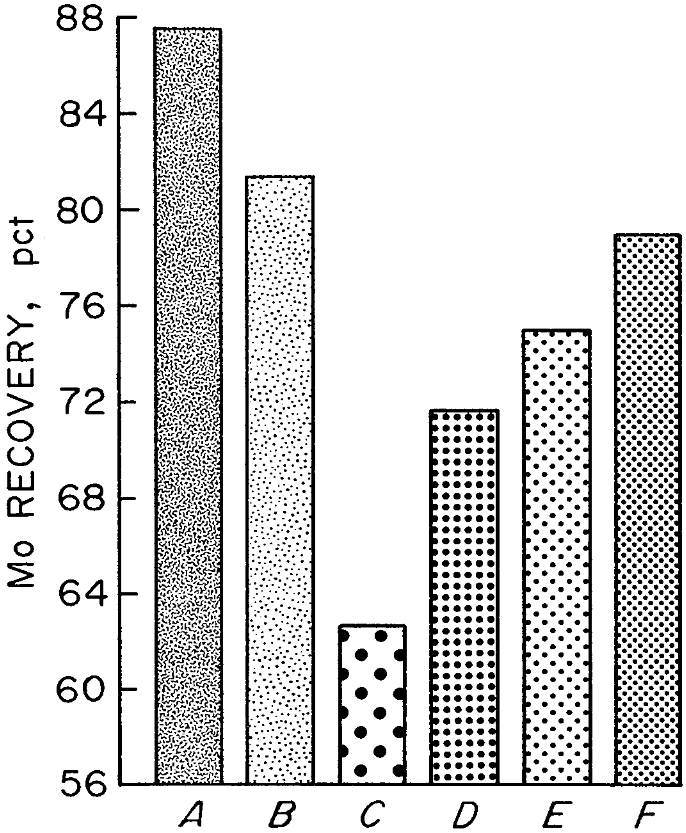
EFFECT OF AERATION TREATMENT ON QUALITY OF WWTP EFFLUENT

Past experience indicated that molybdenum flotation was depressed more by recycling WWTP effluent in the winter months than in the summer months. There was also a possibility that aeration effectiveness might be affected by the ambient temperature. Comparative test series were conducted for winter and spring operations. Aeration was accomplished in a series of three tanks. Figure 7 shows the flotation test results when using treated and untreated water. Molybdenum recovery using WWTP effluent in the spring was not statistically different from that obtained with WWTP effluent in the winter. Aeration significantly improved the water quality for molybdenum flotation, but there was no indication that it was more effective in either season.

Tests described in the previous paragraph showed that the three-step aeration of WWTP effluent significantly improved water quality, but did not restore it to a level equivalent to that of normal feed water. Another test series investigated whether doubling the aeration time by using six stages (fig. 8) would result in a greater increase in water quality. Increasing the number of aeration stages from three to six may have increased water quality slightly (fig. 9), but the increase was not statistically significant.

EFFECT OF COMBINED AERATION PLUS POWDERED CARBON TREATMENT ON QUALITY OF WWTP EFFLUENT

Both the aeration and powdered carbon treatments were shown to significantly improve the quality of the WWTP effluent. Additional test results (fig. 10) indicate the effect of a combined aeration plus



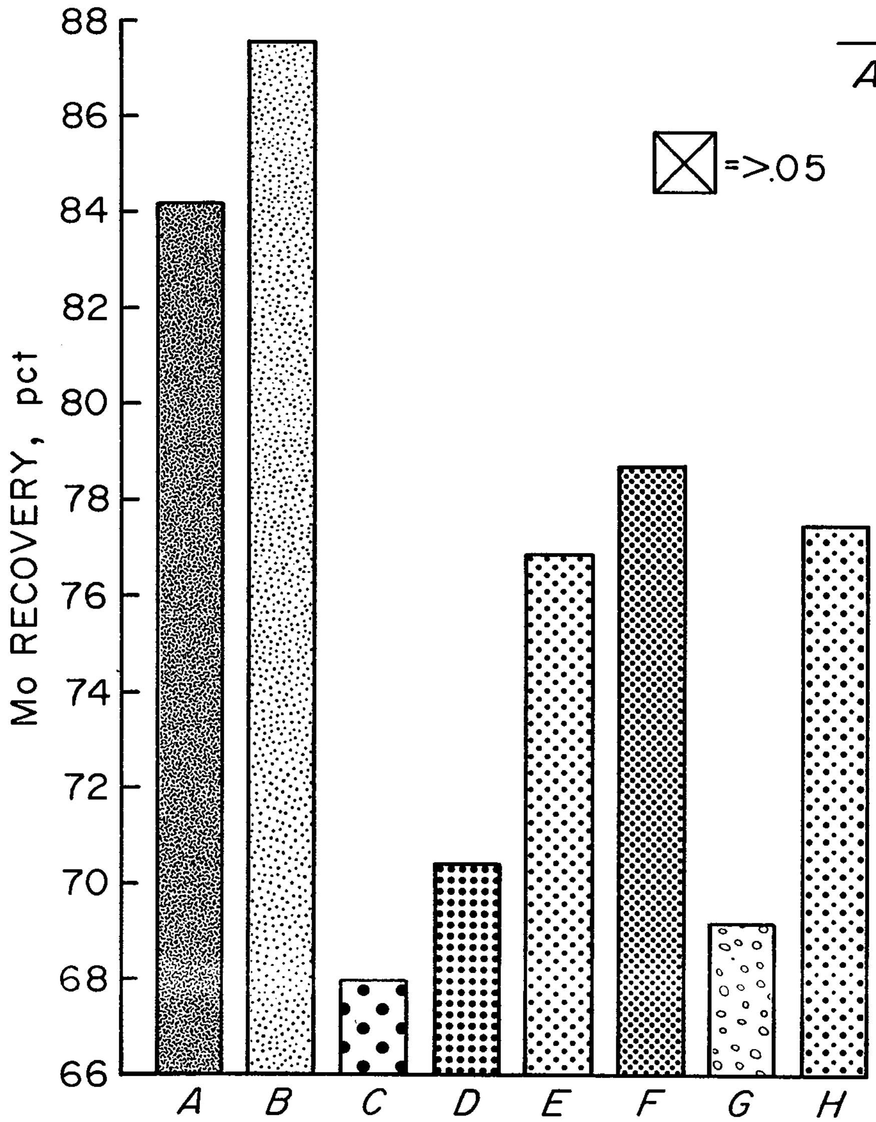
	B	C	D	E	F
A	.01	.01	.01	.01	.01
B		.01	.01	.01	.01
C			.01	.01	.01
D				.01	.01
E					.01

Significance levels of treatment comparisons

KEY

A Culinary water
B Normal process feed water to concentrator
C WWTP effluent
D WWTP effluent treated with 0.1 lb C/1,000 gal
E WWTP effluent treated with 0.25 lb C/1,000 gal
F WWTP effluent treated with 0.5 lb C/1,000 gal

FIGURE 6. - Effect of powdered carbon treatment on quality of WWTP effluent.



⊠ = >.05

	B	C	D	E	F	G	H
A	.01	.01	.01	.01	.01	.01	.01
B		.01	.01	.01	.01	.01	.01
C			⊠	.01	.01	⊠	.01
D				.01	.01	⊠	.01
E					⊠	.01	⊠
F						.01	⊠
G							.01

Significance levels of treatment comparisons

KEY

A Culinary water-winter
B Culinary water-spring
C WWTP effluent-winter
D WWTP effluent-spring
E Aerated WWTP effluent-winter
F Aerated WWTP effluent-spring
G WWTP effluent-overall
H Aerated WWTP effluent-overall

p 23

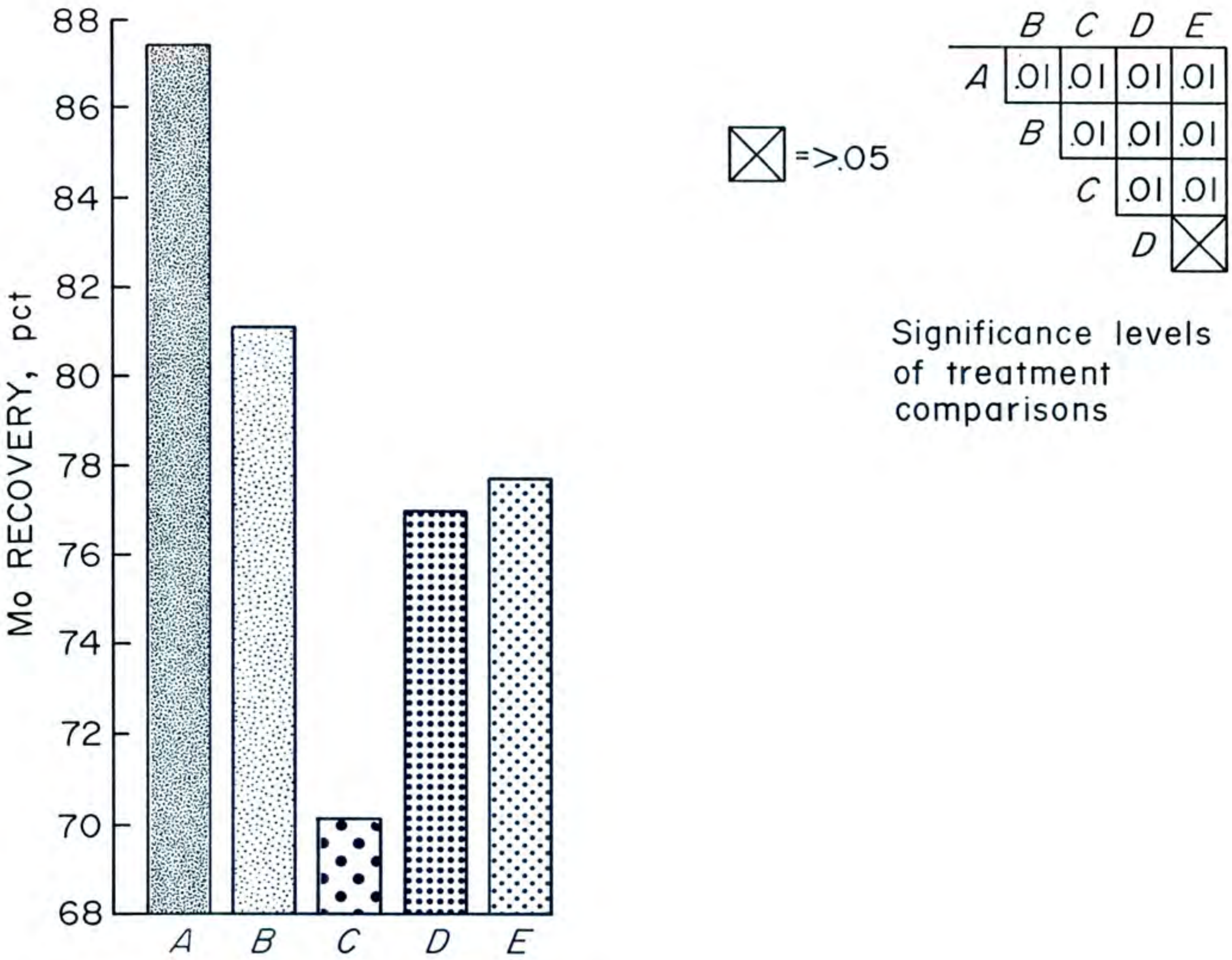
FIGURE 7. - Effect of aeration and season of year on quality of WWTP effluent.

p 24

FIGURE 8. - Aeration system for WWTP effluent treatment.

FIG 8

0-4723-SL



KEY

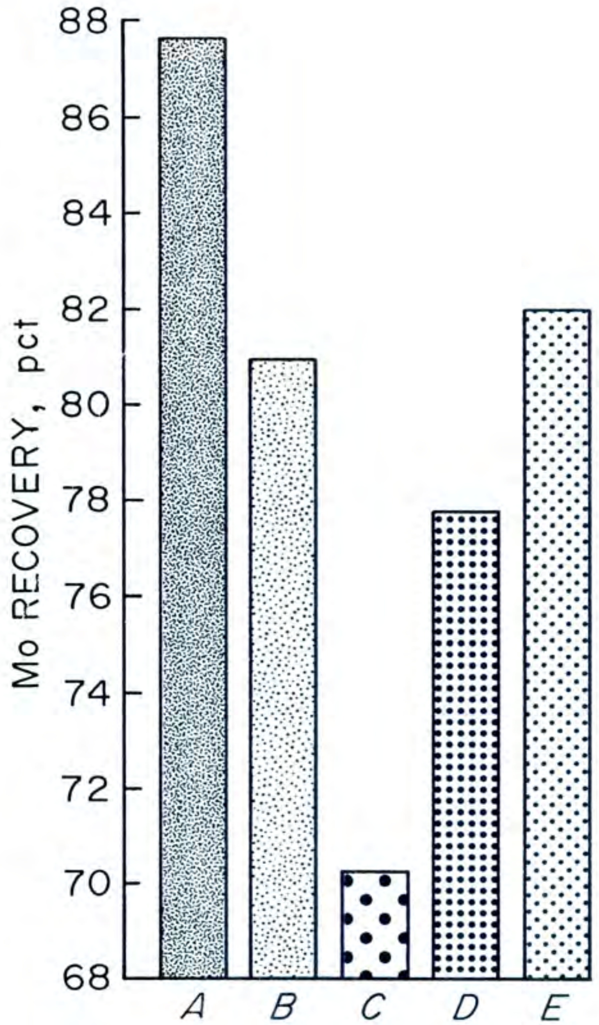
A Culinary water
B Normal process feed water to concentrator
C WWTP effluent
D WWTP effluent-3-stage aeration
E WWTP effluent-6-stage aeration

p 25

FIGURE 9. - Effect of aeration time on quality of WWTP effluent.

FIG 9

D-7438-5C



	B	C	D	E
A	.01	.01	.01	.01
B		.01	.01	X
C			.01	.01
D				.01

X = >.05

Significance levels of treatment comparisons

KEY

A Culinary water

B Normal process feed water to concentrator

C WWTP effluent

D Aerated WWTP effluent

E Aerated WWTP effluent treated with 0.5 lb C/1,000 gal

FIGURE 10. - Effect of aeration plus powdered carbon treatment on quality of WWTP effluent.

powdered carbon treatment. Test procedures were the same as discussed earlier. The combined treatment, using aeration and 0.5 lb powdered carbon per 1,000 gal of WWTP effluent produced water with quality as high as that of normal process feed water.

TEN-DAY POWDERED CARBON DEMONSTRATION RUN

At the conclusion of the pilot-plant and laboratory testing programs, a 10-day full-scale test was performed using powdered carbon to treat the waste water. Powdered carbon was chosen rather than granular carbon because of its higher efficiency in improving water quality and its lower cost. Figure 11 is a photograph of the equipment used for the test. Powdered lignite-based carbon was slurried with culinary water. Then the slurry was pumped into the concentrator effluent stream just before its entry into the junction box where it mixed with the other waste streams entering the WWTP. Carbon dosage was equivalent to approximately 0.5 lb per 1,000 gal of the total flow through the WWTP.

Samples of various streams were collected daily for batch flotation testing. Since the full-scale WWTP did not have facilities for aeration, it was necessary to test for aeration effects in a large tank (approximately 30 gal) on a batch basis. Also, since there was no way to split the streams through the large-scale plant, it was necessary to use batch tests to simulate various streams; this provided baseline results for comparison with actual full-scale test results. The following list describes the various samples processed in flotation tests. Letters refer to the key used in figure 12 to describe the relationship between baseline conditions and the effect of the treatments. All stream samples, except the culinary water, were collected with proportional samples.

A. Culinary water - Ordinary tap water was sampled at the mill site to provide a base of maximum achievable metal flotation.

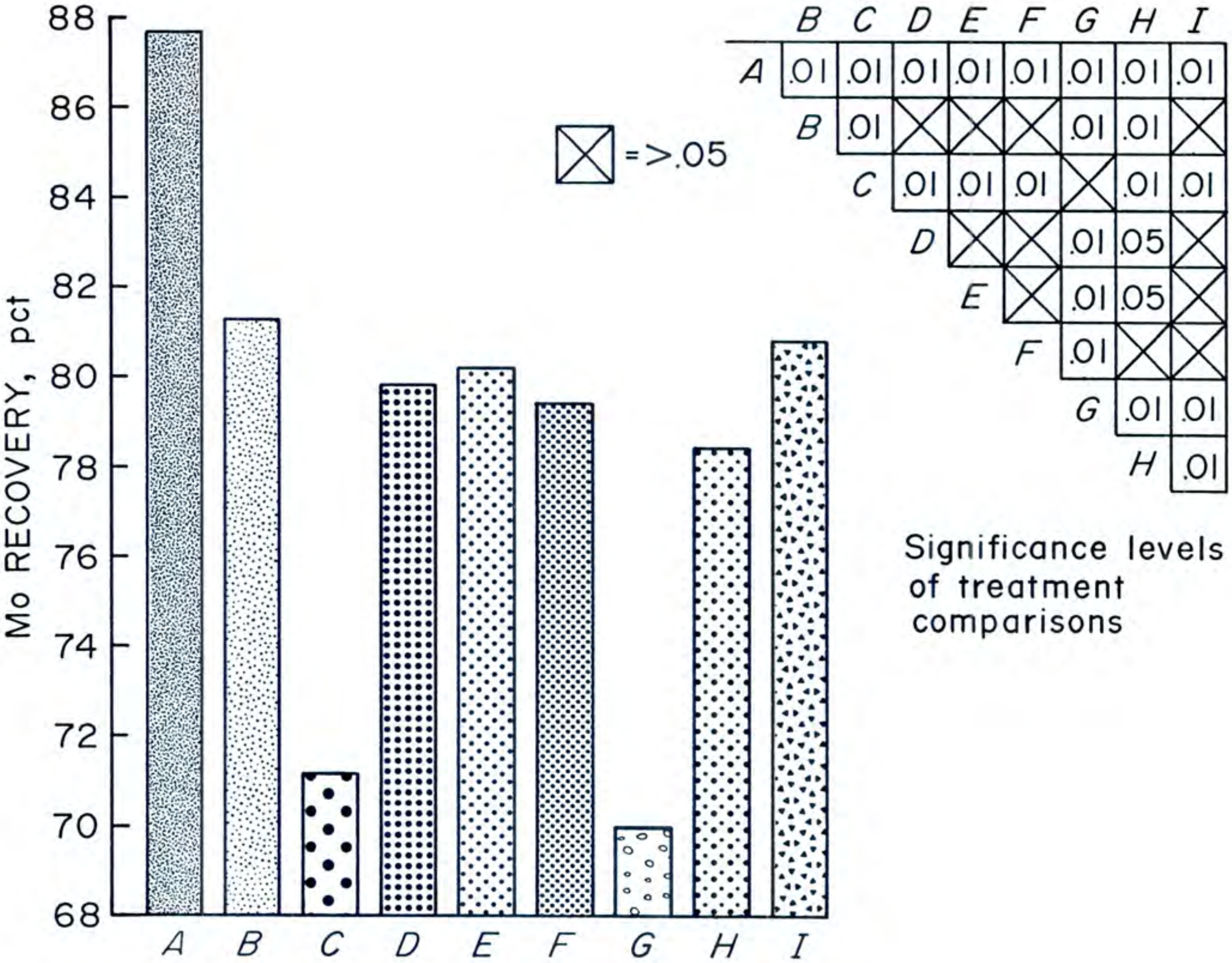
B. Normal process feed water to concentrator - The feed stream to the concentrator was sampled with a proportional sampler; this provided a composite sample of all the water used during a 24-h period.

C. Untreated concentrator effluent - The concentrator effluent stream was sampled before it mixed with the smelter and refinery effluents; this sample was collected at the same time that samples of other streams were collected.

FIGURE 11. - Equipment used for 10-day powdered carbon demonstration run.

FIG 11

D-5112-5L



KEY

A Culinary water
B Normal process feed water to concentrator
C Untreated concentrator effluent
D Filtered carbon-treated WWTP effluent-analyst A-continuous run
E Filtered carbon-treated WWTP effluent-analyst B-continuous run
F Unfiltered carbon-treated WWTP effluent-continuous run
G Limed feed mix(equivalent to untreated WWTP effluent)-batch test
H Limed feed mix with aeration-batch test
I Limed feed mix treated with 0.5 lb C/1,000 gal and filtered-batch test

p 29

FIGURE 12. - Results of 10-day carbon treatment demonstration run.

FIG 12

D-7440-56

D. Filtered WWTP effluent (Analyst A) - Effluent from the full-scale WWTP was sampled daily during the demonstration run; the first of two operators performed flotation tests to provide an indication of possible experimental error between different operators. Samples were filtered to remove any entrained carbon.

E. Filtered WWTP effluent (Analyst B) - Same as D except the flotation tests were performed by the second operator.

F. Unfiltered WWTP effluent - Same as D and E except the samples were not filtered. A comparison of the results from D and E with results from F showed whether entrained carbon would present a problem.

G. Limed-feed mix - A mixture of concentrator, smelter, and refinery effluents was combined in the same proportions as the feed stream to the WWTP and sampled. The mixture was limed to pH 9.0, flocculated, and settled to duplicate WWTP treatment; this also provided a base for comparison with carbon-treated WWTP effluent.

H. Aerated limed-feed mix - Same as G except the limed slurry was aerated for 2 h by sparging air into the slurry in an agitated vessel. This indicated any advantage achieved by aeration of WWTP effluent. equivalent to approximately 0.5 lb per 1,000 gal of the total flow through the WWTP.

I. Limed-feed mix with carbon - Same as G except powdered carbon equivalent to 0.5 lb per 1,000 gal was added to limed slurry, mixed for 30 min, and then filtered. This provided a base for comparison with the results of the continuous flow through the WWTP. This also indicated any advantage achieved by treating WWTP effluent with activated carbon.

All tests on each sample were performed in triplicate to provide an estimate of error. Consequently, two sets of triplicate-filtered effluent samples were submitted daily. Each technician conducted tests on one set of water samples; comparison of results provided an indication of the reproducibility of results between technicians. Figure 12 shows the effect of various treatments on molybdenum recovery. The results plotted are the averages for samples taken each day of the 10-day continuous treatment. Copper recoveries generally followed the same trends as molybdenum recoveries, but were not as pronounced. For example, treatment of limed-feed mix with carbon increased copper recovery from 94.4 to 94.6 pct, and aeration increased copper recovery from 94.4 to 94.9 pct. Molybdenum recovery from concentrator effluent (bar C), limed-feed mix (bar G), and aerated limed-feed mix (bar H) was lower than recovery from normal

process feed water (bar B) at 0.01 significance level. However, the aerated water was significantly higher in quality than the unaerated water. The water quality produced by carbon treatment (bar I) was still higher. Comparison of the carbon-treated limed-feed mix batch (bar I) with continous-flow carbon-treated water (bars D and E) shows that batch treatment of unaerated water with carbon produced water quality comparable to that achieved by continuous treatment with carbon of WWTP influent. These results indicate that comparison of batch test data with data from the 10-day continuous-flow test is valid. Comparison of bar graphs D and E shows that essentially the same results were produced by the different analysts. The absence of any significant differences between filtered (bars D and E) and unfiltered (bar F) samples of treated WWTP effluent indicates that carbon settled out adequately in the WWTP clarifiers. Overall, as in earlier batch tests, carbon treatment (bars D, E, and I) produced WWTP effluent at the quality level of normal process feed water (bar B).

CONCLUSIONS AND RECOMMENDATIONS

Results from the 10-day demonstration run indicated that aeration of the waste water limed to pH 9.0 increased subsequent molybdenum flotation from 70 to 78 pct. Treatment of the unaerated limed-waste water with powdered carbon at 0.5 lb per 1,000 gal increased molybdenum flotation from 70 to 81 pct. Smaller batch tests indicated that a combination of aeration and carbon treatments would produce water of a quality as good or better than normal feed water. Treatment of either the effluent from the flotation concentrator prior to its entry into the WWTP or the effluent from the WWTP was equally effective.

APPENDIX A. - SULFUR DIOXIDE ELIMINATION

Waste water entering the WWTP contained up to 300 ppm dissolved sulfur dioxide. The effect of sulfur dioxide on flotation was not known. However, elimination of sulfur dioxide was desirable in any case. Tests were performed to see how rapidly aeration eliminated sulfur dioxide. Batch and continuous tests were conducted in the laboratory using synthetic sodium sulfate solutions containing either 100 or 300 ppm SO_2. The batch tests comprised stirring the solutions rapidly and sparging air into the stirring solutions through a gas diffusion tube. Periodically, samples were withdrawn and assayed for sulfur dioxide using the standard iodometric method. Continuous tests were conducted in a train of three 30-gal mixers. The solution was agitated rapidly and air was sparged into the bottom of each tank. Effluent from each tank was sampled and assayed after enough solution had passed through the system to assure steady-state conditions.

Batch tests were conducted using 300 ppm SO_2 feed at 15°, 25°, and 35° C and 100 ppm SO_2 feed at 15° C. Data from all batch tests were fitted to the first-order reaction rate equations shown in table A-1. The high correlation coefficients indicate that sulfur dioxide elimination is a first-order reaction. Figure A-1 shows the plots of the data and regression lines. Table A-2 shows the results of the continuous tests together with expected results calculated from batch test results using the method described by Jenny.[1] The continuous test results were better than expected. Although there were some differences between expected and actual results, an adequate continuous system for the elimination of sulfur dioxide could be designed on the basis of batch tests.

Sulfur dioxide in actual WWTP effluent was monitored during aeration tests at the mill site. The water was aerated in a series of three or six agitated vessels, as discussed earlier in this report. Samples of effluent from each tank were assayed for sulfur dioxide; table A-3 shows some typical assays. In all cases, five- or six-stage aerations reduced the sulfur dioxide concentration to less than 4 ppm.

[1]Jenney, T. M. Charts Simplify Job of Designing Your Reactor System. Chem. Eng., Dec. 1955, pp. 198-202.

TABLE A-1. - Reaction rate equations, sulfur dioxide elimination

SO_2 feed, ppm	Temp, °C	Rate equation	Correlation coefficient
100	15	ln C = -.0151 t + 4.489	-.995
300	15	ln C = -.0125 t + 5.433	-.995
300	25	ln C = -.0436 t + 5.486	-.988
300	35	ln C = -.0794 t + 5.953	-.981
300	45	ln C = -.0868 t + 6.143	-.956

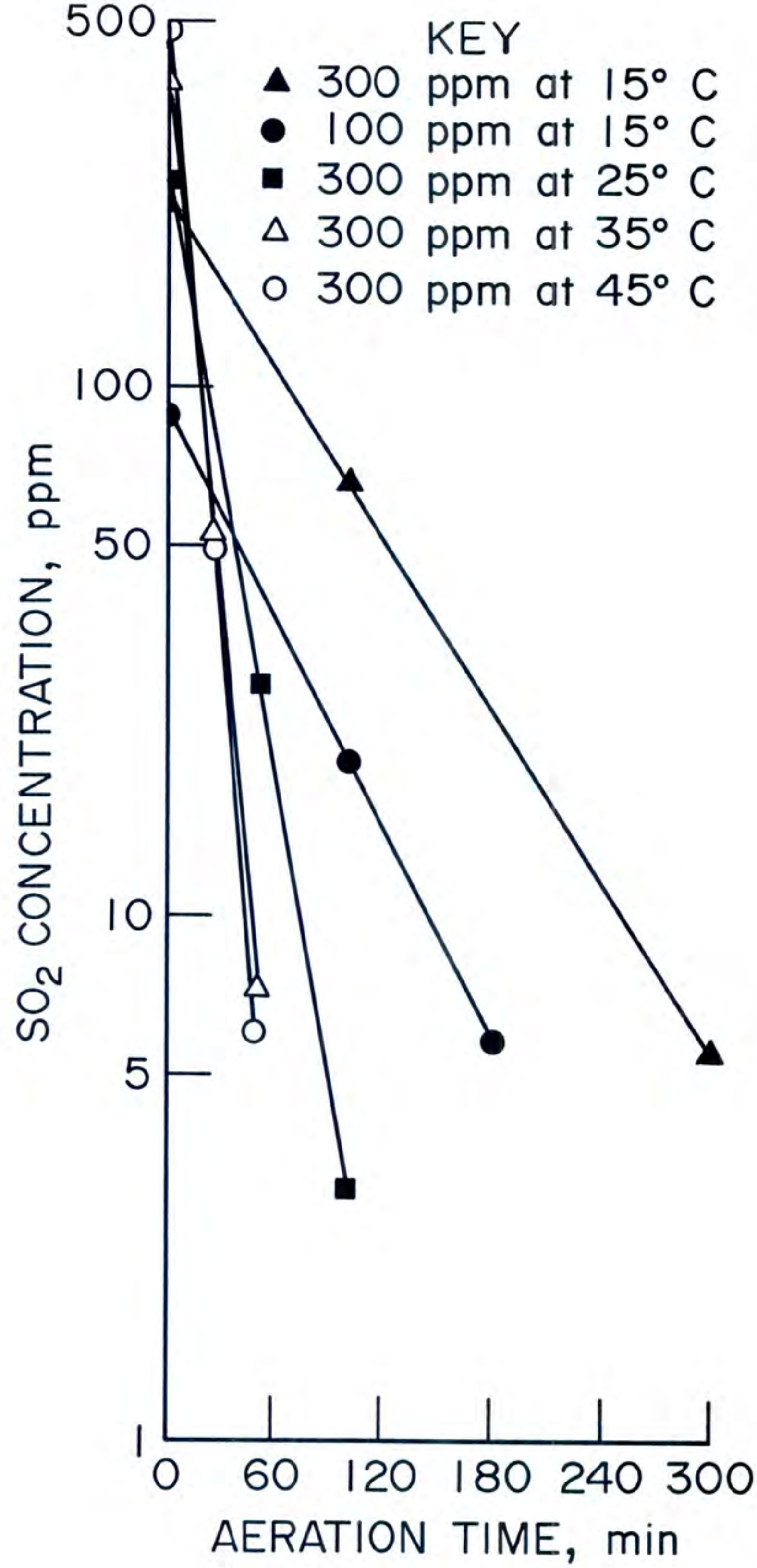
TABLE A-2. - Sulfur dioxide elimination by aeration in continuous flow tests

SO_2 in feed, ppm	Temp, °C	Retention time per stage, min	SO_2 in effluent, ppm					
			Actual SO_2 stage			Expected SO_2 stage		
			1	2	3	1	2	3
300	25	52	88.6	15.1	2.8	90	25.5	8.4
100	25	57	23.4	6.9	2.5	29	8	2.7
100	15	57	73.3	47.9	20.4	65	37	15
300	15	126	83.4	34.8	10.2	114	45	16.5
300	25	81	43.4	9.2	3.2	69	15	8.1

TABLE A-3. - Sulfur dioxide concentrations in aerated WWTP effluent

Date	Feed	SO_2 concentration, ppm Tank No.					
		1	2	3	4	5	6
08/24/78	82.5	3.9	2.3	1.8	1.6	1.5	ND
12/28/78	163.4	20.7	6.1	3	1.9	2.2	ND
01/05/79	158.9	26.1	8.2	4.5	2.4	3	ND
03/30/79	161.3	25.6	15	8.5	5	3.9	2.5
04/06/79	123.8	7.4	4	2.7	2	.8	.7

ND Not determined.


KEY
300 ppm at 15° C
100 ppm at 15° C
300 ppm at 25° C
300 ppm at 35° C
300 ppm at 45° C
500
100
50
10
5
1
SO2 CONCENTRATION, ppm
0
60
120
180
240
300
AERATION TIME, min

p 34

FIGURE A-1. - Effect of temperature on rate of SO_2 elimination.

FIG A-1

D-7441-SL

APPENDIX B.--GAS AND LIQUID CHROMATOGRAPHY

Samples of water from most of the on-site tests were analyzed by gas and liquid chromatography to determine whether any of the troublesome organic compounds could be identified or whether a correlation could be made between the chromatograms and water quality. The chromatograms showed that volatile organics were largely eliminated by aeration and that most volatile and nonvolatile organics were adsorbed by carbon. Attempts to identify specific organic compounds were unsuccessful as were efforts to correlate the chromatograms with water quality.