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## **Copper Exchange Capacity of Clays and Their Potential Effect on In Situ Copper Leaching**

**By J. S. Gomer, S. W. Yopps, S. P. Sandoval, and A. E. Clark**

**UNITED STATES DEPARTMENT OF THE INTERIOR**



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**UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT**

**°C**      degree Celsius

**meq**      milliequivalent

**g**        gram

**mL**      milliliter

**g/L**     gram per liter

**pct**     percent

**h**        hour

# COPPER EXCHANGE CAPACITY OF CLAYS AND THEIR POTENTIAL EFFECT ON IN SITU COPPER LEACHING

By J. S. Gomer,<sup>1</sup> S. W. Yopps,<sup>2</sup> S. P. Sandoval,<sup>3</sup> and A. E. Clark<sup>4</sup>

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## ABSTRACT

The U.S. Bureau of Mines conducted Cu exchange tests for six common clays under simulated in situ leaching conditions. Regression equations were obtained from the data expressing the Cu exchange capacity as a function of Cu concentration, pH, and temperature. Using these equations, an analysis was made of the impact each clay could have on overall Cu recovery. The results suggest that Ca and Na montmorillonite clays could have a major impact on Cu recovery and that attapulgite and illite clays could have a smaller, but still significant, impact. Kaolinite and ripidolite clays pose little threat to loss of Cu from in situ leaching solutions.

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## INTRODUCTION

In situ leaching is an alternative mining technique used to extract metals from ore deposits that preclude conventional methods of mining because of economic, environmental, or other factors. Leaching solutions are applied to the deposit through a grid of injection wells, and the solutions travel through flow channels within the ore body to adjacent solution recovery wells. Metals are dissolved as the leach solution contacts the metal-bearing minerals in the deposit. The metal-containing pregnant solution is pumped to the surface to a metal removal and production facility. The depleted solution is replenished with necessary chemicals for leaching and reinjected into the deposit for further in situ leaching.

There are a number of potential problems associated with in situ leaching of oxidized ores. One of these is the loss of metal from the leaching solution due to cation exchange with clays that are present in the ores. This exchange ability is called the cation exchange capacity (CEC) of the clay and is commonly measured in terms of milliequivalents of ion removed from solution per 100 g of clay. CEC's measured to date have most often been determined at neutral pH and varying ion concentrations. Table 1 gives a range of published CEC's for several clay groups (1).<sup>5</sup> Unfortunately, these values are unsuitable for predicting the effects of clays under acidic in situ leaching conditions since they were determined at pH 7. The CEC values should be lower in an acidic environment because of the severe competition between H<sup>+</sup> ions and the metal cations in solution for the exchange sites in the clay lattice.

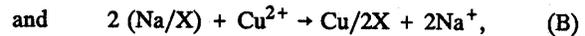
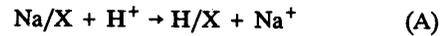
Table 1.—CEC's of clay minerals

Clay	meq per 100 g clay
Montmorillonite ..	80-150
Attapulgite .....	0-30
Illite .....	10-50
Kaolinite .....	3-15
Chlorite .....	10-40
CEC	Cation exchange capacity.

Oxidized Cu deposits are potential candidates for in situ leaching because Cu is easily leached with dilute sulfuric acid solutions and because methods are available commercially to recover the Cu from the solution as salable metal. Consequently, research to determine relevant CEC's of Cu for six common clays under simulated in situ conditions was conducted by the U.S. Bureau of Mines, as part of the Bureau's mission to increase the efficiency and economy of extracting metals from domestic ores.

<sup>5</sup>Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

Clays are composed of a negatively charged repetitive framework of alumina and silica and adsorbed singly or doubly charged cations. Depending on the particular clay, the majority of adsorbed cations are located either in the interlayer positions between the alumina-silica sheet, as in montmorillonite, or on the particle surface, as in kaolinite. When clay particles are placed in an aqueous environment, a fraction of the interlayer or surface cations is quickly replaced by solution cations without appreciable structural damage to the clay material. An example would be the exchange of Cu<sup>2+</sup> and H<sup>+</sup> ions in Cu leach solutions for the exchangeable Na<sup>+</sup> ions of Na montmorillonite. In this case the two competing exchange reactions are



where X = an alumina-silica unit cell.

Assuming chemical equilibrium, then

$$K_1 = \frac{a_{\text{H/X}} \cdot a_{\text{Na}^+}}{a_{\text{Na/X}} \cdot a_{\text{H}^+}}, \quad (1)$$

$$\text{and} \quad K_2 = \frac{a_{\text{Cu/2X}} \cdot (a_{\text{Na}^+})^2}{(a_{\text{Na/X}})^2 \cdot a_{\text{Cu}^{2+}}}, \quad (2)$$

where K = equilibrium constant,

and a = activity.

Multiplying the two equilibrium equations,

$$K_1 K_2 = \frac{a_{\text{H/X}} \cdot a_{\text{Na}^+} \cdot a_{\text{Cu/2X}} \cdot (a_{\text{Na}^+})^2}{a_{\text{Na/X}} \cdot a_{\text{H}^+} \cdot (a_{\text{Na/X}})^2 \cdot a_{\text{Cu}^{2+}}} \quad (3)$$

Taking the log of both sides, then

$$\log K_1 K_2 = \log a_{\text{H/X}} + 3 \log a_{\text{Na}^+} + \log a_{\text{Cu/2X}} - 3 \log a_{\text{Na/X}} - \log a_{\text{H}^+} - \log a_{\text{Cu}^{2+}}. \quad (4)$$

Substituting

$$K = \log K_1 K_2 - \log a_{\text{H/X}} - 3 \log a_{\text{Na}^+} + 3 \log a_{\text{Na/X}} \quad (5)$$

into equation 4 gives

$$K = \log a_{\text{Cu/2X}} - \log a_{\text{H}^+} - \log a_{\text{Cu}^{2+}}. \quad (6)$$

The effect of the final concentration of the displaced cation,  $\text{Na}^+$  in the case of Na montmorillonite, was assumed to be constant and was incorporated as the  $\log a_{\text{Na}^+}$  term in the constant K. Since  $\log a_{\text{Cu}^{2+}}$  is a relative measure of CEC, equation 6, relating CEC to the pertinent variables, becomes

$$\text{CEC} = K + A \log a_{\text{H}^+} + B \log a_{\text{Cu}^{2+}}, \quad (7)$$

where A and B are regression constants.

Since molar concentration,  $M$ , is related to activity by  $a = \lambda M$ , equation 7 becomes

$$\text{CEC} = K' + A \log [\text{H}^+] + B \log [\text{Cu}^{2+}], \quad (8)$$

$$\text{where } K' = K + A \log \lambda_{\text{H}^+} + B \log \lambda_{\text{Cu}^{2+}}, \quad (9)$$

and  $\lambda =$  activity coefficient.

A more detailed explanation of these relationships can be found in references 2 through 4.

The pertinent independent variables in equation 8 are Cu concentration and pH. This research investigated the effect of these variables on ion exchange. In addition, the effect of temperature on the exchange capacity of the clays was studied. Future research will report the effect of competing ions in the general equation.

## EXPERIMENTAL DESIGN AND PROCEDURES

The following clays, which were obtained from the Source Clay Repository of the Clay Mineral Society, a recognized source of homogeneous clay samples, were used in the Cu exchange studies: Ca montmorillonite, Apache County, AZ; Na montmorillonite, Crook County, WY; attapulgite, Gadsden County, FL; illite, Silver Hill, MT; kaolin, Washington County, GA; and ripidolite, a chlorite clay, Flagstaff Hill, El Dorado County, CA. Each clay was thoroughly blended to ensure homogeneity. The ripidolite and illite clay pieces required crushing and pulverizing prior to blending. Typical analyses of each clay mineral are shown in table 2. The size distribution of each clay sample as received is presented in table 3.

Table 2.—Typical analyses of clay minerals, weight percent

Element	Ca montmorillonite	Na montmorillonite	Attapulgit	Illite	Kaolinite	Ripidolite
Al ...	7.9	9.5	4.8	11.7	20.1	10.6
Ca ..	1.7	1.0	1.1	.3	<.3	.046
Cu ..	.012	.009	.008	.013	.008	.016
Fe ..	.97	2.7	2.2	5.1	.17	17.5
K ...	.22	.21	.23	2.5	<.1	<.1
Mg ..	3.3	1.5	5.3	1.5	.04	11.5
Mn ..	.095	.011	.024	.015	.019	.075
Na ..	.11	.84	.063	.085	.074	<.03
P ...	<.1	<.1	.38	.10	<.1	<.1
Si ...	26.5	30.0	27.9	26.1	22.6	13.1
Ti ...	.13	.070	.28	.48	.96	.52
Zn ..	.12	.077	.017	.083	.058	.052

The effects of pH, Cu concentration, and temperature on Cu exchange were determined utilizing a face-centered cube response surface design (5). This approach allowed the effects of experimental variables on the Cu exchange capacity (CuEC) to be determined with a minimal number of experimental tests. After a cursory review of the literature to determine the compositions of typical Cu leach solutions (6-9), experimental ranges were chosen to be 1 to 3 for final pH, 0.5 to 2.0 g/L for final Cu

concentration, and 25° to 75° C for temperature. Test order was randomized to reduce the effects of unknown biases. The experimental parameters for each design are shown in table 4.

Table 3.—Clay size distributions, weight percent

Particle size, mesh ...	+48	-48, +100	-100, +200	-200, +400	-400
	Ca montmorillonite ...	0	1	10	14
Na montmorillonite ...	0	0	0	0	100
Attapulgit	0	5	16	20	59
Illite	38	13	11	6	32
Kaolinite	0	0	0	0	100
Ripidolite	35	10	8	11	36

Table 4.—Experimental parameters for face-centered cube test design

Temp, °C	pH	Cu conc, g/L	Temp, °C	pH	Cu conc, g/L	Temp, °C	pH	Cu conc, g/L
		1	2	.5			1	2.0
		2	2	1.0			2	1.0
		3	2	2.0			3	.5
		3	3	1.0			3	2.0

Preliminary tests for each clay determined the rate and amount of Cu exchanged and the acid consumed over a given period at room temperature. These tests revealed that the Cu exchange equilibrium was achieved within 1 h for each clay. Once the equilibrium time was established, a face-centered cube experiment design was conducted for each clay. Experiments were conducted by mixing untreated clay and copper sulfate-sulfuric acid solution in screw top flasks. Initial Cu and acid concentrations varied depending on acid consumption and Cu exchange for each of the 15 test conditions. The flasks were placed in shaker

baths and agitated at the appropriate temperature. The slurries were vacuum filtered after 1 h of shaking, and equilibrium pH and Cu concentrations of the filtrates were measured to determine the exact experimental conditions. If the pH of a test solution was not within 0.1 or the Cu concentration was not within 0.06 g/L of the desired test parameters, the experiment was repeated utilizing different initial acid and/or Cu concentrations until the design criteria were met.

Each test was run in triplicate and the average CuEC's, pH's, and Cu concentrations at a given temperature were analyzed using multiple regression analysis. With the exception of the clay-to-solution ratio, each clay was subjected to the same experimental procedure. The clay-to-solution ratios were chosen for each clay to allow a detectable change in the concentration of Cu in solution after ion exchange. These ratios are detailed in table 5.

Table 5.—Clay-to-solution ratios

Clay	Clay-to-solution, g:mL
Ca montmorillonite . .	2.5:100
Na montmorillonite . .	2.5:100
Attapulgate . . . . .	5.0:100
Illite . . . . .	5.0: 25
Kaolinite . . . . .	10.0: 25
Ripidolite . . . . .	10.0: 25

The Cu ion concentrations of the initial and equilibrated solutions were determined by atomic absorption spectroscopy. The difference between the two values was the Cu exchanged.

## RESULTS

The CuEC's and the equilibrium conditions for each test are presented in tables 6 through 11. The results show that Ca montmorillonite exhibits the greatest exchange, ranging from 19 to 70 meq per 100 g of clay. Sodium montmorillonite removed from 13 to 42 meq of  $\text{Cu}^{2+}$  ions from solution per 100 g of clay. Attapulgate ranged from 3 to 16 meq per 100 g of clay, illite from 1 to 6 meq, kaolinite from 0.1 to 1.1 meq, and ripidolite from 0.01 to 1.3 meq. Only five tests were reported from the ripidolite series, since no Cu exchange occurred at pH 1 or 2. Under these test conditions, the CuEC of this series of clays varied in the following manner: Ca montmorillonite > Na montmorillonite > attapulgate > illite > kaolinite > ripidolite. Based on these results, Ca and Na montmorillonite have the greatest potential to exchange Cu and, therefore, pose the greatest threat in affecting Cu recovery during in situ leaching. Kaolin and ripidolite clays pose little threat to Cu recovery.

Table 6.—CuEC's for Ca montmorillonite

Temp, °C	Initial		Final		CuEC, meq per 100 g clay	
	pH	Cu conc, g/L	pH	Cu conc, g/L	Ob- served <sup>1</sup>	Cal- culated <sup>2</sup>
25 . . .	0.99	0.63	1.03	0.44	23.9	23.5
	.99	2.41	.95	2.00	52.0	52.6
	1.86	1.34	1.99	.97	47.0	48.3
	2.45	.83	3.00	.48	44.1	44.6
	2.53	2.53	2.92	1.97	70.5	69.8
50 . . .	.98	1.21	1.01	.95	33.1	34.1
	1.88	.77	2.08	.49	35.7	36.3
	1.88	1.32	2.06	.94	47.4	47.8
	1.88	2.49	2.03	1.97	65.1	63.5
	2.52	1.40	3.00	.94	57.9	55.9
75 . . .	.98	2.39	.97	2.01	47.9	49.6
	.99	.63	1.06	.48	18.9	20.8
	1.86	1.34	2.03	.96	47.0	47.3
	2.45	.83	2.90	.48	44.5	45.6
	2.61	2.57	2.99	2.02	68.8	70.8

CuEC Cu exchange capacity.

<sup>1</sup>Calculated as average of triplicate runs.

<sup>2</sup>Calculated based on design values given in Table 4.

Table 7.—CuEC's for Na montmorillonite

Temp, °C	Initial		Final		CuEC, meq per 100 g clay	
	pH	Cu conc, g/L	pH	Cu conc, g/L	Ob- served <sup>1</sup>	Cal- culated <sup>2</sup>
25 ...	0.94	0.62	0.98	0.52	13.0	12.5
	.98	2.21	1.04	1.98	28.5	29.5
	1.75	1.33	2.00	1.04	37.0	35.0
	2.08	.73	2.96	.49	30.6	31.1
	2.08	2.37	2.93	2.06	39.0	40.7
50 ...	1.00	1.16	1.06	.99	21.4	21.8
	1.73	.71	1.97	.51	25.2	26.9
	1.77	1.27	1.98	.99	34.9	35.0
	1.81	2.31	2.03	1.98	41.5	40.2
	2.04	1.30	3.05	1.00	38.2	38.0
75 ...	.94	.62	1.00	.52	13.0	12.5
	.98	2.21	1.05	1.98	29.0	29.5
	1.75	1.33	2.06	1.05	35.3	35.0
	2.08	.73	2.96	.47	32.7	31.2
	2.08	2.33	2.99	2.00	41.1	40.7

CuEC Cu exchange capacity.

<sup>1</sup>Calculated as average of triplicate runs.<sup>2</sup>Calculated based on design values given in Table 4.

Table 8.—CuEC's for attapulgite

Temp, °C	Initial		Final		CuEC, meq per 100 g clay	
	pH	Cu conc, g/L	pH	Cu conc, g/L	Ob- served <sup>1</sup>	Cal- culated <sup>2</sup>
25 ...	0.92	0.55	0.97	0.51	2.7	3.4
	.97	2.10	1.09	2.00	6.6	6.05
	1.58	1.16	1.96	1.05	6.7	5.9
	1.84	.61	3.09	.52	5.7	5.6
	1.95	2.21	3.07	2.03	11.1	11.6
50 ...	.92	1.07	1.05	1.00	4.4	5.0
	1.58	.60	1.99	.53	4.6	5.95
	1.58	1.16	2.04	1.03	8.0	7.4
	2.00	2.14	2.00	2.00	9.0	10.3
	1.89	1.15	3.08	1.00	9.2	9.8
75 ...	.92	.55	1.01	.47	5.0	4.9
	.87	2.12	.93	2.01	6.7	7.6
	1.58	1.16	2.02	1.00	10.3	8.9
	1.86	.60	2.97	.45	9.4	10.1
	2.00	2.24	2.90	1.99	15.9	16.1

CuEC Cu exchange capacity.

<sup>1</sup>Calculated as average of triplicate runs.<sup>2</sup>Calculated based on design values given in Table 4.

Table 9.—CuEC's for illite

Temp, °C	Initial		Final		CuEC, meq per 100 g clay	
	pH	Cu conc, g/L	pH	Cu conc, g/L	Ob- served <sup>1</sup>	Cal- culated <sup>2</sup>
25 ...	0.80	0.61	1.02	0.55	0.90	1.1
	1.78	2.16	1.09	2.02	2.2	2.4
	1.20	1.08	2.03	.96	1.9	1.6
	1.28	.62	3.08	.53	1.3	1.6
	1.36	2.28	3.08	1.99	4.5	5.3
50 ...	.74	1.07	.98	.98	1.4	1.5
	1.10	.56	1.97	.50	.88	.95
	1.12	1.10	2.02	1.00	1.6	1.8
	1.15	2.18	1.99	2.02	2.5	3.5
	1.31	1.21	3.07	1.02	3.0	3.3
75 ...	.75	.58	1.08	.52	.94	1.1
	.76	2.17	1.04	2.01	2.5	2.4
	1.21	1.18	2.04	1.04	2.2	2.1
	1.37	.68	3.08	.53	2.3	2.6
	1.47	2.43	3.09	2.02	6.5	6.3

CuEC Cu exchange capacity.

<sup>1</sup>Calculated as average of triplicate runs.<sup>2</sup>Calculated based on design values given in Table 4.

Table 10.—CuEC's for kaolinite

Temp, °C	Initial		Final		CuEC, meq per 100 g clay	
	pH	Cu conc, g/L	pH	Cu conc, g/L	Ob- served <sup>1</sup>	Cal- culated <sup>2</sup>
25 ...	1.00	0.54	1.03	0.49	0.38	0.32
	.99	2.08	1.04	2.00	.60	.66
	1.86	1.10	2.00	1.05	.41	.59
	2.50	.56	2.94	.48	.60	.54
	2.58	2.15	2.97	2.02	1.06	1.18
50 ...	.95	1.08	.97	1.04	.25	.21
	1.86	.56	2.04	.51	.36	.35
	1.83	1.11	2.04	1.05	.48	.47
	1.87	2.09	2.06	2.00	.74	.72
	2.45	1.11	2.97	1.02	.74	.73
75 ...	.94	.53	.98	.52	.08	.05
	.95	2.05	1.00	2.03	.14	.06
	1.77	1.02	2.00	.95	.57	.35
	2.44	.59	2.90	.50	.72	.57
	2.58	2.15	2.95	2.02	1.03	.98

CuEC Cu exchange capacity.

<sup>1</sup>Calculated as average of triplicate runs.<sup>2</sup>Calculated based on design values given in Table 4.

Table 11.—CuEC's for ripidolite<sup>1</sup>

Temp, °C	Initial		Final		Observed <sup>2</sup> CuEC, meq per 100 g clay
	pH	Cu conc, g/L	pH	Cu conc, g/L	
25 ..	1.18	0.55	3.03	0.54	0.11
	1.21	2.04	3.01	2.01	.26
50 ..	1.15	1.05	3.06	1.01	.34
75 ..	1.20	.56	2.93	.51	.36
	1.21	2.07	2.95	1.91	1.3

CuEC Cu exchange capacity.

<sup>1</sup>Only five tests reported, because no Cu exchange occurred at pH 1 or 2.<sup>2</sup>Calculated as average of triplicate runs.

## REGRESSIONS

An objective of the present work was to develop empirical equations to predict the magnitude of soluble Cu losses during in situ leaching of oxidized deposits. The equations were developed using a stepwise regression procedure with a t-test significance of 0.10 or less required to enter a variable into the equation (10). The details of the modeling procedure are presented in the appendix. The general form of the model is

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2,$$

where  $y$  = CuEC in milliequivalents per 100 g of clay,

$x_1$  = temperature from 25° to 75° C,

$x_2$  = final pH from 1.00 to 3.00,

$x_3$  = final Cu concentration from 0.5 to 2.0 g/L,

and  $b$  = coefficients of variables.

The coefficients of the equations developed for the clays using normalized units are shown in table 12. An equation for ripidolite was not generated because of the very low Cu exchange at pH 1 and 2 noted earlier.

The coefficients of the equations provide useful information about the CuEC's of the clays. The coefficients reveal that final pH and final Cu concentration have the greatest influence on Cu exchange, as was evidenced in equation 8. Copper exchange increases with increasing pH and increasing Cu concentration. The effect of pH is due to the strong competition between H<sup>+</sup> ions and Cu<sup>2+</sup> ions for exchange sites. An increase in final H<sup>+</sup> ion

concentration decreased the total Cu exchanged, while an increase in the final Cu<sup>2+</sup> ion concentration increased the exchange. This was expected because cation exchange is a stoichiometric reaction and the laws of mass action apply.

Table 12.—Coefficients of normalized clay regression equations, milliequivalents per 100 g clay<sup>1</sup>

Coefficient	Ca montmorillonite	Na montmorillonite	Attapulgitite	Illite	Kaolin
$b_0$ ..	52.0	37.6	7.9	2.1	0.6
$b_1$ ..	-1.0	( <sup>2</sup> )	1.5	.4	-.1
$b_2$ ..	10.9	7.5	2.7	1.0	.3
$b_3$ ..	13.7	6.5	2.1	1.2	.1
$b_{12}$ ..	1.1	( <sup>2</sup> )	.8	.3	.1
$b_{13}$ ..	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )	-.05
$b_{23}$ ..	-.9	-1.9	.8	.6	.1
$b_{22}$ ..	-2.8	-5.1	( <sup>2</sup> )	.6	( <sup>2</sup> )
$b_{33}$ ..	-2.7	-4.1	( <sup>2</sup> )	( <sup>2</sup> )	( <sup>2</sup> )

<sup>1</sup>Equation not generated for ripidolite because of very low exchange of Cu at pH 1 and 2.<sup>2</sup>Not statistically significant.

The negative curvature terms of the Ca and Na montmorillonite models reveal that the effects of final pH and final Cu concentration diminish as these variables are increased for these two clays. Temperature and the interaction terms have small effects on the CuEC of the clays.

The accuracy of the equations is measured using two statistics—the coefficient of multiple determination ( $R^2$ ), which measures the accuracy of the equations in predicting the values of the data set used to develop the equations, and the adjusted coefficient of multiple determination (adjusted  $R^2$ ), which estimates the accuracy of the equations in predicting future responses within the range of applicability of the equations. These two statistics, which range from 0 to 100 pct accurate, are shown in table 13 for the clay equations. The statistics show that the models capture to a satisfactory degree the phenomenon of Cu exchange as a function of the three independent variables.

Table 13.— $R^2$  and adjusted  $R^2$  for clay models, percent<sup>1</sup>

Model	$R^2$	Adjusted $R^2$
Ca montmorillonite ..	99	99
Na montmorillonite ..	99	98
Attapulgitite .....	95	92
Illite .....	96	93
Kaolin .....	94	91

<sup>1</sup>Equation not generated for ripidolite because of very low exchange of Cu at pH 1 and 2.

The regression models were transformed into equations that use the natural variable units of temperature in

degrees Celsius, final pH, and final Cu concentration in grams per liter. Details of the conversion from normalized to natural units are given in the appendix. The transformed equations are as follows:

Ca montmorillonite:

$$\begin{aligned} \text{CuEC} = & -8.1 - 0.1T + 21.4\text{pH} + 32.7\text{Cu} \\ & + 0.04(T)(\text{pH}) - 1.3(\text{pH})(\text{Cu}) - 2.8(\text{pH})^2 \\ & - 4.8(\text{Cu})^2 \end{aligned} \quad (10)$$

Na montmorillonite:

$$\begin{aligned} \text{CuEC} = & -26.4 + 31.0\text{pH} + 32.1\text{Cu} - 2.5(\text{pH})(\text{Cu}) \\ & - 5.1(\text{pH})^2 - 7.3(\text{Cu})^2 \end{aligned} \quad (11)$$

Attapulgitite:

$$\begin{aligned} \text{CuEC} = & 1.9 - 0.2\text{pH} + 0.7\text{Cu} + 0.03(T)(\text{pH}) \\ & + 1.1(\text{pH})(\text{Cu}) \end{aligned} \quad (12)$$

Illite:

$$\begin{aligned} \text{CuEC} = & 2.8 - 0.01T - 2.8\text{pH} + 0.1\text{Cu} \\ & + 0.01(T)(\text{pH}) + 0.8(\text{pH})(\text{Cu}) + 0.6(\text{pH})^2 \end{aligned} \quad (13)$$

Kaolin:

$$\begin{aligned} \text{CuEC} = & 0.4 - 0.01T - 0.04\text{pH} + 0.2\text{Cu} \\ & + 0.004(T)(\text{pH}) - 0.003(T)(\text{Cu}) \\ & + 0.1(\text{pH})(\text{Cu}) \end{aligned} \quad (14)$$

The predicted CuEC's of each clay based on the transformed equations are compared with the observed CuEC's in tables 6 through 10.

## IMPACT OF CATION EXCHANGE

The developed CuEC relationships, equations 10 to 14, can be used to predict the impact of cation exchange on Cu recoveries from an in situ leaching operation. Copper losses can be calculated given an ore body grade, type and percentage of clay in the deposit, solution composition, and pH. An example is given in table 14. The calculations are based on the assumption that all of the Cu in the ore body is extracted into solution and that the solution contacts all of the clay in the ore body. Results presented in table 14 suggest that clays can have a large effect on Cu recovery. Even minimal amounts of Ca or Na montmorillonite could potentially decrease the viability of the operation. Minor amounts of attapulgitite in the ore body would decrease the Cu recovery slightly, but larger amounts of attapulgitite could increase the Cu loss measurably. Losses associated with illite would only be noticeable in bodies containing high illite and low Cu grades.

Operating conditions vary from site to site. If the pH and/or Cu concentration of the pregnant solution are greater than those of the test matrix of this report, the Cu losses would increase. Conversely, lower pH and/or Cu concentration would reduce the loss. Changes in temperature would affect Cu recovery slightly.

As mentioned previously, the effect of competing metal ions, such as Al and Mg, that would be present in an actual in situ leaching solution will be examined in a future study. Competing metal ions may exchange in preference to Cu, thereby reducing Cu exchange losses.

## CONCLUSIONS

This investigation demonstrated that the ability of clays to exchange their adsorbed cations for the valuable Cu ions is potentially detrimental to the success of an acidic in situ leaching operation.

The Cu ion exchange capacity of each clay varied from high to low as follows: Ca montmorillonite > Na montmorillonite > attapulgitite > illite > kaolinite > ripidolite. The montmorillonite clays, because of their relatively high CuEC's, have the potential to exchange a major portion of the dissolved Cu and could render an in situ leaching operation unprofitable. Depending on attapulgitite and illite concentrations in an ore body, measurable losses of Cu ions could occur as a result of these clays. Based on CEC's, the presence of kaolinite and ripidolite in Cu ore

deposits would pose little threat to the recovery of solubilized Cu.

Operating at the highest possible acid concentration and minimizing the recirculation of Cu ions to maintain the lowest possible Cu concentration within the ore body minimizes the exchange of Cu ions into clay matrices. Changes in temperature affect the Cu exchange with the clays slightly.

It should be noted that this research was conducted in the absence of competing metal ions, which would be present in actual in situ leaching solutions. Competing metal ions may exchange in preference to Cu, thereby reducing Cu exchange losses. The effect of competing metal ions will be addressed in a future study.

Table 14.—Effect of clay ion exchange on Cu recovery<sup>1</sup>

(Test matrix conditions: pH, 2.5; Cu conc, 1.8 g/L; temp, 65° C)

Clay concentration, pct	CuEC, meq per 100 g clay	Cu loss per 100 g ore, g	Cu loss, <sup>2</sup> pct at pct Cu levels <sup>3</sup> of—			
			0.2	0.4	0.6	0.8
<b>Ca montmorillonite:</b>						
1 .....	65	0.021	10.5	5.2	3.5	2.6
5 .....	65	.103	51.5	25.7	17.2	12.9
10 .....	65	.207	100	51.7	34.5	25.9
<b>Na montmorillonite:</b>						
1 .....	42	.013	6.5	3.2	2.2	1.6
5 .....	42	.067	33.5	16.7	11.2	8.4
10 .....	42	.133	66.5	33.2	22.2	16.6
<b>Attapulgite:</b>						
1 .....	12	.004	2.0	1.0	.7	.5
5 .....	12	.019	9.5	4.7	3.2	2.4
10 .....	12	.038	19.0	9.5	6.3	4.7
<b>Illite:</b>						
1 .....	4	.001	.5	.2	.2	.1
5 .....	4	.006	3.0	1.5	1.0	.7
10 .....	4	.013	6.5	3.2	2.2	1.6
<b>Kaolinite:</b>						
1 .....	0.8	.0002	.1	.05	.03	.002
5 .....	.8	.0013	.6	.3	.2	.2
10 .....	.8	.0025	1.2	.06	.4	.3

CuEC Cu exchange capacity.

<sup>1</sup>Information for ripidolite not given because of very low exchange of Cu at pH 1 and 2.<sup>2</sup>Cu loss to clay ion exchange.<sup>3</sup>Assumes 100 pct of Cu is leached.

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## APPENDIX.—FACE-CENTERED CUBE MODELING PROCEDURE

The three-variable face-centered cube experiment design in matrix form is shown below in normalized units.

Independent variables:  $\bar{x}_1$   $\bar{x}_2$   $\bar{x}_3$

-1	-1	-1
1	-1	-1
-1	1	-1
1	1	-1
-1	-1	1
1	-1	1
-1	1	1
1	1	1
-1	0	0
1	0	0
0	-1	0
0	1	0
0	0	-1
0	0	1
0	0	0
0	0	0
0	0	0

Geometrically, the points correspond to the corners, faces, and center of a cube. The matrix is designed so that independent estimates of the variable coefficients can be obtained using multiple regression analysis. The general form of the model utilized in this analysis is as follows:

$Y = (\text{constant}) + (\text{linear effects}) + (\text{interaction effects})$

$+ (\text{curvature effects})$

$$= b_0 + \sum_{i=1}^p b_i x_i + \sum_{i=1}^p b_{ij} x_i x_j + \sum_{i=1}^p b_{ii} x_i^2,$$

where  $Y =$  predicted value,

$b =$  coefficients of model,

$x =$  normalized level of variable,

and  $p =$  number of independent variables.

The face-centered cube design allows for the estimation of linear, interaction, and curvature effects. For the estimates to be independent estimates of the effects, however, the regression analysis must be conducted using normalized units. If normalized units are not used, the interaction and curvature variables are highly correlated with their respective linear variables, which does not meet the regression analysis assumption that the independent variables are independent of one another. When normalized units are used, correlations between the linear, interaction, and curvature variables are minimized. The normalization equation is

$$\text{normalized level} = \frac{(\text{variable level} - \text{middle level})}{(\text{high level} - \text{low level})/2}$$

Using temperature as an example, the range of 25°, 50°, and 75° C would correspond to -1, 0, and 1 in normalized units. A temperature of 40° C would correspond to -0.4 in normalized units.

The face-centered cube design used in this report was modified slightly in that 1.00 g of Cu per liter (normalized unit = -0.33) was the middle value of Cu concentration tested in the experimentation (see table 4) rather than 1.25 g of Cu per liter. However, 1.25 g of Cu per liter must still be used as the middle value in the normalization equation (see below).

The regression equations in this report were developed using a stepwise regression procedure with a t-test significance of 0.10 or less required to enter a variable into the equation. The equations were developed using normalized units and variable ranges of temperature from 25° to 75° C, final pH from 1.00 to 3.00, and final Cu concentration from 0.5 to 2.0 g/L according to the matrix design shown above.

When using the models to calculate Cu loss predictions, it becomes somewhat repetitive to normalize the independent variable levels for each calculation. One way to avoid this repetition is to substitute the normalization equations into the normalized regression equations and then simplify the result. For the Ca montmorillonite model, the transformation would be as follows:

$$Y = 52.0 - 1.0 \frac{(T - 50)}{(75 - 25)/2} + 10.9 \frac{(\text{pH} - 2.0)}{(3.0 - 1.0)/2} + 13.7 \frac{(\text{Cu} - 1.25)}{(2.0 - 0.5)/2} + 1.1 \frac{(T - 50)}{(75 - 25)/2} \frac{(\text{pH} - 2.0)}{(3.0 - 1.0)/2} \\ - 0.9 \frac{(\text{pH} - 2.0)}{(3.0 - 1.0)/2} \frac{(\text{Cu} - 1.25)}{(2.0 - 0.5)/2} - 2.8 \frac{(\text{pH} - 2.0)}{(3.0 - 1.0)/2} \frac{(\text{pH} - 2.0)}{(3.0 - 1.0)/2} - 2.7 \frac{(\text{Cu} - 1.25)}{(2.0 - 0.5)/2} \frac{(\text{Cu} - 1.25)}{(2.0 - 0.5)/2}$$

When simplified, this function equals equation 10 for the Ca montmorillonite model. Predictions can be calculated using this equation by entering the variable levels in their natural units. Each of the clay models was transformed in this manner. In the transformation calculations, the

coefficients from the normalized regression equations were carried out to the fourth decimal place and divisions and multiplications were not performed until the end of the calculations to avoid rounding error.

