UTILIZATION OF MUNICIPAL WASTE WATER FOR FROTH FLOTATION OF COPPER AND MOLYBDENUM SULFIDES

by
Walter W. Fisher, Assistant Metallurgist
and
Samuel Rudy, Assistant Metallurgist

THE ARIZONA BUREAU OF MINES
MINERAL TECHNOLOGY BRANCH

1976

Circular 17

Price Seventy-five cents

Material contained in this Circular may be quoted or reproduced without special permission provided appropriate acknowledgment is given to the source.

UTILIZATION OF MUNICIPAL WASTE WATER FOR FROTH FLOTATION OF COPPER AND MOLYBDENUM SULFIDES

by
Walter W. Fisher, Assistant Metallurgist
and
Samuel Rudy, Assistant Metallurgist

INTRODUCTION

Water is becoming a more and more controversial subject in Arizona. The problem stems from the fact that the amount of water consumed far exceeds the ability of nature to replace it. In order to meet growing agricultural, industrial, mining and municipal demands, water is being mined from groundwater reservoirs at alarming rates. Statistics presented in Phase I of the Arizona State Water Plan recently released by the Arizona Water Commission indicate that for Arizona, taken as a whole, water is being withdrawn from groundwater storage at 1.7 times the rate at which it is being replaced by natural recharge. In Pima County, where essentially all water consumed is drawn from the groundwater supply, the depletion rate is 4.7 times the recharge rate. Such depletion of the groundwater supply cannot go on indefinitely. Alternatives must be found and implemented to narrow the widening gap between water use and water recharge.

One alternative that could result in a significant reduction in groundwater depletion near metropolitan areas is utilization of municipal waste water. This large source of water is presently used to a very limited extent. For example, in Pima County, the City of Tucson discharges about 33 million gallons per day of municipal waste water into the Santa Cruz River. Part of this water percolates into the ground and will ultimately enter the groundwater reservoir to the north of Tucson. However, a large portion of the water evaporates into the atmosphere. The City of Tucson is currently seeking alternative uses for this water. Of the many possibilities, the one that has received the most public exposure is utilization of the waste water by the four copper mining and processing operations located south of Tucson. This alternative would reduce the groundwater depletion in the area and at the same time provide the local copper industry with a reliable, long term source of water.

Municipal waste water is already utilized to a small extent in several copper processing operations in Arizona. However, the amount used is rather small when it is compared with the total water consumed by each operation and the adverse effects attributable to the waste water are not readily observed in these operations.

The proposed use of waste water by the operations near Tucson is considerably different. The water currently used by these operations would be almost completely replaced with waste water. The mineral processing techniques used by these companies are extremely sensitive to chemical contaminants, and therefore, large scale substitution of waste water could have serious detrimental consequences. Because there is not an industrial precedent for this type of municipal waste water utilization and since experimental studies on the effects of waste water in mineral processing have not been reported, there remains a large gap between proposed utilization and commercial acceptance.

The Arizona Bureau of Mines, under the sponsorship of the Office of Water Research and Technology at The University of Arizona, has for the past two years studied the feasibility of utilizing municipal waste water in mineral processing. The laboratory investigation has been aimed at first identifying potential problems, and then, seeking solutions that would be acceptable to the mineral processing industry. Since this work was prompted by a specific problem in the Tucson area, the investigation has been limited to utilizing City of Tucson municipal waste water in the mineral processing operations south of Tucson. The largest use of water in these operations is in the froth flotation recovery of copper and molybdenum sulfide minerals. Consequently, this entire report is devoted to the utilization of sewage effluent in the flotation process.

The work reported in this paper is by no means an exhaustive study of the problem. Rather, it is an exploratory study meant only to define the problem and point out areas for future concentrated investigation.

Background on Copper-Molybdenum Froth Flotation

Froth flotation is the principal process by which sulfide minerals are recovered from ores to form sulfide concentrates. The copper industry relies almost entirely on froth flotation for its feed to smelters and hydrometallurgical refining processes. The success of the flotation process lies in the carefully controlled addition of small quantities of specific chemicals to the processing system at the correct addition point. As a result, froth flotation is extremely sensitive to small amounts of chemical contaminants that may be present in water supplied to the processing system. Foreign chemical contaminants in the process water can have a significant effect on froth flotation metal recovery.

Flotation recovery of copper sulfide minerals and by-product molybdenum sulfide, as practiced in most copper concentrators, consists of many interdependent flotation stages. Raw ore, having been crushed and ground sufficiently fine, is subjected to the rougher flotation stage. A rougher bulk concentrate is produced which contains most of the copper and molybdenum sulfide minerals, along with other impurities. The rougher concentrate is ground finer, and cleaned two or three times by flotation to remove as much non-sulfide material or gangue as possible and produce a high-grade bulk copper-molybdenum concentrate. Molybdenum sulfide is then separated from copper sulfides by chemical treatment and differential flotation to produce a relatively low grade rougher molybdenum sulfide concentrate and a high grade copper concentrate. The rougher molybdenum concentrate is cleaned by several additional stages of flotation to further reject copper sulfides and gangue to produce a high-grade final molybdenum concentrate.

This report is devoted solely to the determination of the effects of sewage effluent on bulk rougher flotation. Therefore, the results presented serve only to identify the gross and most obvious effects of sewage effluent. Determination of the effects of sewage effluent on the integrated copper-molybdenum froth flotation processing scheme is beyond the scope of this report, and in fact, can probably only be determined with certainty in a pilot plant of sufficient size to allow scale up to commercial practice.

EXPERIMENTAL PROCEDURE

Ore, Water and Reagents

The investigation was conducted using an ore obtained from the Cyprus Pima Mining Company open pit mine located south of Tucson. Approximately 800 pounds of ore was collected in the concentrator from conveyors feeding three grinding mills in the primary grinding circuit. The ore was stage crushed in the laboratory to minus 10 mesh, mixed, split into 1000 gram dry test charges, and stored in plastic bags for later use. Since the ore samples were ground in a laboratory ball mill prior to each flotation test to produce an ore pulp containing about 47 percent finer than 200-mesh, oxidation of the sulfides in the minus 10-mesh ore during storage was not considered to be a significant problem. Chemical analysis showed the sample to contain 0.49 percent copper, 4.40 percent iron and 0.011 percent molybdenum. Chalcopyrite, pyrite, and molybdenite were identified microscopically as the main sulfide minerals present.

Demineralized water generated with a high-capacity Barnstead demineralizing column was used for the standard flotation tests. (Use of product or company names in this report is made for identification only and does not serve as an endorsement by the Arizona Bureau of Mines.) Water obtained by this procedure was designated standard water in subsequent flotation tests, and was used to establish a reference flotation response from which direct comparisons of flotation results could be made. Sewage effluent was obtained at the City of Tucson's Roger Road sewage treatment facility from one of the activated sludge units. All samples were collected from the same treatment unit between the hours of 8 and 9 A.M. so that the flow rate through the plant was essentially the same for each sample.

Flotation reagents used throughout the study were standard laboratory chemicals in general use by flotation laboratories. Potassium amyl xanthate (Z-6) and methyl iso-butyl carbanol (MIBC) were used as the primary collector and frother respectively. In some tests, American Cyanamid AERO PROMOTER 3302 was used as the collector. A mixture of 50 percent kerosene and 50 percent Number 2 diesel fuel constituted the fuel oil mixture. Hydrated lime assaying 93 percent $Ca(OH)_2$ was used as the pH modifying agent.

Flotation Procedure

Flotation tests were conducted in the following manner. One thousand grams of ore containing suitable additions of desired reagents were ground at 67 percent solids for 10 minutes in a 7.5 by 8-inch laboratory ball mill containing 30 pounds of steel balls of various sizes. The ground pulp was transferred to a Denver D-1 2.5 liter laboratory flotation cell and diluted to 2.2 liters or about 35 percent solids. The pH of the slurry was determined using a Corning Model 7 pH meter. The slurry was then conditioned for 2 minutes with the air valve of the flotation mechanism in the open position, after which time frother was added and the slurry conditioned another minute without introducing air. The conditioned pulp was subjected to rougher flotation with the impeller of the flotation machine rotating at 1800 RPM. Froth was drawn on 10 second intervals for 8 minutes. The sides of the flotation cell were washed on 2 minute intervals, and the pulp level was adjusted after 4 minutes by adding 100 milliliters of water. Rougher concentrate and rougher tailings were filtered, dried, weighed, and analyzed for copper and molybdenum using an atomic absorption method. Iron determinations were made by a standard volumetric method.

The procedure of conducting a standard flotation test with each series or set of sewage effluent tests was adopted to allow a direct comparison of results of the various test sets.

Experimental Approach

Most of the copper processing operations use complex reagent schedules that have been devised through several years of laboratory evaluation and plant operating experience. In general, each reagent schedule is tailored to fit the ore on which it is used with optimum flotation response as the goal. If an

optimum, multi-component reagent schedule was used in this investigation, some of the effects of sewage effluent might have been masked by the compensating ability of the reagent schedule. Therefore, a very simple reagent schedule was chosen for the initial flotation tests, so that the full effects of sewage effluent would be apparent.

RESULTS AND DISCUSSION

Development of the Standard Flotation Test

The development of a standard laboratory flotation reagent schedule and establishment of a standard flotation response was necessary to provide a basis from which comparisons could be made and metallurgical differences could be determined between sewage effluent and standard demineralized water flotation systems. Adequate liberation of sulfide minerals from host rock was the first consideration. Laboratory grinding studies indicated that a 10 minute grinding time provided adequate liberation and produced a particle size distribution that generally paralled that which mining companies in the area achieve. Table 1 shows the particle size distribution obtained for a 10 minute grind.

Table 1

Screen Analysis of Ground Ore

Tyler Screen Fraction	Weight Percent Retained	Cumulative Weight Percent Retained
+ 35	1.8	1.8
- 35+ 48	4.7	6.5
- 48+ 65	11.9	18.4
- 65+100	11.3	29.7
-100+150	10.4	40.1
-150+200	13.1	53.2
-200	46.8	100.0

Potassium amyl xanthate and methyl iso-butyl carbanol were chosen as the collector and frother respectively, because of their wide use in industry. Figure 1 shows copper and molybdenum recovery as a function of collector dosage at a pH of 11.5 with 0.04 pound per ton of frother. A collector addition level of 0.04 pound per ton was adopted as the standard collector dosage to be held constant throughout the study.

Flotation recovery for copper and molybdenum is shown as a function of pH for standard water and sewage effluent systems in Figures 2 and 3. These figures indicate that a pH in the range of 11.0 to 12.0 is optimum for copper and molybdenum recovery in both standard water and sewage effluent systems. A pH of 11.5 was thus selected as the pH at which the standard test would be conducted. Figures 2 and 3 also show that sewage effluent effects molybdenum recovery far more than it does the recovery of copper.

Iron in the rougher concentrate is contributed by both chalcopyrite and pyrite. Pyrite is generally an undesirable constituent of the concentrate and therefore flotation conditions are adjusted to reject as much pyrite as possible. A decrease in the iron content of the concentrate is an indication of pyrite rejection. Figure 4 shows the effect of flotation pH on the amount of iron contained in rougher concentrate for the standard water and sewage effluent systems. Pyrite depression is substantial but not complete at a pH of 11.5. In practice, a more complete depression of pyrite is generally achieved in the cleaner flotation section.

Table 2 summarizes the standard test reagent schedule developed during the initial stage of the investigation for comparing sewage effluent with standard water.

Table 2

Reagent Schedule for Standard Water and Sewage Effluent Flotation Tests

Addition Point	Reagents, pounds per ton					
	Standard Water			Sewage Effluent		
	Lime	MIBC	Z-6	Lime	MIBC	Z-6
Grind	3.5	----	0.04	4.0	----	0.04
Condition	---	0.04	----	---	0.03	----

The lime requirement necessary to attain a pH of 11.5 was greater for sewage effluent than for standard water. In addition, less frother was required to achieve optimum frothing conditions in the sewage effluent system than in the standard water system.

Standard Water and Sewage Effluent Test Results

Table 3 shows a comparative metallurgical summary for eight standard water and eight sewage effluent flotation tests conducted on different dates over a period of several months. The table illustrates the small but measurable detrimental effect on copper recovery, and a substantially larger detrimental effect on molybdenum recovery when utilizing secondary treated sewage effluent as process water in the systems studied. The percent recovery values have been calculated at the 95 percent confidence level. The magnitude of the losses attributable to sewage effluent can be dramatically reduced by the addition of certain supplemental flotation chemicals to the system, especially in the case of molybdenum.

In addition to the quantitative metallurgical differences between sewage effluent and standard water systems evident from Table 3, a very significant difference in frothing characteristics exists between the two systems. Sewage effluent causes a voluminous, dull grey colored initial froth (without the

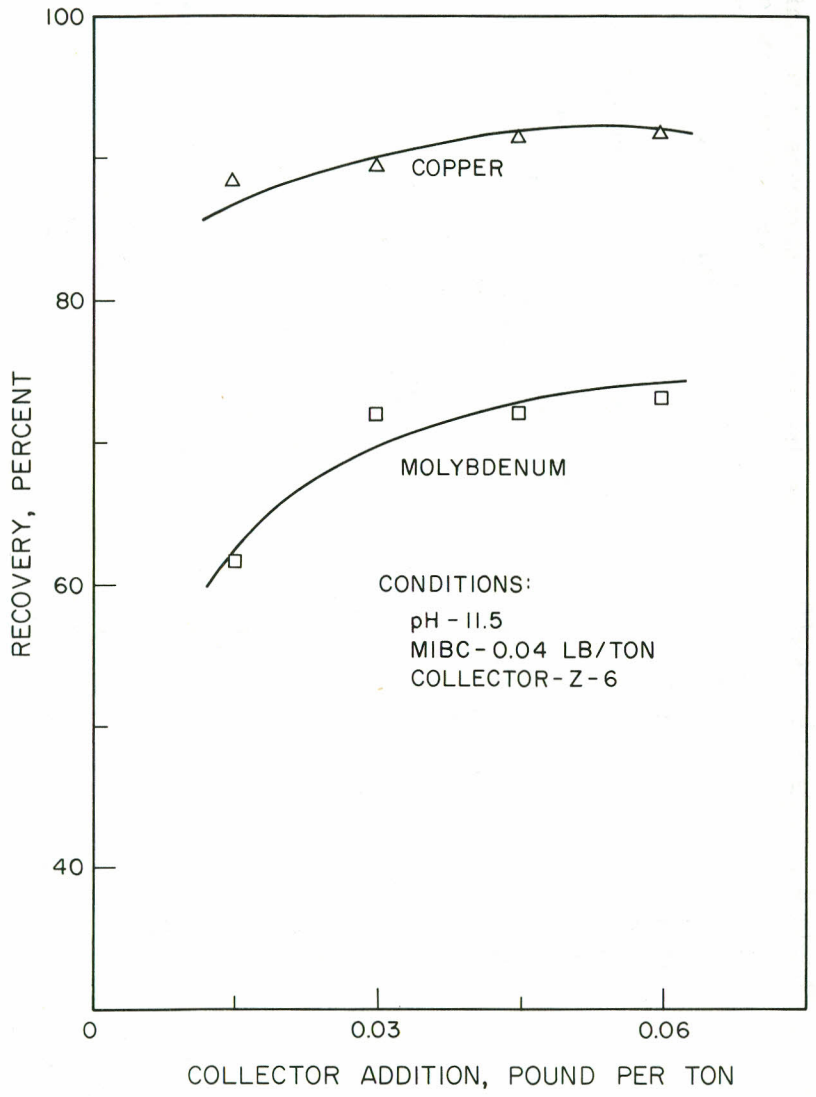

Figure 1. Copper and molybdenum recovery vs. collector addition in demineralized water.

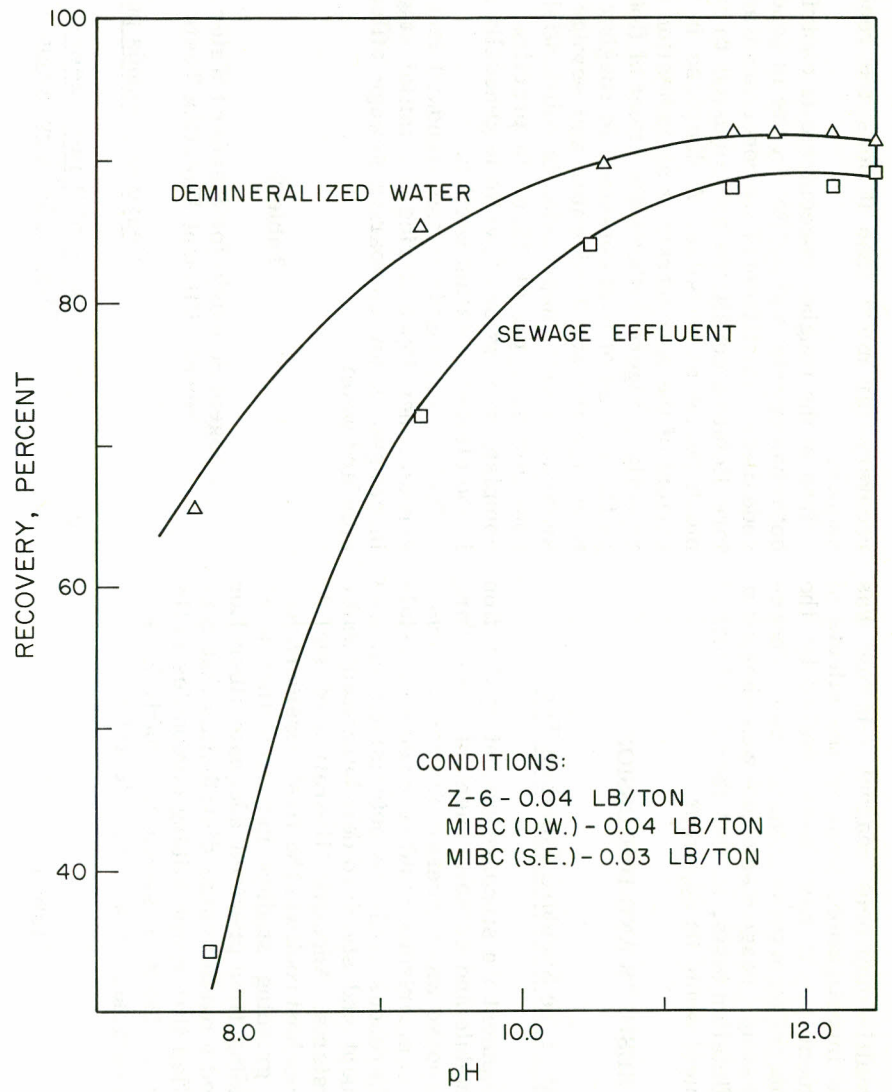

Figure 2. Copper recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.).

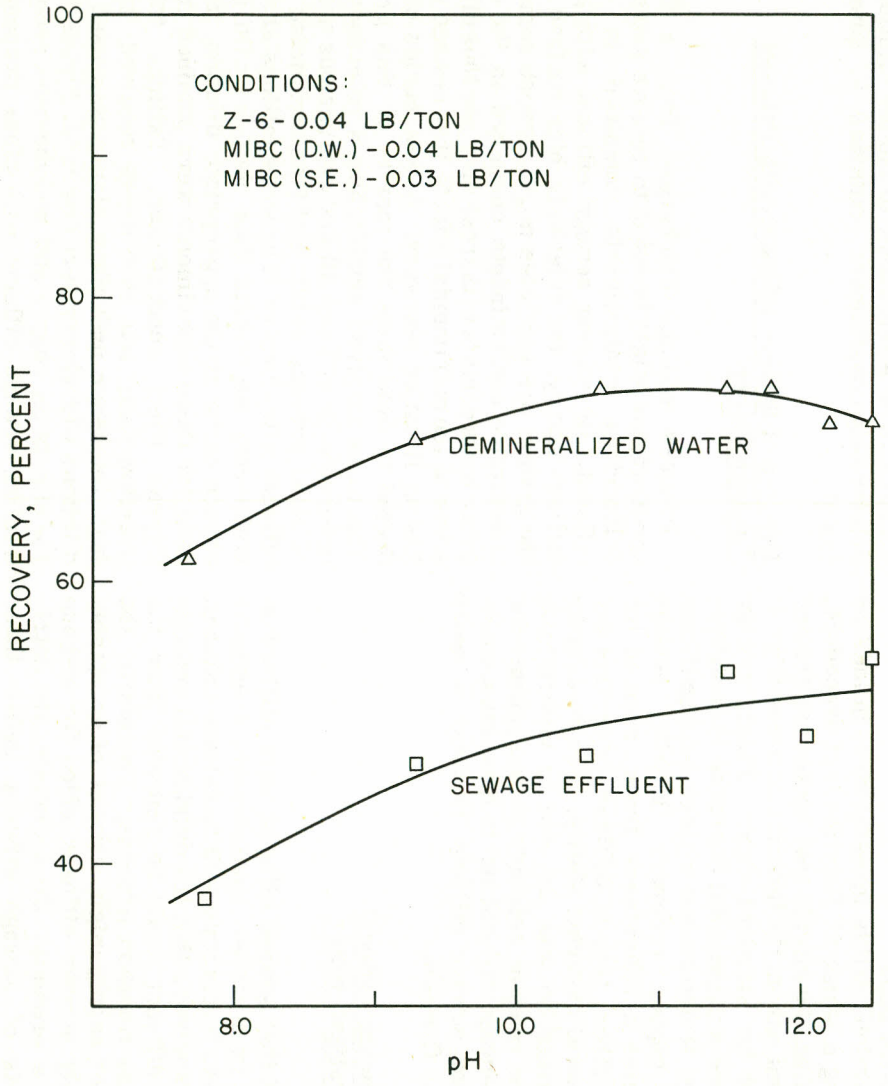

Figure 3. Molybdenum recovery vs. pH for demineralized water (D.W.) and sewage effluent (S.E.).

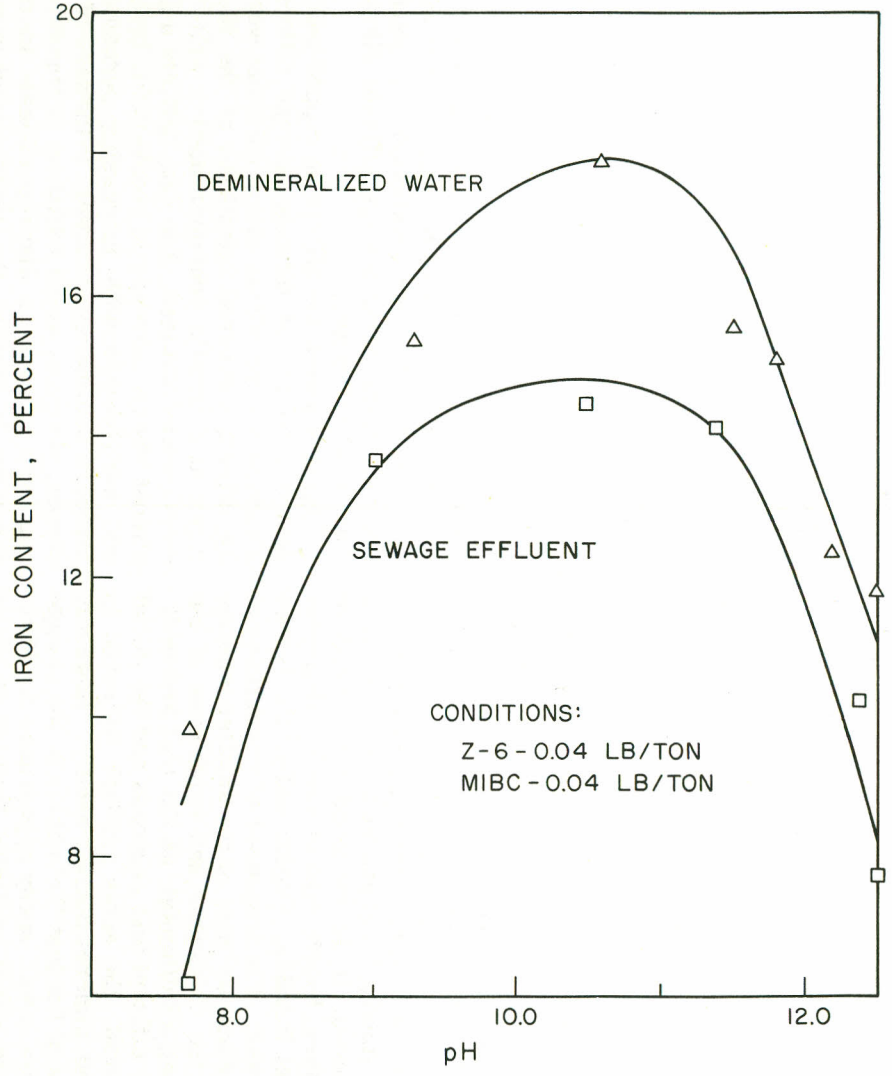

Figure 4. Percent iron in rougher concentrate vs. pH for demineralized water and sewage effluent.

Table 3

Comparative Metallurgical Summary for Standard Water and Sewage Effluent Flotation Systems

Water Type	Concentrate			Tail		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard	6.8	6.52	0.120	0.055	0.0035	89.7 ± 1.2	71.7 ± 1.0
Sewage	8.5	5.09	0.078	0.069	0.0058	87.3 ± 0.9	55.5 ± 1.7

addition of frother) that has little mineral carrying capability and is difficult to control. The initial froth in the standard test is smaller in volume, and is heavily laden with a coating of bright, brassy chalcopyrite. As the standard test proceeds and the initial froth is removed, it is replaced by a froth of relatively uniform bubble size of smaller diameter than the initial bubbles. Occasionally, the larger bubbles reappear. The frequency of occurrence of the larger bubbles, the size of the smaller uniform bubbles, and the thickness and brightness of the mineral coating all diminish as the test proceeds. As the sewage effluent test proceeds and the initial froth is removed, the same gradual decrease in bubble size and mineral coating occurs. However, toward the end of the test the bubbles in the sewage effluent test give a wet, sudsy appearance and seem to contain more slime particles than the standard froth at the same point.

The first sections of this investigation, in addition to establishing a standard flotation test procedure, served to define the effects that secondary treated sewage effluent has on the flotation process when it is substituted for standard water. First, sewage effluent causes a substantial decrease in molybdenum recovery. It also causes a small but significant decrease in copper recovery. Finally, sewage effluent creates a voluminous froth, even in the absence of frother, that is difficult to control and has little mineral carrying ability. The remainder of this investigation was devoted to determining changes in the reagent schedule to compensate for the effect of sewage effluent and to examining methods of treating sewage effluent to make it more acceptable for flotation.

Dilution of Sewage Effluent with Demineralized Water

In the event that sewage effluent were utilized on a large scale by a copper concentrator, eventually the entire water inventory would be sewage effluent. It is likely, however, that the detrimental constituents of the effluent would be removed from the system by the flotation process. Therefore, the recycled water supply might consist of acceptable water and only sewage effluent added for makeup would create a problem. Consequently, the detrimental effects of sewage effluent under these conditions might not be as severe as those encountered with complete replacement with sewage effluent as practiced in tests previously reported. This possibility was evaluated by performing flotation tests using sewage effluent diluted with demineralized water.

Figure 5 shows the effects on copper and molybdenum recovery of diluting sewage effluent with standard demineralized water. Dilutions were made by mixing measured quantities of the two water types in a plastic container until a well blended solution was obtained. The data indicate a gradual, almost linear, increase in recovery for both copper and molybdenum with increasing percentages of standard demineralized water. In the case of molybdenum, however, small additions of standard water appeared to cause a disproportionate increase in recovery. In general, the improvement in recovery appears to be attributable to simple dilution of the deleterious constituents contained in sewage effluent.

Dilution of Sewage Effluent with Process Tailings Slurry

Process tailings discharged from a flotation concentrator might be used to remove some of the deleterious contaminants contained in sewage effluent. By mixing sewage effluent with process tailings slurry, the relatively high surface area of the ground ore particles might adsorb some of the undesirable contaminants contained in the effluent prior to its contact with fresh ore, and thus eliminate some of the detrimental effects that sewage effluent has on flotation recovery. A test series was conducted to determine the merits of this proposal. The tests involved establishing a reference curve using sewage effluent diluted with various quantities of clear process water, and then combining sewage effluent with samples of process tailings slurry and comparing the results thus obtained with the reference curve at the appropriate dilution. Samples used for these experiments were obtained from the Cyprus Pima concentrator. Tailings thickener overflow water was used where required, and tailings thickener underflow slurry was used where dilutions with slurry were required. Figure 6 shows the effects on copper and molybdenum recovery of diluting sewage effluent with clear process water

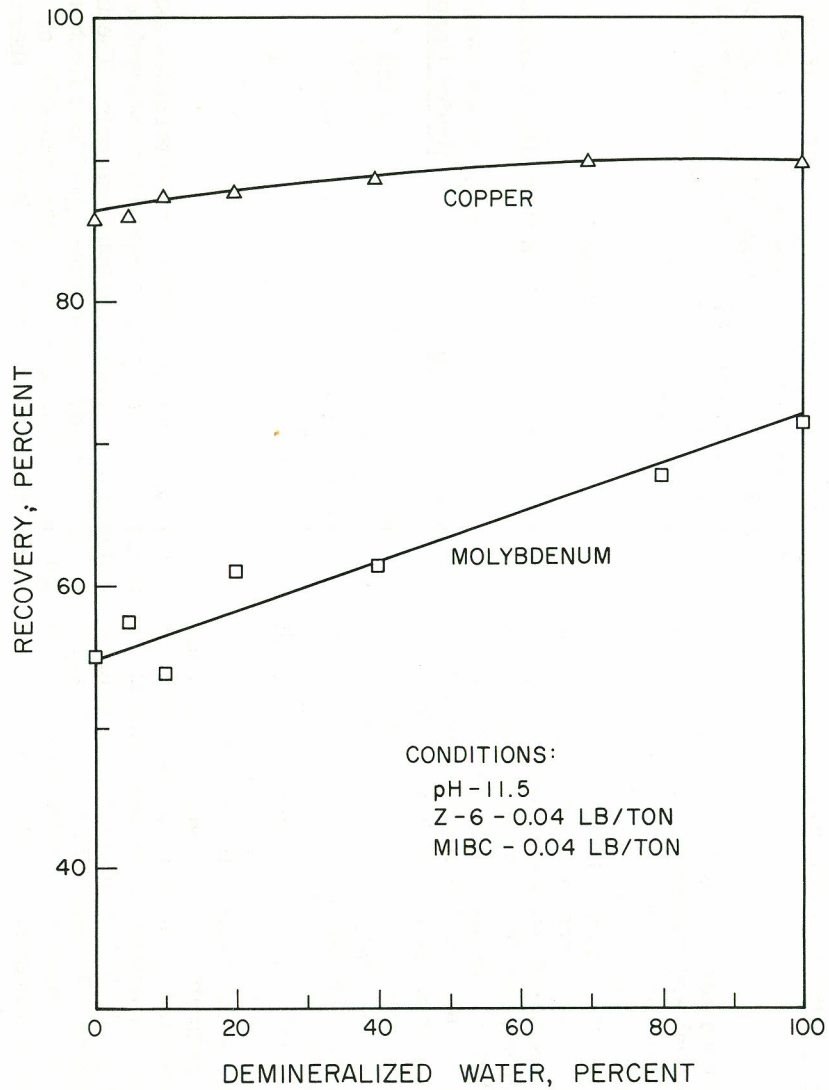

Figure 5. The effect of diluting sewage effluent with demineralized water.

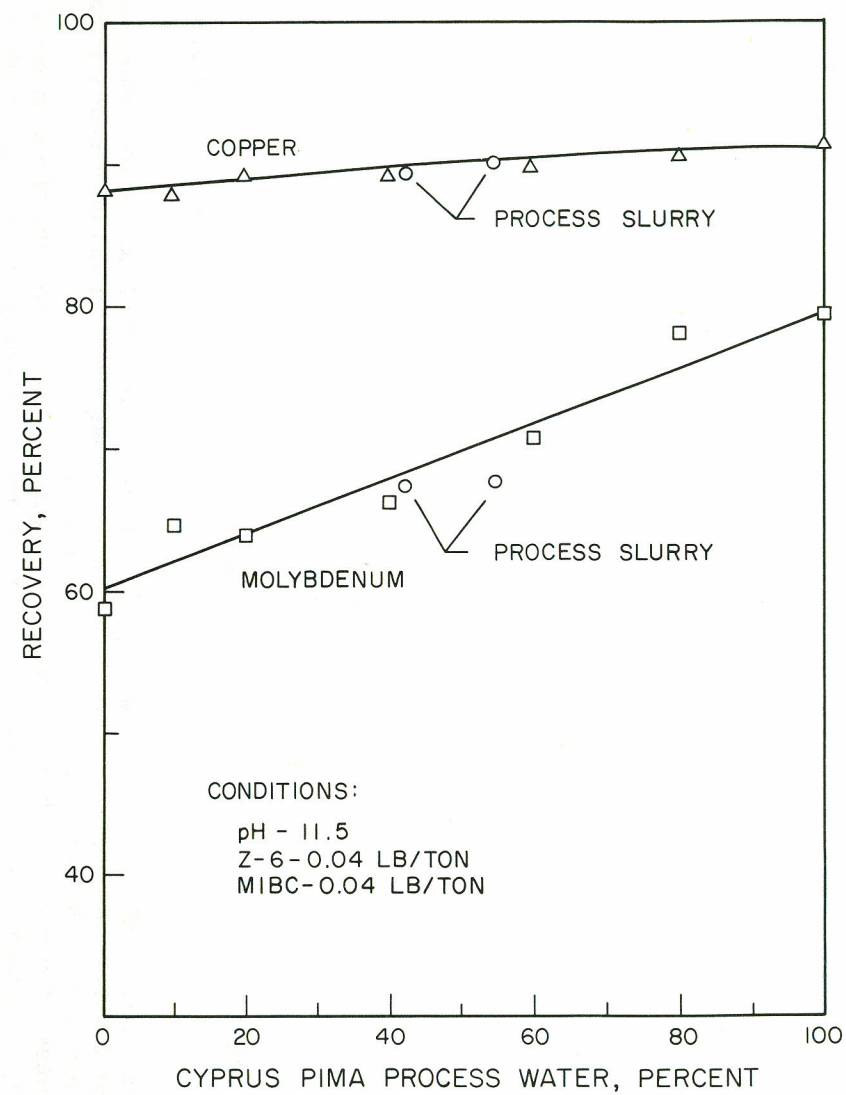

Figure 6. The effect of diluting sewage effluent with Cyprus Pima process water and process slurry.

Table 4

South Tahoe Public Utility District
Estimated Overall Plant Efficiency

Quality Parameter	Raw Waste Water Influent	Activated Sludge Effluent	Reclamation Plant: Separation Bed Effluent	Reclamation Plant: Chlorinated Carbon Column Effluent
BOD, mg/1	200-400	20-100	1	1
COD, mg/1	400-600	80-160	30-60	3-16
Suspended solids, mg/1	160-350	5- 20	0.5	0.5
Turbidity, units	50-150	20- 60	0.5	0.5
Phosphate, mg/1	15- 35	10- 30	0.4-2.0	0.2-1.0
Chlorine Demand, mg/1	Over 50	10- 50	5-10	1-3
Odor	Odor	Odor	Odor	Odorless

and process slurry. The addition of process tailings slurry to sewage effluent had no beneficial effect on flotation recovery, and the deleterious constituents contained in sewage effluent apparently do not adsorb on the surface of ground ore particles to any measurable extent. Furthermore, aging the slurry-sewage effluent solution for 2 days had no effect on water quality in terms of flotation response.

Activated Carbon Treatment of Sewage Effluent

A method sometimes employed to improve the quality of industrial and municipal waste waters is treatment with activated carbon. Granular activated carbon treatment of large quantities of waste water began in the early 1960s (Hager, 1974). The development of granular activated carbon with the capability of regeneration and reuse made adsorption an economic alternative for removal of dissolved organics and other contaminants from waste water. At Lake Tahoe, California, the South Tahoe Public Utility District uses activated carbon for tertiary treatment of more than 2.5 mgd of activated sludge effluent prior to discharge to the environment (McDonald, 1965). The water discharged from the plant has been characterized as being colorless, odorless, and crystal clear. The water reclamation plant's estimated overall plant efficiency is summarized in Table 4 (McDonald, 1965).

A laboratory activated carbon column was constructed and operated to determine the effect of activated carbon treatment of sewage effluent on flotation recovery. Table 5 summarizes the column operating conditions. Sewage effluent was pumped upward through the column at a controlled rate with a contact time of 2 minutes. No attempt was made to maximize the efficiency of the column and no chemical analysis of column influent or effluent was performed.

Figures 7 and 8 show the effect on copper and molybdenum recovery of treating sewage effluent with activated carbon. The results indicate a significant increase for both copper and molybdenum recovery when sewage effluent is treated with granular activated carbon. Further improvements in sewage effluent quality may be obtained with longer carbon contact times. Indeed, mining company personnel have indicated that they have generated water from sewage effluent using activated carbon treatment that is of a quality equal to their standard process water in terms of flotation response (Khan, 1975).

Table 5

Activated Carbon Column Operating Conditions

Carbon Description	6X16 mesh Pittsburgh Activated Carbon
Column Diameter, ft.	0.125
Area, sq. ft.	0.0123
Carbon Weight, lb.	0.77
Bed Depth, ft.	2.3
Flow Rate, gpm	0.074
Residence Time, min.	2.0

The detrimental frothing characteristics associated with sewage effluent appeared to be significantly reduced by activated carbon treatment. The initial froth generated on conditioning without frother was not as voluminous and unmanageable as with untreated sewage effluent. However, there did

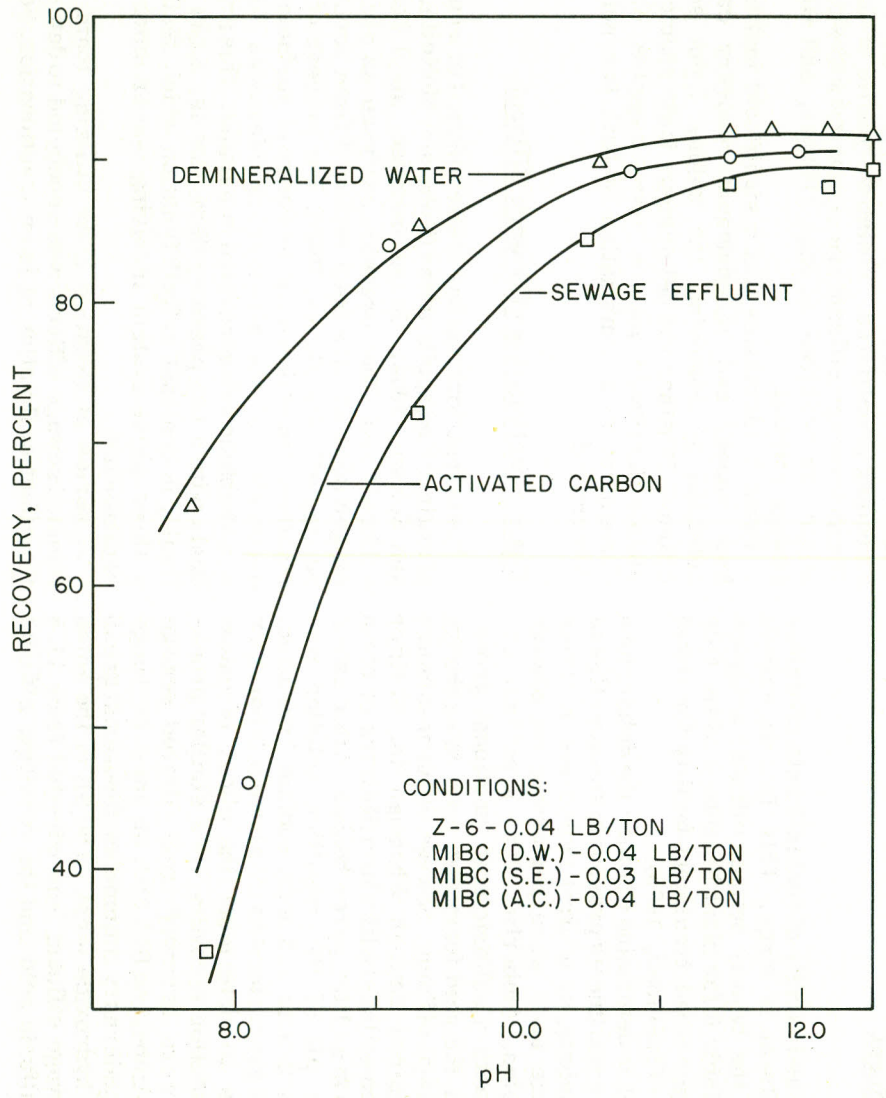

Figure 7. Copper recovery vs. pH for demineralized water (D.W.), sewage effluent (S.E.), and activated carbon (A.C.) treated sewage effluent.

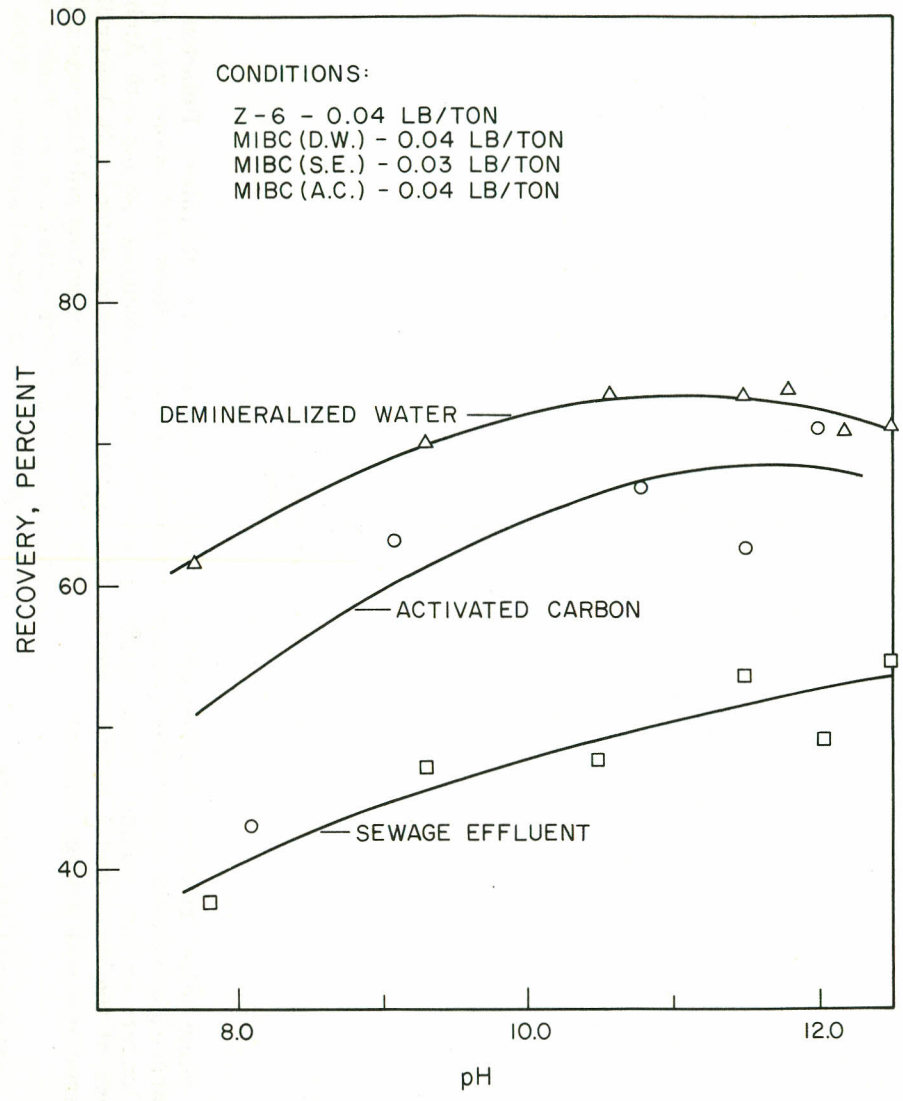

Figure 8. Molybdenum recovery vs. pH for demineralized water (D.W.), sewage effluent (S.E.), and activated carbon (A.C.) treated sewage effluent.

Table 6

Analysis of Plant Number 3 Effluent
for Fiscal Year 1974-75

Quality Parameter	Concentration, PPM	Quality Parameter	Concentration, PPM
Total Solids	656	NH_3-N	18.9
Suspended Solids	36	NO_2-N	0.2
Dissolved Solids	620	NO_3-N	0.5
Fixed Residue	469	Organic N	8.2
Volatile Residue	151	Calcium	66
Total Alkalinity		Magnesium	17
($CaCO_3$)	277	Hardness	325
pH	7.7	Chloride	92
BOD	28	Bicarbonate	338
COD	68	Phosphate, ortho	28
MBAS	0.9	Sulfate	146
Grease	9	Sodium and	
		Potassium	116

appear to be some minor residual frothing characteristics that are associated with untreated sewage effluent. A longer carbon contact time might eliminate most of the detrimental frothing characteristics associated with sewage effluent.

Ion Exchange Removal of Contaminants in Sewage Effluent

The number and variety of contaminants contained in sewage effluent is large. This fact is evident from viewing the typical sewage effluent analyses presented in Table 6 for plant Number 3 of the City of Tucson Roger Road treatment facility for fiscal year 1974-75 (Trueblood, 1975).

In an attempt to determine whether the deleterious constituent or constituents present in sewage effluent are cations, anions, or neutral molecules, a series of ion exchange tests were performed on sewage effluent samples. Amberlite 200, a cationic exchange resin with a sulfonic acid functional group, was loaded in the acid form and used to exchange cations in sewage effluent. Sewage effluent samples were first filtered through Whatman No. 50 filter paper, and then agitated with 250 milliliters of resin for 30 minutes in a 4 liter pyrex beaker. After cation exchange, the pH of the resulting solution was adjusted from 2.8 to 7.5 with sodium hydroxide. The water thus generated was then used in laboratory flotation tests to determine the effect of cation removal on flotation recovery. In a similar procedure, anions were removed from filtered sewage effluent using Amberlite IRA 900, an anion exchange resin with a quaternary ammonium functional group loaded in the hydroxide form. The pH of the anion exchanged sewage effluent was adjusted from 11.5 to 7.6 with sulfuric acid and the resulting effluent solution was used in laboratory flotation tests. Exchange of both cations and anions was accomplished by first exchanging cations with Amberlite 200, and then exchanging anions with Amberlite IRA 900. The pH of the resulting solution was adjusted from 10.7 to 6.7 with sulfuric acid. Table 7 shows a comparative metallurgical summary of the flotation results obtained with water generated by the foregoing procedures. Flotation results of ion exchanged sewage effluent are compared with standard water, as received sewage effluent, and filtered sewage effluent.

Table 7 illustrates that a significant increase in both copper and molybdenum recovery can be achieved by removing the anions from sewage effluent. Whether the deleterious ionic species is a simple inorganic ion, a more complex organic derivative, or a combination of both has not been determined.

Foam Fractionation of Sewage Effluent

Foam fractionation has been employed in a number of engineering applications (Kobe and McKetta, 1962 and Schoen, 1962). In one instance, alkyl benzene sulfonate and other organics analyzed as chemical oxygen demand have been removed from secondary sewage effluent (Rubin, 1963). The process of foam fractionation utilized the tendency of surfactants to accumulate at the air-aqueous interfaces formed when bubbles are generated in a liquid. This process deals with a two phase system; that is, a gas and a liquid, in contrast to froth flotation which deals with a three phase system involving one or more solid constituents.

A series of flotation tests utilizing foam fractionated sewage effluent was conducted to determine the effect on flotation of foam fractionation. Sewage

Table 7

Comparative Metallurgical Summary
for Ion Exchange Test Series

	Concentrate			Tails		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard Water	6.8	6.52	0.120	0.055	0.0035	89.7	71.7
Sewage Effluent	7.5	5.80	0.085	0.069	0.0053	87.2	56.5
Filtered Effluent	6.7	6.40	0.091	0.068	0.0051	87.2	56.3
Cationic Exchange	6.6	6.58	0.115	0.067	0.0044	87.5	64.9
Anionic Exchange	7.5	5.90	0.111	0.056	0.0035	89.5	71.9
Cationic-Anionic Exchange	6.6	6.95	0.117	0.059	0.0036	89.2	69.6

Table 8

Comparative Metallurgical Summary for
Foam Fractionation Test Series

Water	Concentrate			Tails		% Recovery	
	Wt. %	% Cu	% Mo	% Cu	% Mo	Cu	Mo
Standard Water	6.8	6.52	0.120	0.055	0.0035	89.7	71.7
Sewage Effluent	7.4	5.86	0.093	0.065	0.0060	87.8	55.4
Foam Fractionated Sewage Effluent	7.2	5.96	0.098	0.060	0.0060	88.4	55.8

effluent was foam fractionated for 10 minutes in a laboratory flotation cell without frother. Table 8 shows a comparison of flotation results obtained for standard water, sewage effluent and foam fractionated sewage effluent.

The results indicate that foam fractionation did not improve the quality of sewage effluent in terms of flotation metal recovery. There was, however, a noticeable improvement of frothing qualities. The voluminous, unmanageable froth associated with sewage effluent appeared to be significantly reduced. Foam fractionation could be employed as one approach to froth control when utilizing sewage effluent.

Substitution of an Alternate Collector for Potassium Amyl Xanthate

A collector frequently employed in copper and molybdenum flotation is the allyl ester of amyl xanthate (S-3302). This water insoluble, oily collector is sometimes used in combination with a xanthate, fuel oil, and a frother, to give optimum copper and molybdenum rougher flotation results. Because this type of collector is also in wide use in industry, a series of flotation tests were conducted using the same procedure previously described with the exception that 0.04 pound per ton of S-3302 was added to the grinding mill in place of 0.04 pound per ton of Z-6. Figures 9 and 10 show the effect on copper and molybdenum recovery, respectively, of substituting S-3302 for Z-6 in demineralized water and sewage effluent flotation systems. Figure 9 indicates that copper recovery with S-3302 is less sensitive to pH change than is Z-6 in both standard demineralized water and sewage effluent. Above a pH of about 9 to 9.5, copper recovery is adversely affected by the substitution of S-3302 for Z-6 in both standard water and sewage effluent systems. Figure 10, on the other hand, shows that molybdenum recovery is increased dramatically over the entire pH range studied for both demineralized water and sewage effluent systems. In fact, the recovery versus pH curve for S-3302 in the sewage effluent system lies almost directly on the recovery versus pH curve for Z-6 in standard demineralized water. Figure 11 shows a comparison of the percent of iron contained in the rougher concentrate for Z-6 and S-3302 in demineralized water. Since S-3302 is already widely used by industry, the results of this test series are of fundamental interest.

Fuel Oil in Combination with Potassium Amyl Xanthate

A study of this nature could not be complete without determining the effect of fuel oil addition on molybdenum recovery in both the sewage effluent and demineralized water flotation systems. Fuel oil is almost universally used in commercial molybdenum flotation as a molybdenum promoter. Table 9 summarizes the results of a test series (using Z-6 as the collector) to determine the effect of fuel oil addition on copper and molybdenum recovery.

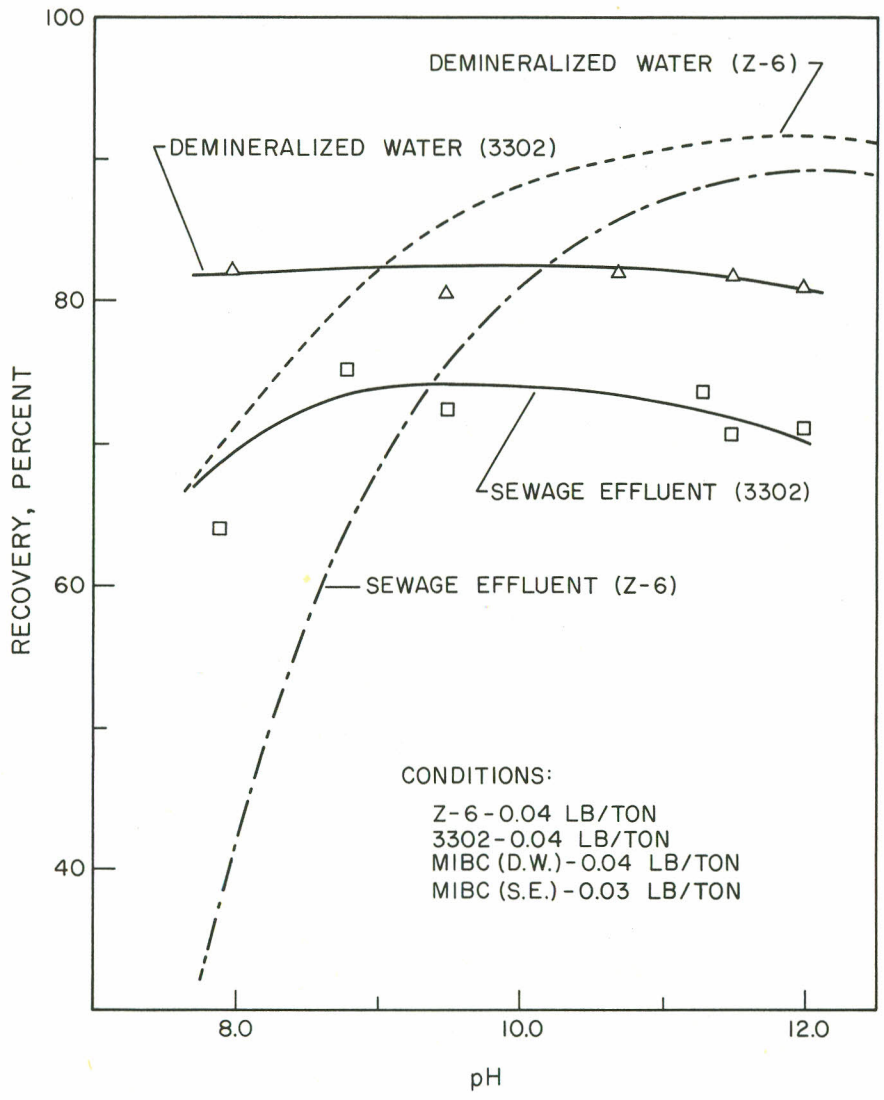

Figure 9. Comparison of copper recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.) using Z-6 and 3302 as collectors.

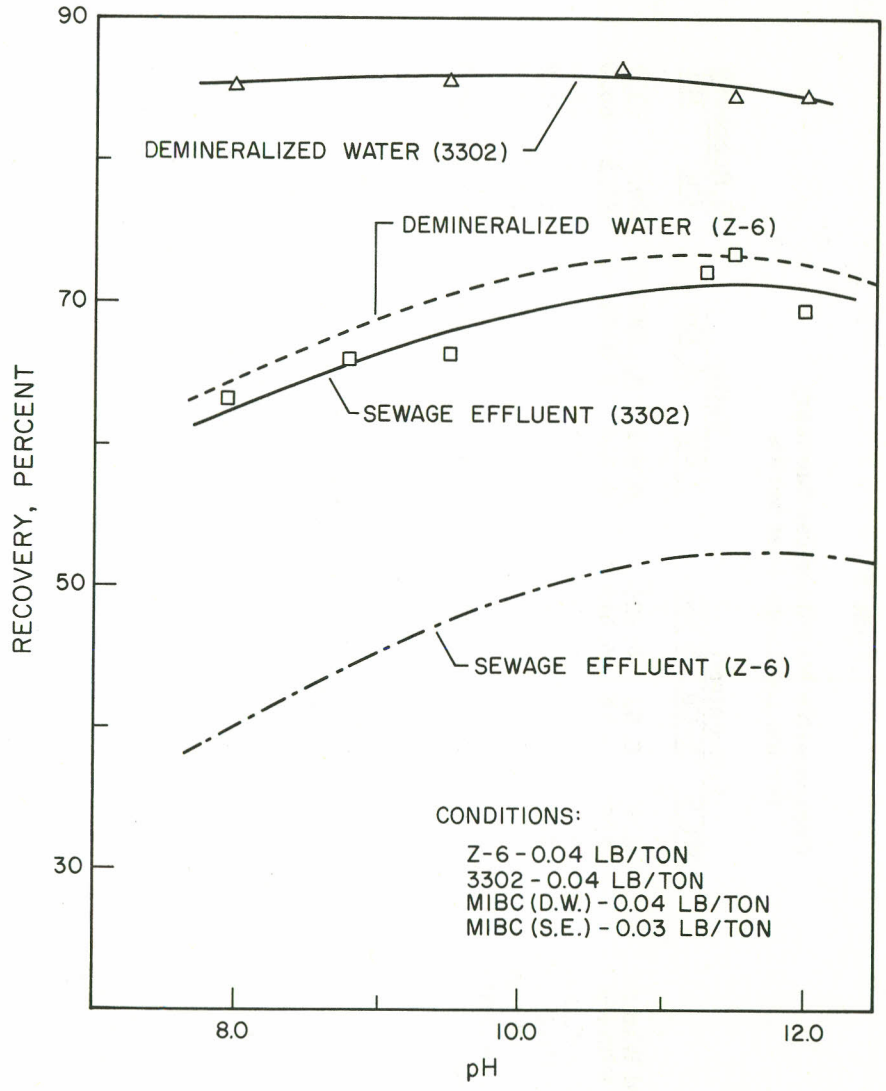

Figure 10. Comparison of molybdenum recovery vs. pH for demineralized water (D. W.) and sewage effluent (S. E.) using Z-6 and 3302 as collectors.

Table 9

Effect of Fuel Oil Addition on Copper and Molybdenum Recovery in Demineralized Water and Sewage Effluent Flotation Systems

Fuel Oil, Lb/Ton	Water Type: Demineralized, % Recovery, Cu	Demineralized, % Recovery, Mo	Sewage Effluent, % Recovery, Cu	Sewage Effluent, % Recovery, Mo
0	89.2	68.7	89.1	52.8
0.025	89.7	70.8	90.3	59.5
0.05	90.0	75.7	88.8	63.1
0.10	90.0	78.4	89.0	68.3
0.20	91.2	81.0	90.2	73.9
0.40	--	--	89.9	69.3

This table clearly indicates the beneficial effect of fuel oil addition on molybdenum flotation in both standard water and sewage effluent systems. The magnitude of molybdenum losses attributed to sewage effluent are substantially reduced by the addition of fuel oil to the system. However, the molybdenum losses attributable to sewage effluent are still significant. There appears to be no appreciable effect on copper recovery by the addition of fuel oil to the systems studied.

A Multicomponent Reagent Schedule

Most concentrators in the vicinity of Tucson employ a flotation reagent combination consisting of a primary collector, a supplemental collector, fuel oil, and a frother for the recovery of copper and molybdenum sulfides. A single "optimum" reagent combination that works equally well for all copper-molybdenum ores does not exist, and consequently, reagent schedules differ from concentrator to concentrator. The metallurgical staff for a particular operation may have invested years developing and refining a reagent combination that satisfies their operating requirements most of the time. With the foregoing in mind, an attempt was made to establish the effect of sewage effluent on copper and molybdenum recovery using a multicomponent reagent system. The emphasis in this test series was placed on reducing the large detrimental effect that sewage effluent has on molybdenum recovery.

Table 10

Multicomponent Reagent Schedule

Reagent	Quantity, Lb / Ton
Z-6	0.013
S-3302	0.027
Fuel Oil	0.025
MIBC	0.03

Previous testwork in which S-3302 was substituted for Z-6 established that a very significant increase in molybdenum recovery could be obtained by using S-3302. Since this reagent is widely used by the copper industry, it was chosen as the supplemental collector.

In the development of the multicomponent reagent schedule, the effect of S-3302 addition level on flotation response was determined. Figure 12 shows the results obtained from a test series devoted to this end. The most significant features of this figure are the large increases in molybdenum recovery accompanied by corresponding decreases in copper recovery.

To determine the interaction of Z-6 and S-3302 when both are used simultaneously as collectors, a series of tests using various combinations of these flotation reagents was conducted. The results of this series are shown in Figure 13. All tests were carried out in standard water at a pH of 11.5, with 0.04 pound per ton total collector addition, using MIBC as the frothing agent at a level of 0.04 pound per ton. Since the objective of this section of the study was to increase molybdenum recovery, a ratio of S-3302 to Z-6 of 2:1 was chosen as an acceptable collector combination. This choice was obviously a compromise between the desired higher molybdenum recovery and reduced, but reasonable, copper recovery.

The reagent schedule listed in Table 10 was selected on the basis of the cumulative experience gained in this investigation with the emphasis on minimizing molybdenum losses.

Table 11

The Effect of Sewage Effluent on Copper and Molybdenum Recovery in a Simple Reagent System and a Complex Multicomponent Reagent System

Water Type	% Recovery, Simple System, Cu	Simple System, Mo	Cu	Mo
Standard	89.7 ± 1.2	71.7 ± 1.0	83.1 ± 0.6	77.3 ± 1.2
Sewage	87.3 ± 0.9	55.5 ± 1.7	80.1 ± 1.0	71.9 ± 1.3

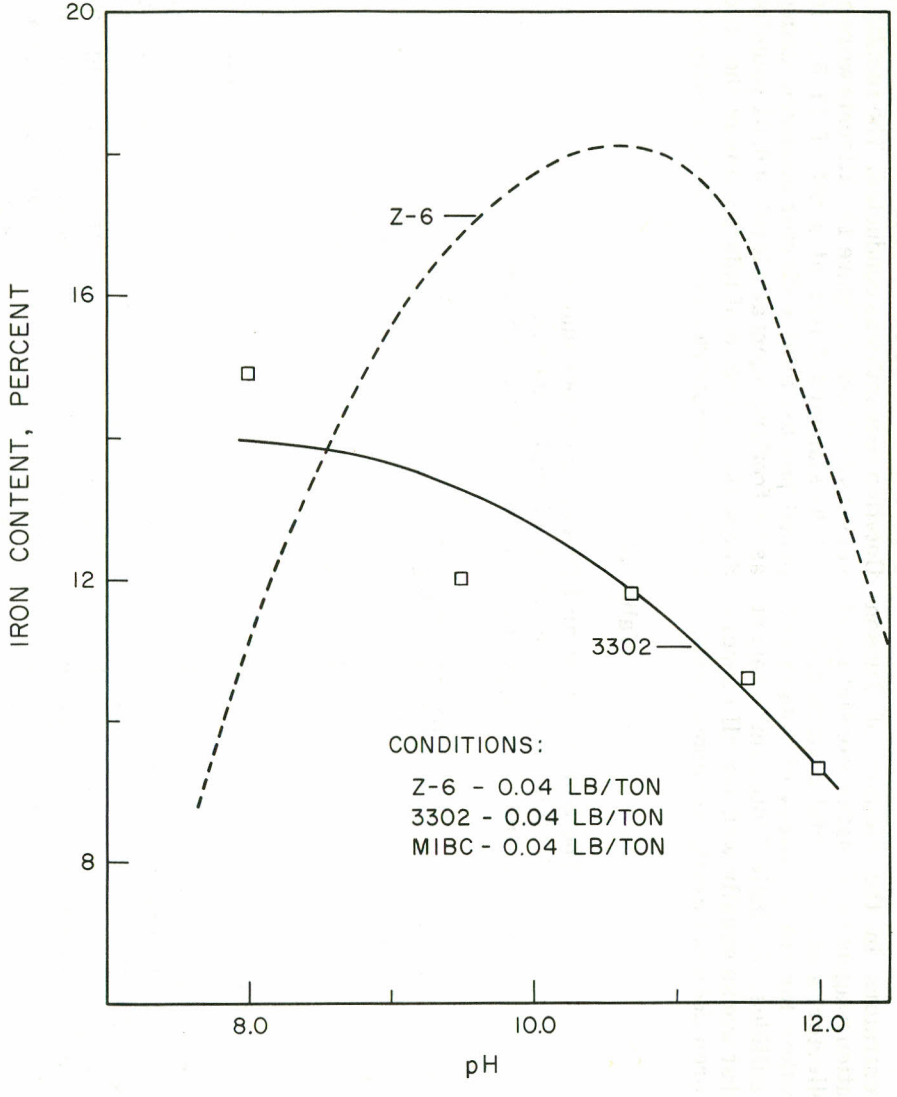

Figure 11. Comparison of percent iron in rougher concentrate vs. pH for demineralized water using Z-6 and 3302 as collectors.

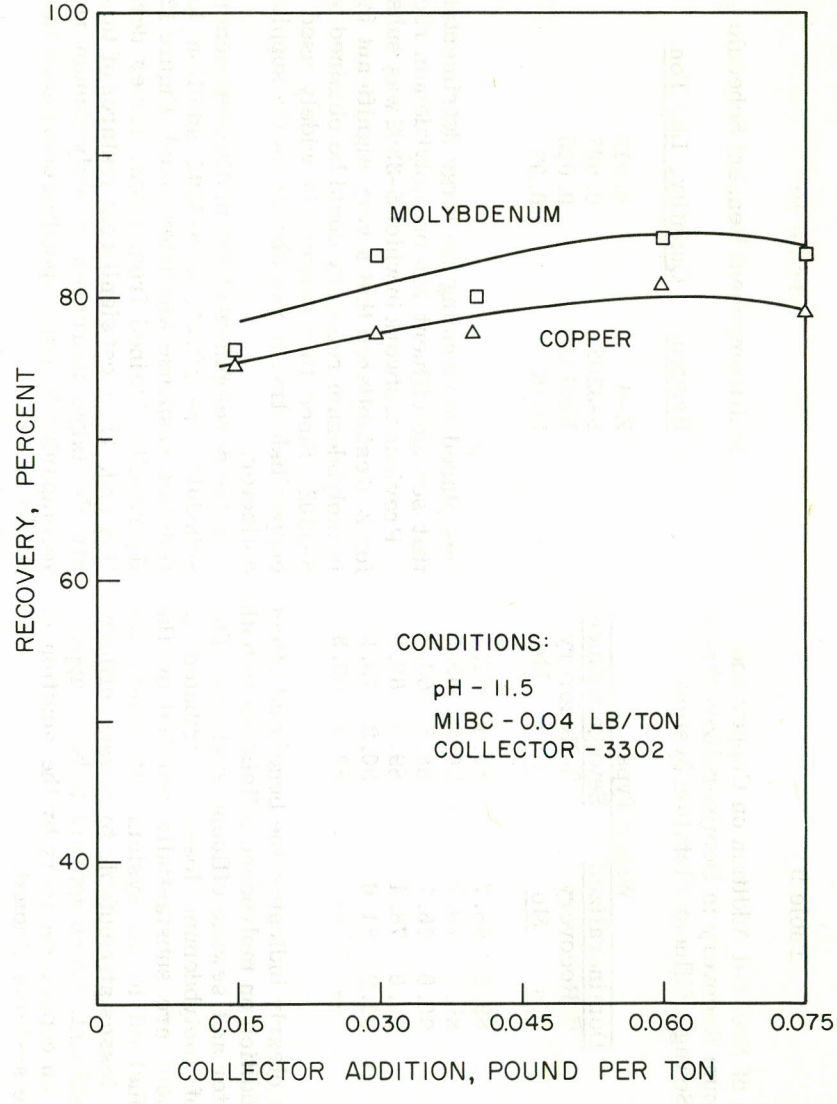

Figure 12. Copper and Molybdenum recovery vs. collector addition in demineralized water.

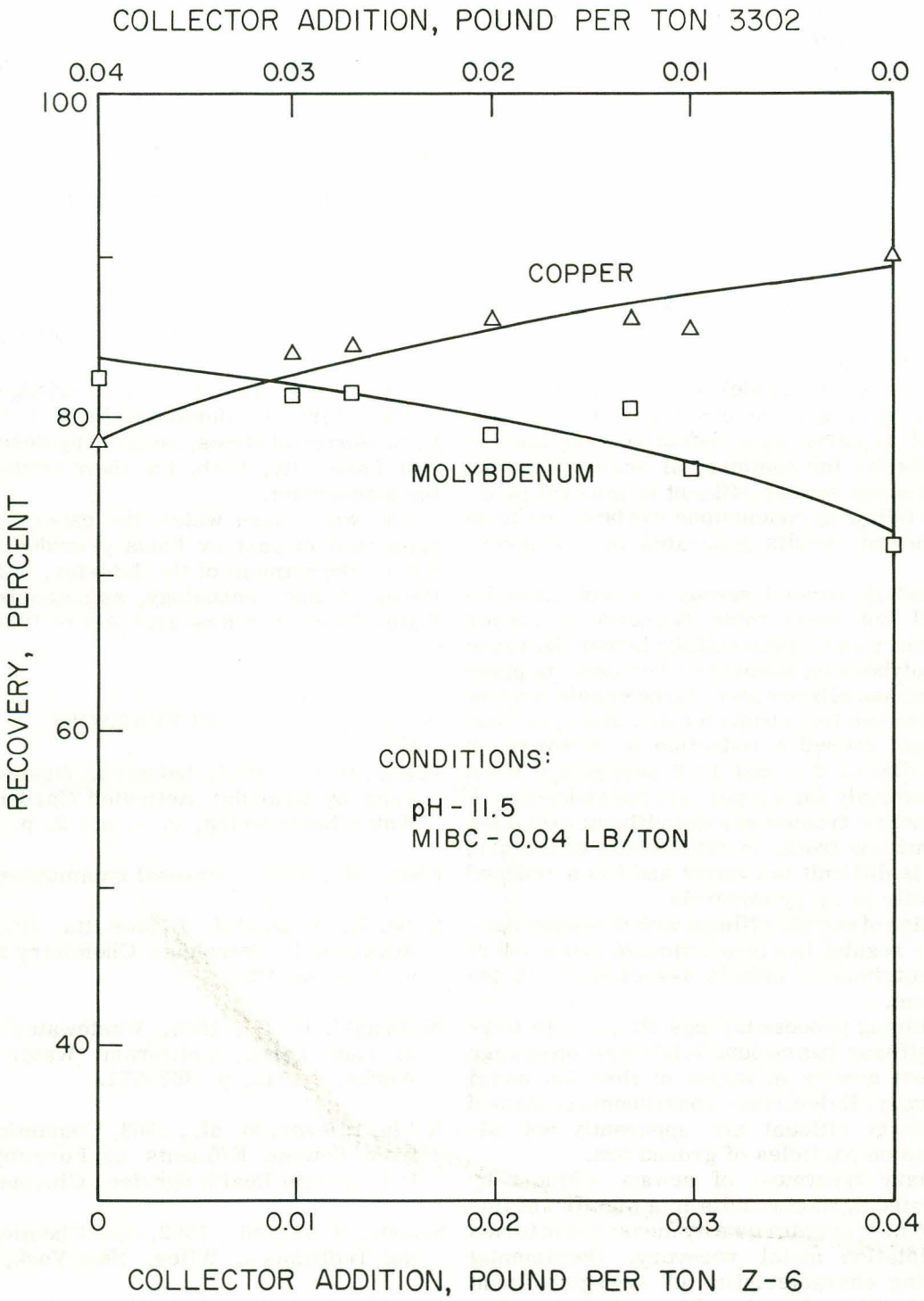

Figure 13. Copper and molybdenum recovery as a function of combined Z-6 and S-3302 at a total collector addition of 0.04 lb/Ton.

Table 11 shows a comparison of recoveries at the 95 percent confidence level obtained in standard water and sewage effluent systems for the simple Z-6 reagent schedule and the multicomponent reagent schedule described above. All tests were conducted at a pH of 11.5. Although the multicomponent reagent schedule is effective in improving molybdenum recovery, the loss of molybdenum in the sewage effluent system remains significant and the reduction in copper recovery is unacceptable.

CONCLUSIONS

The conclusions drawn from this study are intended to serve as a guideline and reference from which future investigations can proceed. They are not intended to serve as a definitive prediction of operating results for commercial scale utilization of City of Tucson sewage effluent in mineral processing. The following conclusions can be drawn from the experimental results generated in this investigation.

1. Secondary treated sewage effluent caused a small but measurable decrease in copper recovery and a substantially larger decrease in molybdenum recovery when used in place of demineralized water. In the simple reagent system used as a basis for this study, sewage effluent caused a reduction in recovery on the order of 2.4 and 16.2 percentage units respectively for copper and molybdenum.
2. Secondary treated sewage effluent creates a voluminous froth, in the absence of frother, that is difficult to control and has a reduced capacity to carry minerals.
3. Dilution of sewage effluent with demineralized water results in a proportionate reduction of the detrimental effects associated with the effluent.
4. Combining process tailings slurry with sewage effluent has no beneficial effect on sewage effluent quality in terms of flotation metal recovery. Deleterious constituents contained in sewage effluent are apparently not adsorbed on particles of ground ore.
5. Tertiary treatment of sewage effluent by activated carbon results in a significant improvement in water quality measured in terms of flotation metal recovery. Detrimental foaming characteristics of sewage effluent are significantly reduced by activated carbon treatment.
6. Ion exchange removal of anions contained in sewage effluent results in a significant improvement in water quality in terms of both copper and molybdenum recovery. In addition, the foaming attributed to sewage effluent is significantly reduced. This result indicates that the species detrimental to metal recovery are anions.
7. Foam fractionation does not improve the quality of sewage effluent in terms of flotation metal recovery. There is, however, an improvement in the deleterious frothing characteristics associated with the effluent.
8. Use of a multicomponent reagent schedule results in a significant improvement in molybdenum recovery using both demineralized water and sewage effluent. However, this reagent system causes an unacceptable loss in copper recovery.

ACKNOWLEDGMENTS

The authors gratefully acknowledge George M. Potter, Jerry L. Huiatt and Rees D. Groves of the U. S. Bureau of Mines, Metallurgy Research Center, Salt Lake City, Utah, for their critical reading of the manuscript.

The work upon which the paper is based was supported in part by funds provided by the United States Department of the Interior, Office of Water Research and Technology, as authorized under the Water Resources Research Act of 1964.

REFERENCES

Hager, D. G., 1974, Industrial Wastewater Treatment by Granular Activated Carbon: Industrial Water Engineering, v. 8, no. 2, p. 14-28.

Khan, M., 1975, Personal communication.

Kobe, K. A., and J. J. McKetta, Jr., ed., 1962, Advances in Petroleum Chemistry and Refining, v. 7, p. 66-135.

McDonald, K. R., 1965, Wastewater Reclamation at Lake Tahoe, California: Water and Sewage Works, v. 112, p. 367-371.

Rubin, Eliezer, et. al., 1963, Contaminant Removal from Sewage Effluents by Foaming: AWTR-5, U.S. Public Health Service, Cincinnati, Ohio.

Schoen, H. M., ed., 1962, New Chemical Engineering Techniques, Wiley, New York, p. 319-385.

Trueblood, E. J., 1975, Personal communication.

THE ARIZONA BUREAU OF MINES

W. H. Dresher, Director
W. W. Fisher, Assistant Metallurgist
J. D. Forrester, Director Emeritus
S. B. Keith, Geologist
R. T. Moore, Principal Geologist
R. T. O'Haire, Associate Mineralogist
H. W. Peirce, Geologist
D. D. Rabb, Mining Engineer
G. H. Roseveare, Metallurgist Emeritus
Samuel Rudy, Assistant Metallurgist
J. S. Vuich, Assistant Geologist

The Arizona Bureau of Mines was created in 1915 and placed under the authority of the Arizona Board of Regents by an act of the State legislature. Under the functions mandated by the enabling legislation, the Bureau regularly provides wide ranging-service in the fields of geology, metallurgy, and mining in response to both public inquiries and requirements of the management agencies of State government. In order to carry out these diverse functions, two basic operational subdivisions have been established in the Bureau.

GEOLOGICAL SURVEY BRANCH

This branch is charged with the responsibility of acquiring, disseminating, and applying basic geologic and mineralogic history and to assist in determining the short and long range influence these have on human activity and the relative merits of alternative land use plans, and (b) assist in developing an understanding of the important controls influencing the location of both metallic and nonmetallic mineral resources and mineral fuels in Arizona.

MINERAL TECHNOLOGY BRANCH

This branch conducts research and investigations into, and provides information about, the development of Arizona's mineral resources, including the extraction, refinement, and utilization of metallic and nonmetallic mineral deposits. These activities are directed toward the efficient recovery of Arizona's mineral resources as well as insuring that the recovery methods will be compatible with the environmental aspects of the state.

1-6/76SH15/445