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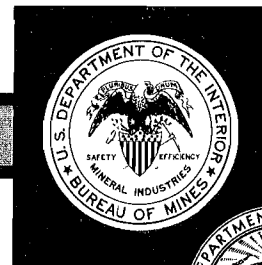
**U.S. BUREAU OF MINES
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Effect of Nonionic Surfactants on Chalcopyrite Leaching Under Dump Chemical Conditions

By S. P. Sandoval, D. L. Pool and L. E. Schultze

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**UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C degree Celsius

g/L gram per liter

L liter

mg/L milligram per liter

mL milliliter

ppm part per million

pct percent

EFFECT OF NONIONIC SURFACTANTS ON CHALCOPYRITE LEACHING UNDER DUMP CHEMICAL CONDITIONS

By S. P. Sandoval,¹ D. L. Pool,² and L. E. Schultze³

ABSTRACT

Several researchers have shown that the surface of chalcopyrite becomes hydrophobic under oxidizing conditions. Because dissolution of copper from chalcopyrite in dump leaching occurs under oxidizing conditions, the U.S. Bureau of Mines studied the effect of surfactants on chalcopyrite leaching under dump chemical conditions. Surfactants were selected for study because they can lower interfacial tension. The tests were conducted in shaking water baths using 250-mL Erlenmeyer flasks in statistical experimental design formats. The addition of nonionic surfactants increased copper extraction in the ferric sulfate leaching of chalcopyrite when sufficient Fe^{3+} was present. A positive interaction between Fe^{3+} concentration and surfactant concentration was demonstrated. Copper concentration in the leaching solutions was increased by as much as 100 pct at 25° and 50° C by adding nonionic surfactants. Ionic surfactants decreased leaching. The structure of the nonionic surfactants and their hydrophilic-lipophile balance (HLB) influenced surfactant performance. The branched hydrophile of an ethoxypolyol was beneficial to surfactant performance. The ethoxypolyol was the superior surfactant at 25° C, but became unstable at 50° C. Four surfactants, an ethoxyalcohol and three block copolymers, performed best at 50° C.

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INTRODUCTION

Use of ferric sulfate to leach copper sulfide minerals has been known since prior to the turn of the century and has been employed, in various forms, since at least 1890 (1).⁴ While the leaching system has been extensively studied and a great deal of information has been obtained, inherent defects, such as slow and incomplete copper leaching, have never been satisfactorily resolved. The major commercial usage of ferric sulfate leaching has been to recover additional copper from those portions of sulfide ore bodies too low in copper grade to be suitable for concentration by flotation. The low-grade ore is normally placed in large piles of uncrushed run-of-mine material called dumps. The ore is sprayed with dilute sulfuric acid, which percolates through the dump and is collected as it exits. The exiting solutions contain both copper and iron, the copper being recovered by cementation or solvent extraction and the acidic iron sulfate being recycled to the top of the dump. While dump leaching is a low-cost method for increasing copper recovery, it is not an efficient leaching technique. It is not unusual for 25 pct of the contained copper to be recovered from a dump during the first 6 months of operation, but several years are required to recover an additional 25 pct. According to Hiskey and Bhappu (2), 30 to 50 pct of the copper in chalcocitic ores will be recovered in 4 to 5 years but only 6 to 15 pct of the copper in chalcopyritic ores will be recovered over the same time frame. A number of explanations for the leaching behavior in copper dumps have been proposed, and numerous studies to test the explanations have been done. Published results of the studies have often appeared to be contradictory, and attempts to apply published conclusions to dump leaching operations have failed to yield significant improvements in copper recovery.

Because ferric sulfate leaching of copper sulfide is an oxidation-reduction reaction, consideration has been given to the availability of oxygen in copper dumps. Madsen and Groves (3) reported that injection of oxygen to a chalcocitic column leaching test after 47.1 pct of the copper had been leached caused the leaching rate to increase from near zero to rates similar to those recorded at the beginning of the test. An additional 40.7 pct of the copper was then leached. The authors concluded that the improvement was due to stimulation of the growth of both iron-oxidizing and sulfur-oxidizing bacteria. Hiskey and Bhappu (2) reported that aeration was tried in two field tests and that some improvement in copper recovery was noted in one of the tests. Because the results of the field tests have never been published and current practice does not employ aeration of copper dumps, one can only assume that the improvements were not significant or that additional problems were encountered that negated the positive aspect of improved copper recovery.

Another possible explanation for the leaching behavior would be copper accessibility, as proposed by many

authors including Cathles and Apps (4). They suggest that the decrease in copper leaching over time is due to leaching of the more available copper during the first 7 months and that leaching solutions must diffuse through barren zones to contact additional copper sulfides. The explanation is very reasonable when one considers that the material in a dump can range up to several feet in diameter. One question, however, whether accessibility is rate controlling when other authors have reported similar decreases in copper leaching rate in studies dealing with ground ore or pure mineral specimens (1, 5-6). These studies suggest that the change in leaching rate is due to a change in reaction mechanism.

Some authors have suggested that the decrease in copper leaching over time is caused by the formation of elemental sulfur coatings that result as a reaction product (7-9). The sulfur is thought to act as a diffusional barrier limiting ingress and egress of leaching solutions. Other authors are opposed to this hypothesis, concluding that, while a surface film does form in the course of leaching, the film is a copper sulfide, formed as a reaction intermediate and more stable than chalcopyrite (10-11). Additionally, Linge (12) states that the rate of diffusion through the sulfur layer is four times higher than the rate of chalcopyrite dissolution, indicating that the sulfur coatings are not rate limiting.

Recently, several researchers have shown that the surface of chalcopyrite becomes more hydrophobic under certain chemical conditions (13-15). Heyes and Trahar found that the surface of chalcopyrite is rendered more hydrophobic in an oxidizing environment. Gardner and Woods concluded that the presence of sulfur, which forms on the chalcopyrite surface as a result of anodic oxidation, produces the observed hydrophobicity. Since in dump leaching the chalcopyrite is oxidized in order to release the copper, it was reasoned that the resulting hydrophobicity might contribute to the poor leaching rates observed in dump leaching. The present study was undertaken to investigate the application of surfactants as leaching aids in the dump leaching of chalcopyrite with ferric sulfate. This work supports the goal of the U.S. Bureau of Mines to make better use of domestic mineral resources by increasing the efficiency and economy of extraction techniques.

Surfactants were selected for study because they can lower interfacial tension. A surfactant is defined by Leja (16) as an amphipatic molecule, or a molecule of dual character. The surfactant molecule possesses a dual character in that it is made up of a polar and a nonpolar group. The polar group is hydrophilic in character and may or may not be ionized. The nonpolar group is hydrophobic in character and is typically made up of a hydrocarbon chain. If the hydrophile of the surfactant is ionized, the surfactant is called an anionic or a cationic surfactant, depending on the sign of the charge. If the hydrophile is not ionized, the surfactant is called a non-ionic surfactant. In anionic and cationic surfactants, the hydrophile is typically a single charged group, such as a

⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

sulfide, sulfonate, or sulfate group for anionic surfactants or an amine group for cationic surfactants. In nonionic surfactants, the hydrophile is typically made up of chains of polyethylene oxide.

Previous research by Duncan, Trussell, and Walden (17-18) tested the effect of the addition of surfactants on the *Thiobacillus ferrooxidans* leaching of chalcopyrite. The premise for testing the surfactants was that they might aid the bacteria in contacting the mineral. The tests were conducted by exposing specimen-grade chalcopyrite to *Thiobacillus ferrooxidans* in a modified 9K nutrient medium in which the iron solution was replaced with

distilled water. The researchers found that the addition of nonionic surfactants, particularly Tween 20, aided the bacterial leaching process. When chalcopyritic ores were leached under the same conditions, only two of the eight ores tested responded to the addition of Tween 20. Mineralogical analyses of the ores tested were not given, making a comparison difficult. The work of Duncan, Trussell, and Walden proved that the nonionic surfactants were not lethal to *Thiobacillus ferrooxidans*, which is important in considering the application of nonionic surfactants to dump leaching because these bacteria are a major factor in the dump leaching process.

MATERIALS AND PROCEDURES

Mineral leaching studies were conducted in statistical experimental design formats (19). The two designs utilized were "factorial" and "completely randomized" designs. The completely randomized designs were used to compare the performance of different surfactants. The factorial designs were used to determine the effects of variables such as pH, Fe^{3+} concentration, and surfactant concentration on leaching. The results of the completely randomized design comparisons were subjected to statistical tests of significance in order to decide whether a true difference existed between the performance of the surfactants included in the comparison, or whether the observed differences could be attributed to experimental error. The two tests of significance employed were the analysis-of-variance F-test and the least significant difference (LSD) test, both at the 0.05 level of significance (20-21). The F-test compared the variation due to the influence of the surfactants with the variation due to experimental error. If the surfactant variation was sufficiently larger than the error variation, then the F-test was significant, indicating that a true difference existed between the performance of the surfactants included in the comparison. A significant F-test did not indicate which surfactants in the comparison were different, only that a difference existed. The LSD test was utilized to indicate where the differences were by organizing the surfactants included in the comparison into homogeneous subsets, as will be shown. The results of the factorial designs were subjected to regression analyses and presented in X_1 - X_2 -Y (contour) plots. Contour plots represent predictions of the response (Y) as a function of two variables (X_1 and X_2) and are derived by plotting the regression equation. The tests of significance used in the regression analyses were the t-tests associated with the regression coefficients at the 0.05 level of significance.

In the mineral leaching studies, ground chalcopyrite was exposed to 50 mL of leaching solution in 250-mL Erlenmeyer flasks while being agitated in a shaking water bath. The chalcopyrite mineral was freshly prepared for leaching before each design; it was ground to minus 100 mesh with a mortar and pestle and homogenized on a rolling cloth. A typical size distribution was 34 pct minus 100 plus 200 mesh, 24 pct minus 200 plus

325 mesh, and 42 pct minus 325 mesh. The chalcopyrite used was specimen-grade mineral from Transvaal, Republic of South Africa. A mineralogical analysis revealed that the mineral was 88 pct chalcopyrite, 10 pct quartz, and 2 pct epidote, with trace pyrite and bornite. Each design was made up of 9 to 16 flask tests. Because the chalcopyrite was homogenized before being loaded into the flasks, each flask within a design received a uniform particle size distribution in addition to equal mass. Because no effort was taken to ensure a uniform particle size distribution between experimental designs, conclusions should be drawn only within each design and not between designs. The general level of copper extractions observed varied from design to design because of differences in particle size distribution and chalcopyrite sample. These variables were controlled within each design. The leaching solutions were made with deionized-distilled water and reagent-grade ferric and in some cases ferrous sulfate. When Fe^{2+} was added, the flasks were evacuated with nitrogen to inhibit the air oxidation of Fe^{2+} to Fe^{3+} . The amount of solids was 0.5 or 1.0 pct. The surfactants tested were industrial samples obtained from their manufacturers. Surfactant solutions were freshly mixed for each experiment design by weighing the desired amount and adding it to 1 L of deionized-distilled water. The temperatures studied were 25° and 50° C, the typical range of temperatures found in a dump. Sulfuric acid was added to adjust the pH.

During the course of the mineral leaching studies, six hypotheses were outlined for testing (table 1). Hypotheses 1 through 3 were tested using the three surfactants shown in table 2. The surfactants differ with respect to the ionic nature of their hydrophiles. The hydrophile of Dow 2A1 is made up of two anionic sulfonate groups. The hydrophile of Aerosol C-61 is made up of a cationic amine group. The hydrophile of Tween 20 is made up of chains of polyethylene oxide, which are nonionic in nature. The hydrophobe in each of the surfactants is made up of a hydrocarbon chain. Each surfactant was tested separately in a $2 \times 2 \times 4$ factorial design at 25° C, 1 pct solids, and 10 days of leaching. The independent variables of the design and their normalized levels are shown in table 3.

Because Fe^{2+} is also present in a dump leaching solution, total iron was maintained at 2 g/L Fe with ferrous sulfate while the amount of Fe^{3+} in the leaching solutions was varied for the design. Four levels of surfactant concentration were studied because of the uncertainty involved in picking an appropriate level. The pH, Fe^{3+} , and total iron levels were chosen as those typically found in a dump.

Table 1.—Hypotheses tested in chalcopyrite leaching studies

1	Lowering the interfacial tension with anionic, cationic, or nonionic surfactant addition will improve copper extraction in the ferric sulfate leaching of chalcopyrite under dump conditions.
2	The pH of the leaching solution will influence surfactant performance.
3	Fe^{3+} concentration will influence surfactant performance.
4	The hydrophile-lipophile balance (HLB) of nonionic surfactants will influence their performance.
5	The structure of nonionic surfactants will influence their performance.
6	The temperature of the leaching solution will influence nonionic surfactant performance.

Table 2.—Three surfactants used to test hypotheses 1, 2, and 3

Class	Trade name	Chemical name
Anionic	Dow 2AI	Alkylsodium sulfonate diphenyl oxide.
Cationic	Aerosol C-61	Alkylamine-guanidine polyoxyethanol.
Nonionic	Tween 20	Polyoxyethylene sorbitan monolaurate.

Table 3.— $2 \times 2 \times 4$ factorial design variables and levels

Variable	Normalized level ¹			
	-1	-0.96	-0.6	+1
X1: pH	1.0	—	—	2.0
X2: Fe^{3+} g/L	0.2	—	—	1.0
X3: surfactant ppm	0	1	10	50

¹Only the -1 and +1 levels of X1 and X2 were studied in the $2 \times 2 \times 4$ design.

Hypothesis 4 was tested by comparing the performance of Tween 20, Tween 40, and Tween 60 nonionic surfactants in a completely randomized experiment design at 10 ppm surfactant, 25° C, pH 2, 1 pct solids, and 10 days of leaching. The three surfactants contain the same number of moles of hydrophile, which is made up of ethylene oxide, in their structures but differ in hydrophobe chain length, as shown in table 4. The HLB value represents the amount of hydrophile in a nonionic surfactant structure relative to the amount of hydrophobe in the structure. The larger the HLB, the greater the proportion of hydrophilic groups in the structure relative to hydrophobic

groups. Three designs were conducted at 1, 2, and 0.02 g/L Fe^{3+} with total iron = 2 g/L. The number of replicates used in the designs was three.

Table 4.—Tween surfactants used to test hypothesis 4

Surfactant	Number of carbons in hydrophobe	HLB
Tween 20	11	17
Tween 40	15	16
Tween 60	17	15

HLB Hydrophile-lipophile balance.

Hypotheses 5 and 6 were tested using completely randomized experiment designs at 1.0 g/L Fe^{3+} , 10 ppm surfactant, pH 2, 0.5 pct solids, and 8 and 4 days of leaching at 25° and 50° C, respectively. No ferrous sulfate was added in these designs in order to simplify the procedure. The number of replicates used in the designs was three at 25° C and four at 50° C. The surfactants included in the comparisons are shown in table 5. The classes included in the comparisons represent five of the eight major classes of nonionic surfactants identified by Schick (22). The three classes not represented are ethoxysters of fatty acids, ethoxyamines, and ethoxyamides. The ethoxysters of fatty acids were not tested because their structure is very similar to that of the ethoxyalcohols. The amines and amides were not tested because they can take on cationic properties. The hydrophile in each of the surfactants in table 5 is made up of chains of polyethylene oxide. The surfactant class identifies the source of the hydrophobe. In block copolymers, the hydrophobe is made up of chains of polypropylene oxide. The surfactants in table 5 are divided up into groups according to HLB value. An attempt was made to keep the molecular weights of the surfactants within a group as constant as possible. Each group was included in a single comparison to test the effect of surfactant structure. The best performers from each group were included in a final comparison to identify the overall best performers at 25° and 50° C.

Table 5.—Nonionic surfactants included in the comparisons to test hypotheses 5 and 6

Surfactant	Class	Source	Molecular weight	HLB
S218	Ethoxymercaptan	Alcolac	700	14
NP20	Ethoxyphenol	Mazer Chemicals	1,100	16
LA23	Ethoxyalcohol	do.	1,200	16
T40	Ethoxypolyol	ICI Americas Inc.	1,300	16
L44	Block copolymer	BASF Corp.	2,200	12-18
10R5	do.	do.	1,950	12-18
304	do.	do.	1,650	12-18
50R8	do.	do.	10,200	12-18
NP100	Ethoxyphenol	Maser Chemicals	4,600	19
G4280	Ethoxypolyol	ICI Americas Inc.	3,900	19
L35	Block copolymer	BASF Corp.	1,900	18-23
10R8	do.	do.	4,550	18-23
F38	do.	do.	4,700	>24
707	do.	do.	12,200	>24

HLB Hydrophile-lipophile balance.

The overall best performers at 25° and 50° C were tested over a broader Fe^{3+} concentration range using 3×3 factorial designs with surfactant concentration and

Fe^{3+} concentration as the independent variables of the designs. The designs were conducted at pH 2 and 1 pct solids. No ferrous sulfate was added in these designs.

RESULTS AND DISCUSSION

The results for hypotheses 1 through 3 are shown in figures 1 through 3. The contours represent predicted copper concentrations as a function of Fe^{3+} concentration and surfactant concentration and were derived by fitting a second-order regression equation to the factorial data and then plotting the equation. The goodness-of-fit of the regression equations to the data, given by the coefficient of determination, R^2 , was greater than 90 pct in each of the regression models obtained, except that shown in figure 2, which has an R^2 of 81 pct. Figure 1, which contains the results for Tween 20 at pH 2 and pH 1, shows that the addition of the nonionic surfactant increases copper extraction. At pH 2 and 0.2 g/L Fe^{3+} , copper concentration in the leaching solution increases from 60 mg/L at 0 ppm Tween 20 to 130 mg/L at 25 ppm Tween 20. At

1.0 g/L Fe^{3+} , copper concentration increases from 90 mg/L at 0 ppm Tween 20 to 220 mg/L at 25 ppm surfactant. Tween 20 additions beyond 25 ppm did not increase leaching. The results for Tween 20 at pH 1 are similar to those at pH 2, except that above 25 ppm Tween 20, copper leaching begins to decrease rather than remain level.

The addition of Aerosol C-61 causes a decrease in copper leaching at pH 2 and pH 1, as can be seen in figure 2. At pH 2 and 0.2 g/L Fe^{3+} , copper concentration decreases from 70 mg/L at 0 ppm Aerosol C-61 to 45 mg/L at 50 ppm Aerosol C-61. At 1.0 g/L Fe^{3+} , Aerosol C-61 has practically no effect on leaching. The results for Aerosol C-61 at pH 1 are similar to those at pH 2. The addition of Dow 2A1 surfactant also decreases copper

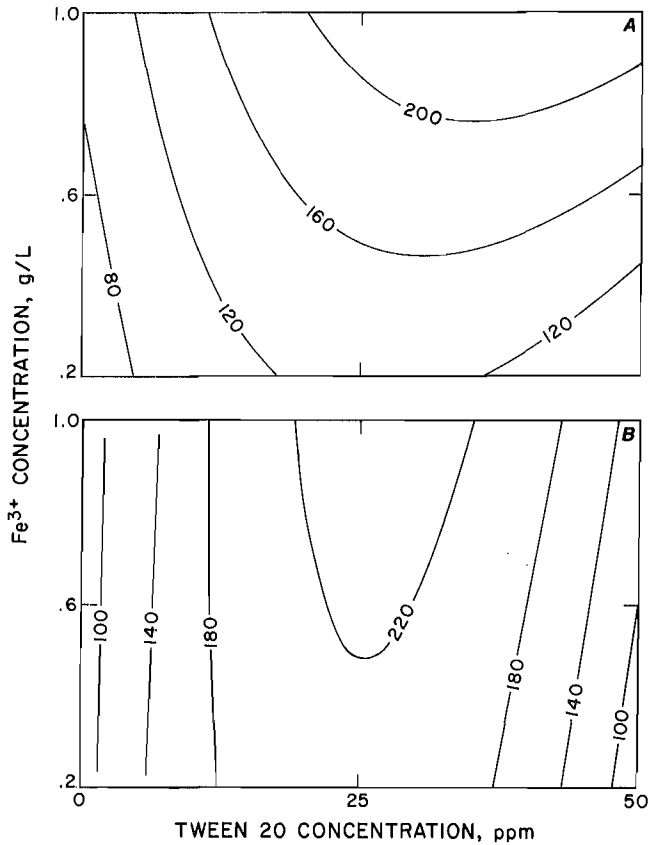


Figure 1.—Effect of Tween 20 concentration and Fe^{3+} concentration on copper leaching after 10 days at (A) pH 2 and (B) pH 1, 25° C, 1 pct solids, and total iron = 2 g/L. Contour lines are copper concentration, in milligrams copper per liter.

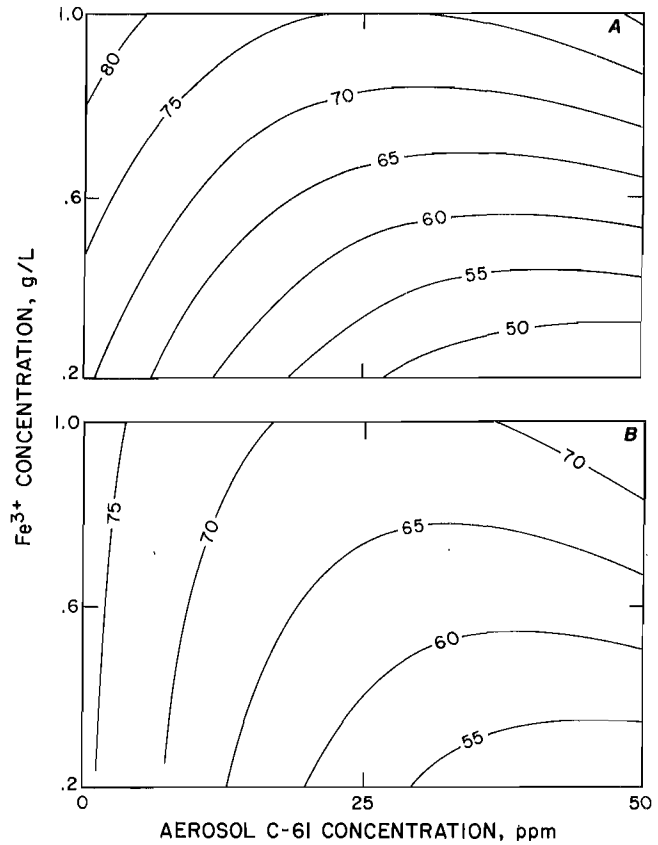


Figure 2.—Effect of Aerosol C-61 concentration and Fe^{3+} concentration on copper leaching after 10 days at (A) pH 2 and (B) pH 1, 25° C, 1 pct solids, and total iron = 2 g/L. Contour lines are copper concentration, in milligrams copper per liter.

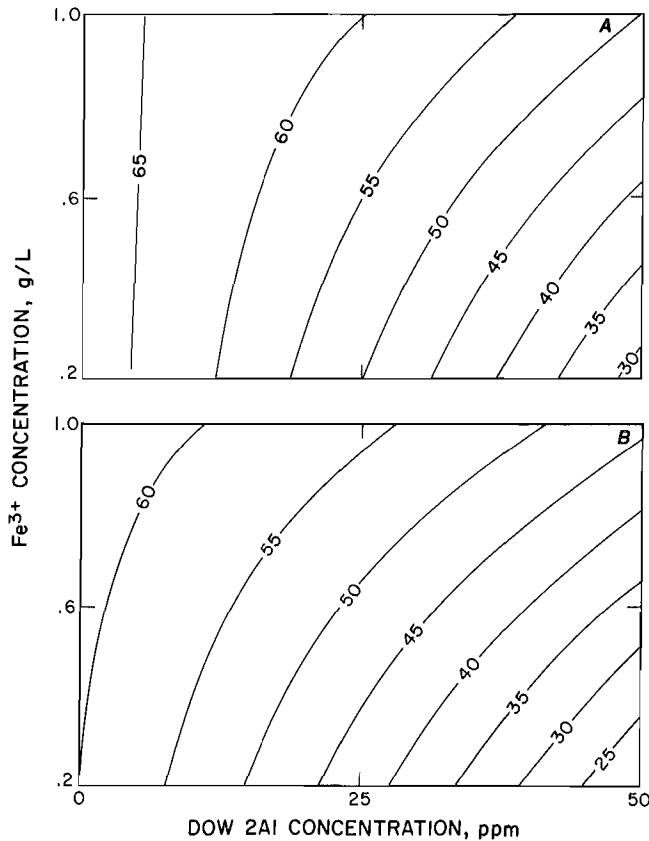


Figure 3.—Effect of Dow 2A1 concentration and Fe^{3+} concentration on copper leaching after 10 days at (A) pH 2 and (B) pH 1, 25° C, 1 pct solids, and total iron = 2 g/L. Contour lines are copper concentration, in milligrams copper per liter.

extraction at pH 2 and pH 1, as can be seen in figure 3. At pH 2 and 0.2 g/L Fe^{3+} , copper concentration decreases from 68 mg/L at 0 ppm Dow 2A1 to 28 mg/L at 50 ppm Dow 2A1. At 1.0 g/L Fe^{3+} , copper concentration decreases from 68 mg/L at 0 ppm Dow 2A1 to 50 mg/L at 50 ppm surfactant. The results for Dow 2A1 at pH 1 are similar to those at pH 2.

Given the results in figures 1 through 3, hypothesis 1 is accepted for the nonionic Tween 20 and rejected for the ionic Aerosol C-61 and Dow 2A1. Lowering the interfacial tension with surfactant addition does improve copper extraction in the ferric sulfate leaching of chalcopyrite under these conditions if the hydrophile of the surfactant is the nonionic polyethylene oxide. With the ionic hydrophiles, the effect of the surfactants is detrimental. Hypothesis 2 is accepted for the nonionic Tween 20 and rejected for the ionic Aerosol C-61 and Dow 2A1. At the lower pH, the strong negative curvature associated with Tween 20 concentration became evident, whereas it was not evident at pH 2. Although there were small differences in the performance of Aerosol C-61 and

Dow 2A1 at the two pH levels tested, these were not statistically significant at the 0.05 level of significance in the regression analyses.

Hypothesis 3 is accepted for each of the three surfactants tested. It is apparent that a positive interaction exists between Fe^{3+} concentration and surfactant concentration. This interaction was statistically significant at the 0.05 level in the regression analyses for each surfactant. An interaction between two variables occurs when the effect of one of the variables is dependent on the level of the other variable. In this case, the effect of surfactant addition on the leaching of chalcopyrite is dependent on the level of Fe^{3+} present. The positive effect of Tween 20 addition is larger at 1.0 g/L Fe^{3+} than at 0.2 g/L Fe^{3+} . The negative effects of Aerosol C-61 and Dow 2A1 additions are smaller at 1.0 g/L Fe^{3+} than at 0.2 g/L Fe^{3+} . This change in the magnitude of the surfactant effect at different Fe^{3+} concentration levels constitutes the interaction. It is interesting to look at this interaction from the opposite perspective. At 0 ppm surfactant concentration, the effect of increasing Fe^{3+} concentration on copper extraction is small. At 50 ppm surfactant, increasing Fe^{3+} concentration produces a larger positive effect on copper extraction.

The interaction between Fe^{3+} concentration and non-ionic surfactant concentration is further evidenced in figure 4, which shows the influence of surfactant HLB (hypothesis 4) at three different Fe^{3+} concentrations with total iron = 2 g/L. The three surfactants differ with respect to HLB value (table 4). At 1 and 2 g/L Fe^{3+} , the addition of the nonionic surfactants increases copper extraction by decreasing the passivation of the chalcopyrite surface that occurs with time in the control tests. This supports the conclusion that some of the passivation is due to a change in the wettability of the chalcopyrite surface during leaching. These results, however, are for initial leaching rates only and do not rule out other sources of passivation, as have been pointed out by the several researchers previously mentioned. At 0.02 g/L Fe^{3+} , the addition of the surfactants decreases copper extraction compared with that of the control tests. The results support the conclusion that the addition of the nonionic surfactants will be beneficial to the ferric sulfate leaching of chalcopyrite under these conditions if a base level of Fe^{3+} is present. Of the three surfactants, Tween 40 produces the best results.

A statistical comparison of the data from the three designs is presented in table 6 for the results in figure 4. The three comparisons consider the data points at 10 days of leaching only. The comparisons are organized into subsets that are statistically different based on the F and LSD tests. For those surfactants in different subsets, there is sufficient evidence to conclude that the observed differences are not due to experimental error. For those means within a subset, there is not sufficient evidence to conclude that the observed differences are not due to experimental error. At 1.0 g/L Fe^{3+} , the four mean

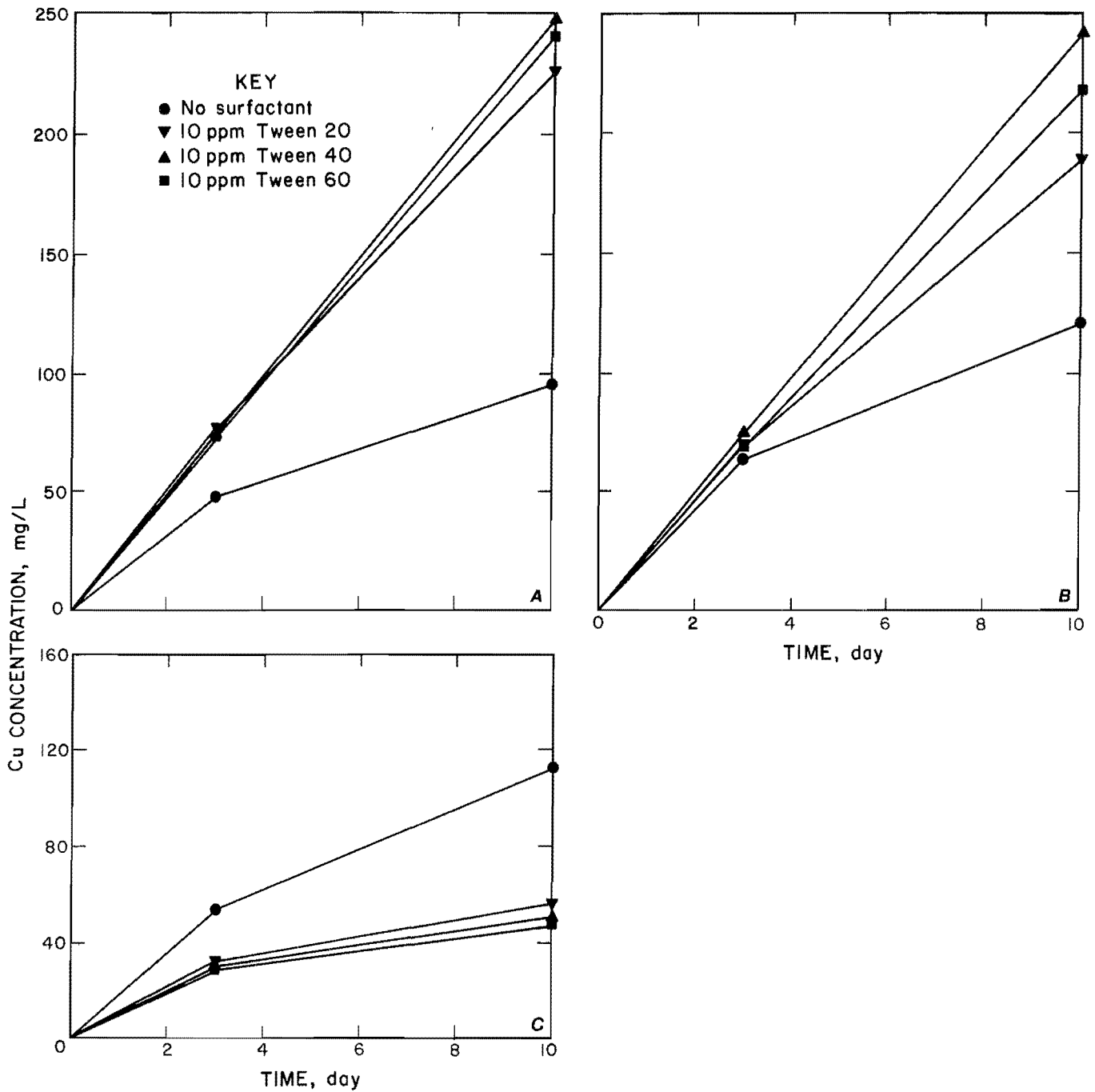


Figure 4.—Effect of Tween 20, Tween 40, and Tween 60 surfactants on copper leaching at (A) 1.0, (B) 2.0, and (C) 0.02 g/L Fe³⁺, 10 ppm surfactant, 25° C, pH 2, 1 pct solids, and total iron = 2 g/L. Each point represents the mean of three replicates.

responses are organized into three subsets. Tween 40 and Tween 60 are statistically the same in performance and are superior to Tween 20. Tween 20 produces a result that is statistically better than the control tests, which do not have any surfactant. At 2.0 g/L Fe^{3+} , the order is the same except that Tween 40 proves itself to be statistically better than Tween 60. Table 6 shows that at 1.0 and 2.0 g/L Fe^{3+} , the HLB value of the Tween surfactants influences their performance in leaching. Hypothesis 4 is therefore accepted. At 0.02 g/L Fe^{3+} , the four treatments are divided into two subsets. The three surfactants perform the same statistically at this Fe^{3+} concentration, regardless of HLB value. The decrease in copper leaching at this Fe^{3+} concentration caused by the addition of the surfactants is statistically significant, indicating the importance of Fe^{3+} concentration to the surfactant effect.

Table 6.—Statistical comparison of data in figure 4 at 10 days of leaching

Subset	Surfactant	Cu mean response, mg/L
1.0 g/L Fe^{3+}		
A	Control	95
B	Tween 20	227
C	Tween 60	241
	Tween 40	249
2.0 g/L Fe^{3+}		
A	Control	121
B	Tween 20	188
C	Tween 60	218
D	Tween 40	242
0.02 g/L Fe^{3+}		
A	Tween 60	48
	Tween 40	49
	Tween 20	56
B	Control	112

Table 7 shows the structures of the nonionic surfactants included in the comparisons to test the influence of surfactant structure and temperature (hypotheses 5 and 6). In the structures, the hydrophiles are the chains of ethylene oxide, " $-\text{OCH}_2\text{CH}_2-$ ". The hydrophobes are the hydrocarbon chains, " $-\text{C}_x\text{H}_y$ ". In the case of the block copolymers, the hydrophobes are the chains of propylene oxide, " $-\text{OCHCH}_2\text{CH}_2-$ ". The results of the comparisons are presented in tables 8 through 11. In table 8, the comparison of surfactants S218, NP20, LA23, and T40 (Tween 40) at 25° and 50° C is presented. At 25° C, the performance of all four surfactants is statistically different.

Hypothesis 5 is, therefore, accepted. The structure of the nonionic surfactants influences their performance. T40 is the superior performer of the four surfactants tested in this comparison. The hydrophile of T40 is a branched orientation of ethylene oxide around a sorbitan ring structure, whereas the hydrophiles of the other three surfactants are linear chains. The branched structure is beneficial to surfactant performance. The NP20 and LA23 structures differ in that NP20 has a benzene ring in the linkage between the hydrophile and hydrophobe of the structure, whereas LA23 does not. The presence of the benzene ring is detrimental to surfactant performance. The poor performance of S218 may be due to its low HLB value. The producer of S218 did not make ethoxymercaptans at higher HLB values.

The estimate of experimental error was larger in the comparisons at 50° C than in the comparisons at 25° C. As a result, clean classifications, in the sense that each surfactant appeared in only one subset, were not obtained in the comparisons at 50° C. At 50° C, T40, NP20, and LA23 are statistically different in performance, whereas S218 is not statistically different from T40 or NP20. The fact that S218 appears in both subsets A and B indicates that in light of experimental error the differences between S218 and T40 and between S218 and NP20 were not large enough to determine in which subset S218 should be placed based on the LSD test. LA23 is the best performer of the four surfactants included in the comparison. The poor performance of T40 at 50° C is due to the weak nature of the ester linkage, " $-\text{OOC}-$ ", that connects the hydrophobe to the hydrophile, as will be shown later. The ester linkage is susceptible to hydrolysis, which is accelerated at higher temperature. This breaks the linkage, causing T40 to lose its surface-active properties. The ether linkage, " $-\text{O}-$ ", and the thioether linkage, " $-\text{S}-$ ", of the other three surfactants in this comparison are more stable at 50° C under the acid-oxidizing conditions of these tests (23). Hypothesis 6 is, therefore, accepted. The temperature of the leaching solution influences nonionic surfactant stability.

Table 9 compares four block copolymers with HLB values of 12 to 18 at 25° and 50° C. The HLB system was developed for nonionic surfactants with hydrocarbon hydrophobes, whereas block copolymers utilize polypropylene oxide as the hydrophobe. Nonionic surfactants with polypropylene oxide as the hydrophobe exhibit different behavior than do nonionic surfactants with hydrocarbon hydrophobes. As a result, the HLB values of polypropylene oxide surfactants do not correlate exactly with those of hydrocarbon surfactants. Their HLB values are expressed in ranges because the effective HLB of these surfactants varies with the system.

Table 7.—Structures of nonionic surfactants included in the comparisons to test hypotheses 5 and 6

Surfactant	Class	Structure
S218	Ethoxymercaptan	$H(OCH_2CH_2)_{11}SC_{12}H_{25}$
NP20	Ethoxyphenol	$H(OCH_2CH_2)_{20}O Q C_9H_{19}$, ¹
LA23	Ethoxyalcohol	$H(OCH_2CH_2)_{23}OC_{12}H_{25}$
T40	Ethoxypolyol	$O (CH_2CH_2O)_xOH$ $C CHCH_2(CH_2CH_2O)_yOCC_{15}H_{31}$ $HO(CH_2CH_2O)_wHC CH(CH_2CH_2O)_zOH$
L44	Block copolymer	CH_3 $HO(CH_2CH_2O)_x(CH_2CHO)_y(CH_2CH_2O)_xH$
10R5	.. do.	CH_3 CH_3 $HO(CH_2CHO)_x(CH_2CH_2O)_y(CH_2CHO)_xH$
304	.. do.	CH_3 CH_3 $H(OCH_2CH_2)_y(OCHCH_2)_x (CH_2CHO)_x(CH_2CH_2O)_yH$ NCH_2CH_2N $H(OCH_2CH_2)_y(OCHCH_2)_x (CH_2CHO)_x(CH_2CH_2O)_yH$ CH_3 CH_3
50R8	.. do.	CH_3 CH_3 $H(OCHCH_2)_y(OCH_2CH_2)_x (CH_2CH_2O)_x(CH_2CHO)_yH$ NCH_2CH_2N $H(OCHCH_2)_y(OCH_2CH_2)_x (CH_2CH_2O)_x(CH_2CHO)_yH$ CH_3 CH_3
NP100	Ethoxyphenol	$H(OCH_2CH_2)_{100}O Q C_9H_{19}$, ¹
G4280	Ethoxypolyol	Same type as T40.
L35	Block copolymer	Same type as L44.
10R8	.. do.	Same type as 10R5.
F38	.. do.	Same type as L44.
707	.. do.	Same type as 304.

¹"Q" designates a benzene ring.

Table 8.—Statistical comparison of surfactants S218, NP20, LA23, and T40 at 25° and 50° C

Subset	25° C		50° C	
	Surfactant	Cu mean response, mg/L	Surfactant	Cu mean response, mg/L
A	S218	35	T40 S218	165 179
B	NP20	40	S218 NP20	179 200
C	LA23	45	LA23	240
D	T40	68		

Table 9.—Statistical comparison of surfactants L44, 10R5, 304, and 50R8 at 25° and 50° C

Subset	25° C		50° C	
	Surfactant	Cu mean response, mg/L	Surfactant	Cu mean response, mg/L
A	304	55	10R5 L44	161 166
B	50R8	58	L44 50R8	166 193
C	10R5 L44	61 62	50R8 304	193 207

Table 10.—Statistical comparison of surfactants NP100, G4280, L35, and 10R8 at 25° and 50° C

Subset	25° C		50° C	
	Surfactant	Cu mean response, mg/L	Surfactant	Cu mean response, mg/L
A	L35	136	G4280 L35 NP100	225 234 254
B	10R8 NP100	142 143	NP100 10R8	254 270
C	G4280	147		

Table 11.— Statistical comparison of surfactants T40, L44, G4280, F38, and 707 at 25° C and surfactants LA23, 304, 10R8, and F38 at 50° C

Subset	25° C		50° C	
	Surfactant	Cu mean response, mg/L	Surfactant	Cu mean response, mg/L
A	F38 707 L44	55 56 58	LA23 10R8 F38 304	185 220 220 234
B	G4280	71		
C	T40	83		

At 25° C, surfactants 10R5 and L44 are the superior performers. At 50° C, surfactants 50R8 and 304 are the superior performers. Surfactants 50R8 and 304 are branched structures, whereas 10R5 and L44 are linear chains. The block copolymers are symmetrical arrangements of the hydrophilic (-OCH₂CH₂-) and hydrophobic (-OCHCH₃CH₂-) groups utilized. Surfactants L44 and 304 have the hydrophilic groups positioned on the ends of the structure chains. Surfactants 10R5 and 50R8 have the hydrophobic groups positioned on the ends of the structure chains. At the HLB values in this comparison, the linear chains perform better at the low temperature and the branched structures perform better at the high temperature. The positioning of the hydrophilic and hydrophobic groups in the structure chains does not affect surfactant performance in this case.

Table 10 compares four surfactants with HLB values in the range of 18 to 23. At 25° C, G4280 performs better than the ethoxyphenol, NP100, and the two block copolymers. G4280 is in the same class as T40 and possesses the branched hydrophile. NP100 is in the same class as NP20, which is a linear chain with a benzene ring in the hydrophile-hydrophobe linkage. At 50° C, surfactants 10R8 and NP100 are the superior performers. G4280 is

unstable at the higher temperature, as will be shown below. At both temperatures, 10R8 is statistically better than L35. These two block copolymers are linear chains but differ in the positioning of the hydrophilic and hydrophobic groups. Surfactant 10R8 has two hydrophobic chains positioned on either side of a hydrophilic chain. L35 is the reverse, having two hydrophilic chains positioned on either side of a hydrophobic chain. The structure of 10R8 produces a better orientation of the block copolymer at the mineral-solution interface than does the structure of L35. At the HLB values of this comparison, the positioning of the hydrophilic and hydrophobic groups along structure chains does influence block copolymer performance. This was not the case with the HLB range of 12 through 18 (table 9).

The surfactant with the best mean response was selected from each of the groups shown in tables 8 through 10 to be included in final comparisons at 25° and 50° C. Table 11 contains the final comparisons and includes surfactants T40, L44, G4280, F38 and 707 at 25° C and surfactants LA23, 304, 10R8, and F38 at 50° C. The two surfactants in the HLB group of >24, F38 and 707, had not been included in any previous comparison and were added to the final comparison. Surfactants F38 and 707 were compared in a separate design at 50° C and were found to perform the same statistically. Therefore, of the two, F38 was selected to be included in the final comparison at 50° C.

At 25° C, T40 proves to be the superior performer. Surfactant G4280 possesses the same structure as T40 except with longer polyethylene oxide chains. Increasing the HLB value of the structure of T40 decreases its performance. This was seen previously in figure 4, where T40 (Tween 40) outperformed Tween 20, which is a step above it in HLB value. The branched hydrophile of T40 sets it apart from the other surfactants tested. The block copolymers included in the final comparison at 25° C perform at the same level regardless of structure and HLB value. At 50° C, no statistical difference between the four surfactants was uncovered. Surfactant 304 produced the highest mean response.

Surfactants T40 and 304 were selected for testing as the overall best performers at 25° and 50° C, respectively. T40 was selected because it was statistically better in performance than any other surfactant tested at 25° C. Surfactant 304 was selected because it produced the highest mean response in the final comparison at 50° C. The results of the 3×3 factorial design for T40 (Tween 40) are shown in figure 5. The three levels of surfactant concentration studied were 0, 10, and 20 ppm. The three levels of Fe³⁺ concentration studied were 0.1, 1.05, and 2.00 g/L. The positive interaction between Fe³⁺ concentration and nonionic surfactant concentration is clearly evident in

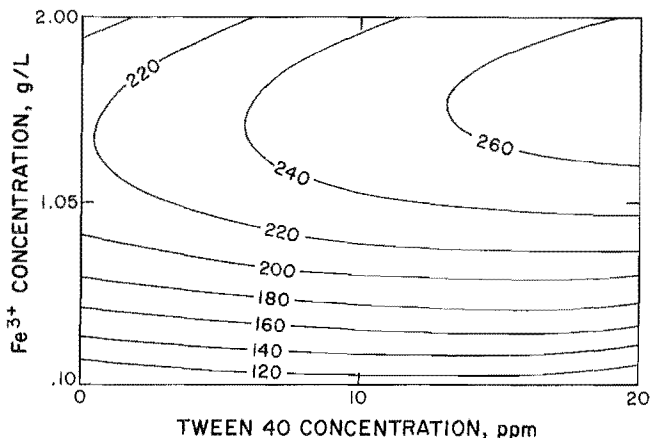


Figure 5.—Effect of Tween 40 concentration and Fe³⁺ concentration on copper leaching after 8 days at 25° C, pH 2, and 1 pct solids. Contour lines are copper concentration, in milligrams copper per liter.

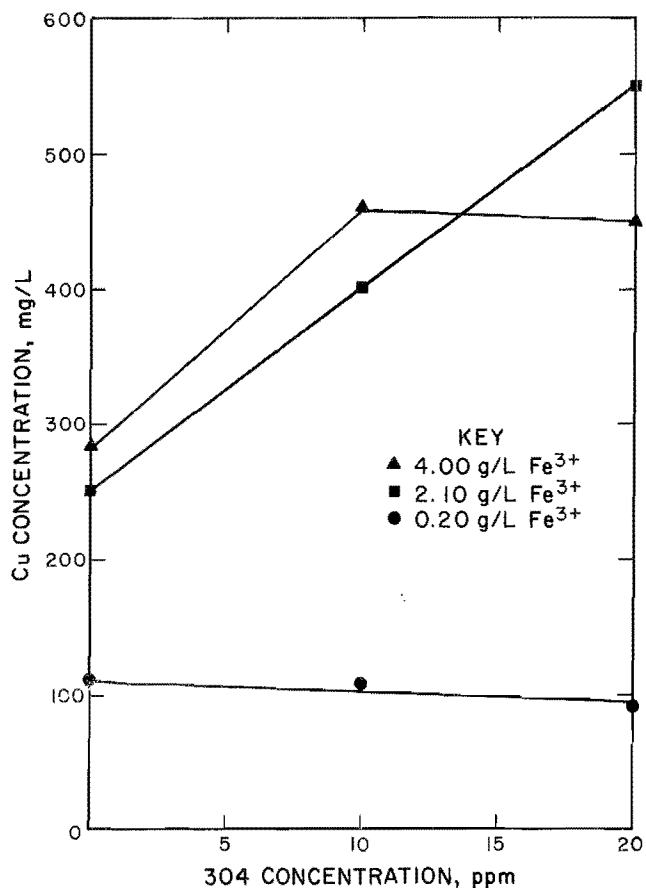


Figure 6.—Effect of Tetrionic 304 concentration and Fe³⁺ concentration on copper leaching after 4 days at 50° C, pH 2, and 1 pct solids.

figure 5. At the higher Fe³⁺ concentrations, T40 addition is beneficial to leaching, whereas at the lower Fe³⁺ concentrations T40 produces no benefit. Beyond 1.05 g/L Fe³⁺, no increase in copper leaching occurs with increasing Fe³⁺ concentration. This is true whether surfactant is present or not.

The 3x3 factorial results for surfactant 304 (Tetric 304) are shown in figure 6. The three levels of surfactant concentrations studied were 0, 10, and 20 ppm. The three levels of Fe³⁺ concentration studied were 0.20, 2.10, and 4.00 g/L. The results are displayed in X-Y format rather than X1-X2-Y (contour) format in order to emphasize the negative curvature associated with the surfactant concentration effect at 4.00 g/L Fe³⁺. At 4.00 g/L Fe³⁺, copper leaching levels off after 10 ppm 304. At 2.10 g/L Fe³⁺, copper leaching increases linearly over the entire 304 concentration range. This design was repeated to ensure that the change in slope at 4.00 g/L Fe³⁺ was not a random occurrence. The change at 4.00 g/L Fe³⁺ may be due to the 304 structure. Because the structure has nitrogen atoms in its linkage, the surfactant may exhibit some cationic properties. These properties may interact negatively with increasing ferric sulfate concentration. At 0.2 g/L Fe³⁺, the addition of 304 produces a slight decrease in copper leaching. The positive interaction between Fe³⁺ concentration and nonionic surfactant concentration is again clearly evident in this figure.

A comparison was conducted to test whether the surfactants with an ester linkage are unstable at 50° C. Two identical surfactant solutions were prepared containing 1 g/L Fe³⁺ and 20 ppm T40 at pH 2. One was heated to 50° C for 20 h and then allowed to cool, while the other remained at room temperature. A comparison was then conducted between a control solution with no surfactant, the surfactant solution that had been heated, and the surfactant solution that had not been heated. The comparison was conducted at 25° C, 1 pct solids, and 8 days of leaching. Results are shown in table 12. All three treatments gave statistically different results. The T40 solution that was not heated was the most effective. Heating the solution of T40 decreased its surface activity by accelerating the degradation of the ester linkage. The T40 solution that was heated produced slightly better results than the control tests.

Table 12.— Statistical comparison of data testing ester linkage instability at higher temperatures

Subset	Condition	Cu mean response, mg/L
A	Control	109
B	Heated	118
C	Not heated	150

CONCLUSIONS

Lowering the interfacial tension by adding a nonionic surfactant (Tween 20) increased copper extraction from chalcopyrite. The addition of the two ionic surfactants tested was detrimental to leaching. The pH of the leaching solution did not affect the performance of the two ionic surfactants tested, but did affect the performance of the nonionic Tween 20, producing a stronger negative curvature in the Tween 20 concentration effect at pH 1 than at pH 2. A positive interaction between surfactant concentration and Fe^{3+} concentration was observed for the nonionic, cationic, and anionic surfactants tested.

The addition of the Tween 20, Tween 40, and Tween 60 nonionic surfactants improved copper extraction from chalcopyrite when sufficient Fe^{3+} was present in the leaching solution. This further evidenced the existence of a positive interaction between Fe^{3+} concentration and nonionic surfactant concentration. Tween 40 was found to be superior to Tween 20 and Tween 60, indicating that the HLB of a nonionic surfactant influences its performance in chalcopyrite leaching. The change in chalcopyrite surface wettability in the acid and ferric sulfate leaching solution was found to contribute to the passivation of the surface toward leaching under the conditions studied.

The structure of a nonionic surfactant influences its performance in chalcopyrite leaching. At 25° C, Tween 40

was determined to possess the superior structure of the 14 surfactants compared. The branched hydrophile of Tween 40 was beneficial to surfactant performance, compared with a linear chain hydrophile. Adding more ethylene oxide to the Tween 40 structure decreased its performance. The Tween 40 structure became unstable at higher temperatures and lost its surface-active properties. Two of the surfactants tested had a benzene ring in the hydrophile-hydrophobe linkage, which was detrimental to surfactant performance. At an HLB range of 18 through 23, the positioning of the hydrophilic and hydrophobic groups within the block copolymer structure became important. The structure of 10R8, which has the hydrophobic groups on either side of the hydrophilic group, performed better than L35, which has the reverse orientation. At 50° C, the four surfactants included in the final comparison performed equally well based on the statistical test. Tetronic 304, a block copolymer with a branched structure, produced the highest mean response of the group.

Tween 40 and Tetronic 304 surfactants were selected as the overall best performers at 25° and 50° C, respectively. At 4.00 g/L Fe^{3+} , the positive effect of Tetronic 304 leveled off after a concentration of 10 ppm.

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