

## USE OF ZEOLITE TO TREAT ACID ROCK DRAINAGE FROM BRITANNIA MINESITE

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### ABSTRACT

Zeolite mineral is one of the few natural materials which has the inherent capability for ion exchange. A proposal was made and a study carried out to investigate the use of natural zeolite to treat acid rock drainage (ARD) from the abandoned Britannia Minesite. The heavy metal uptake by several zeolites was determined using shake flask and column testing. The most effective zeolite in absorbing copper was a phillipsite from Pine Valley, NV. which is capable of an ARD treatment rate of 410 L per kilogram giving a total copper loading of 760 mg/kg zeolite. Regeneration of zeolite by seawater was also investigated. Sea water elution of the phillipsite was able to remove 95% of the copper loaded. Based on these findings and the average quantity of copper contained in the effluent, it is estimated that 311 tonnes of phillipsite will be required to remove copper from one day's flow of ARD from this site.

## INTRODUCTION

Acid rock drainage (ARD) was first observed at the Britannia Minesite, British Columbia in 1928. The drainage, which contains the heavy metals copper and zinc, is currently discharged into Howe Sound after treatment in a can plant to remove copper. The present precipitation plant is inefficient at removing copper below 20 mg/L, and although zinc can be tolerated in sea water, copper is relatively toxic. Studies in Howe Sound reveal that invertebrate and fish populations are suffering below 140 m depth. Lime treatment could be implemented but only at considerable expense. If copper alone could be removed the water quality would be significantly improved to a point where harmful effects to the environment would be minimal.

Zeolites are a naturally occurring industrial mineral which are capable of exchanging heavy metals and iron for alkali earth metals such as calcium, sodium and magnesium. Due to this capability, the use of zeolite has been proposed for treatment of ARD. Although, free sulphuric acid is generally not neutralised by ion exchange, the buffering capacity of the receiving sea water will mitigate the effects of the acidity. The heavy metals can be eluted from the "loaded" zeolite with sodium chloride or sea water. The process could be very cost effective with sea water being readily available.

## SAMPLE COLLECTION

Twenty litres of sea water were collected from a dock at Horseshoe Bay, and 140 L of ARD water were collected upstream from the can plant at the Britannia Mine Site on January 19, 1992.

Ten zeolite samples from the Allenby Zeolite Deposit near Princeton were provided by T.L. Sadlier-Brown, Suite 500 - 342 Water Street, Vancouver B.C. Three samples with the best cation exchange capacity (CEC) were selected for initial shake flask tests. Three samples were obtained from Ms. Monica Zamzow, Reno Research Center, Bureau of Mines, Reno, NV. One sample was obtained from New World Mines in Idaho. All samples were received screened and dried.

Samples tested are listed in Table 1 with their respective size fraction and CEC.

## METHODS

### Cation Exchange Capacity

Cation exchange capacity for copper was provided by Zamzow and Murphy (1991). The method employed consisted of loading copper solution at a flow rate of 1.3 cm/min (linear flowrate) in a 30 cm by 1.0 cm glass column containing zeolite. The column was repeatedly topped with 500 mL of head solution until the effluent concentration was equal to the influent.

Total cation exchange capacity was conducted on the Allenby samples by the ammonium acetate method described in Black et al. (1965). Total cation exchange capacity and exchange capacity for copper are shown in Table 1.

### Shake Flask Tests

To compare the relative exchange capacity, 2-5 g of zeolite were added to 100 mL of ARD in a 250 mL Erlenmeyer flask. The samples were agitated for 2 h on a gyratory shaker, filtered and analyzed for metal content and pH.

## Column Tests

Two sets of column tests were conducted. The initial test was carried out on columns 3 cm diameter by 40 cm long. One hundred grams of 20-40 mesh AZ-5 zeolite from the Allenby deposit were added to each column. The height of zeolite in the column was approximately 14 cm. Britannia ARD was added to the columns with peristaltic pumps at an initial flow rate of 9 mL/min (equivalent to 12.8 L/m<sup>2</sup>/min). However, due to column plugging the flow rate was decreased to 2.1 mL/min. Flow restriction was thought to be due to precipitant in the ARD which was subsequently filtered after the initial 250 mL was added. ARD was added to the columns until the effluent copper concentration was within 90% of the influent concentration. Elution of the columns was conducted at the same flow rate with sea water to one column and 3% sodium chloride to the other. Samples were taken periodically for copper analysis. Elution was continued until the column effluent copper concentration was equal to the copper concentration in the ARD. Individual aliquot samples were collected during the loading and elution cycles. Composite samples were prepared from aliquots and analyzed for metals. The column loading and elution cycles were repeated 3 times. For the final elution sea water and 3% sodium chloride solution were added until the effluent copper concentration was <0.5 mg/L. The zeolite was then removed from the columns, washed with distilled water, filtered and dried. Zeolite that had been eluted with 3% sodium chloride was screen assayed.

The second column test was conducted in a single column with 50 g of washed phillipsite zeolite. Due to flow restriction and possible contaminate ions experienced with the Allenby column test, the zeolite was washed with distilled water, to remove fines, followed by sea water to remove any exchangeable contaminate cations. The zeolite was then dried at 105°C for 4 h. The column was 60 cm long by 1.3 cm in diameter. The height of zeolite in the column was 51.5 cm. Filtered ARD was pumped into the bottom at a flow rate of 1.7 mL/min (equivalent to 12.8 L/m<sup>2</sup>/min), providing a contact time of 16 minutes. ARD was applied until the effluent copper concentration was equal to the influent. The column was then eluted with sea water, pumped into the bottom of the column at a flow rate of 0.85 mL/min, equivalent to a contact time of 30 minutes. Elution was continued until the effluent copper concentration was <0.5 mg/L. The zeolite was then removed, washed with distilled water, dried and weighed.

## RESULTS AND DISCUSSION

Table 2 shows the water quality of the Britannia Mine ARD and sea water. The concentration of copper, zinc and calcium in the ARD was 13.4, 26 and 397 mg/L, respectively. Sea water contained 7,500 mg/L sodium, equivalent to 1.9% sodium chloride. Calcium was relatively low at 297 mg/L.

Table 2 lists mineralogy, size fraction, Si/Al ratio, CO<sub>2</sub> and CEC of the zeolite samples tested. All samples are clinoptilolites except the Pine Valley sample which is a phillipsite. The cation exchange capacity for copper was 273, 131 and 113 meq/100 g for the Pine Valley, Barstow and Death Valley zeolites, respectively. The total cation exchange capacity for the Allenby samples ranged from 77 to 82 meq/100g. The particle size fraction for the Allenby and New World Mines samples was 20 to 40 mesh, whereas the samples received from the US Bureau of mines were 20 to 65 mesh.

## Initial Shake Flask Tests

Table 3 shows the results of the initial shake flask tests. Of the three Allenby samples AZ-5

showed that greatest affinity for copper, loading 140 mg/kg. Zinc loading was 150 mg/kg for all samples. The impact on pH showed a slight increase from 3.59, for the ARD water, to 3.73 for all Allenby samples. Iron in the ARD water decreased from 1.06 to 0.12 mg/L for the AZ-5 sample. Potassium was also exchanged suggesting this cation may interfere with heavy metal absorption. Potassium decreased from 48 mg/L in the ARD water to the 11 to 15 mg/L range for the Allenby samples. Calcium changed only moderately whereas sodium, the exchanging ion, increased from 6.9 mg/L in the ARD to 41 to 60 mg/L in the Allenby samples. The AZ-5 sample was selected for the column tests to compare sea water and 3% sodium chloride elution. The New World Mines (NWM) sample loaded only 78 mg Cu/kg and 200 mg Zn/kg.

Of the samples received from the US Bureau of mines the Pine Valley phillipsite had the highest affinity for copper at 236 mg/kg absorption compared to 184 and 196 mg/kg for the Barstow and Death Valley samples, respectively. The difference in copper loading for these zeolites is not as great as would be suggested by their CECs shown in Table 1; indicating that interfering ions affect each zeolite's copper loading capacity differently. This is partly due to the ion sieve affect of the zeolite structure (Breck 1974). Zamzow (1991) found that calcium above 310 mg/L interfered with copper uptake from a solution containing 10 mg/L copper. Zinc loading was highest for the Death Valley sample with 300 mg/kg compared to 240 and 260 mg/kg for the Barstow and Pine Valley samples, respectively. Calcium removed from the ARD water by the Death Valley and Barstow clinoptilolites was 209 and 213 mg/L, respectively, compared to only 119 mg/L for the Pine Valley phillipsite.

The relative exchange capacity of the cations analyzed in the shake flask tests for the Allenby samples ranged from -1.84 to 1.97 meq/100 g, indicating that most of the exchangeable ions were accounted for by the cations analyzed. The Death Valley, Barstow and Pine Valley samples with net exchanges of -7.57, -7.20 and -20.53 meq/100g suggest that ions not included in the analysis, were exchanged with sodium (e.g. barium, strontium, nickel or cadmium). In addition, the change in pH, as noted in Table 3, from 3.59 for the ARD to 4.72, 4.55 and 5.02 for the Death Valley, Barstow and Pine Valley treated samples, respectively; indicates that hydrogen ion was exchanged for sodium ions. Hydrogen ion loading based on pH change indicates that 1.19, 1.14 and 1.23 meq/100g were exchanged by the Death Valley, Barstow and Pine Valley zeolites, respectively.

The relative exchange capacity for metals is a function of the initial metal concentration and ion selectivity. For the metals analyzed in this study the relative decreasing selectivity is: Fe > Cu > Zn > Ca > Mg > Na > K (Breck 1974). The selectivity of copper, zinc and calcium are very similar, but since the calcium concentration is almost 30 times higher than copper, the meq of calcium exchanged is much higher. The data shows that calcium interferes with copper and zinc loading. Nevertheless, when comparing the relative percent removal of iron, copper, zinc and calcium, as shown in Table 4, the order of selectivity is verified with maximum percent removal occurring with iron and least percent removal occurring with calcium. Zinc and calcium selectivity was reversed for the Barstow and the Pine Valley zeolites. The percent removal data shows that, for the Britannia ARD water, calcium interferes more with zinc uptake than it does with copper, and that the interference from iron would be very significant if it were present at higher concentrations. Iron in the ARD was in the Fe<sup>+3</sup> oxidation state as indicated by the high Eh (600 mV) shown in Table 2. The ion exchange capacity for ferrous iron is probably considerably less than it is for ferric iron. Consequently, the successful treatment of other ARD sites which contain high iron may depend on the iron oxidation state. For the Britannia ARD it follows that if calcium could be removed from the ARD prior to ion exchange, the uptake of copper and zinc would be much higher. Attempts were made to remove calcium by bubbling in carbon dioxide;

however, at the low pH, calcium carbonate would not precipitate. In addition, phosphate was added as trisodium phosphate to remove calcium, but again, due to low pH calcium phosphate would not precipitate until the pH was above 6.0 where copper was also precipitating.

### Column Tests

Column tests to compare 3% sodium chloride with sea water elution were conducted with the Allenby AZ-5 sample. Table 5 shows the results of copper analysis of aliquot samples taken during the first loading and elution tests. The columns were designated as "sodium chloride" and "sea water" to indicate the eluent used. The volume of ARD applied to the columns before the effluent copper concentration was within 90% of the feed concentration was 2,347 and 2,298 mL, with copper loadings of 128 and 130 mg/kg for the sodium chloride and sea water columns, respectively. The results are consistent with the shakeflask test loading which was 140 mg/kg (Table 3).

Elution with sodium chloride solution and sea water was conducted until the effluent copper concentration was equal to that contained in the ARD. The amount of copper eluted was the same for both columns with 55% removal. Copper analysis of aliquot eluent samples showed maximum copper concentrations of 55.4 and 54.2 mg/L in the sodium chloride and sea water columns with an overall 4 fold increase in copper concentration over the ARD water. Approximately 70 mL of eluent was applied in both cases. The results are summarized in Table 5 along with the second and third loading/elution cycles.

On the second cycle both columns loaded considerably more copper even though 45% of the copper was left on the zeolite after the initial elution. Loading for the sodium chloride and sea water columns was 314 and 339 mg/L, respectively. Accounting for the 45% copper not eluted, total loading was 372 and 398 mg/kg for the sodium chloride and sea water columns, respectively. The second elution removed 58 and 54% of the copper from the sodium chloride and sea water columns, respectively. On the third and final loading 237 and 244 mg/L copper were loaded on the columns, and when accounting for copper not eluted during the first and second elutions the total loading was 428 and 427 mg/L for the sodium chloride and sea water columns, respectively. Copper eluted in the third cycle was carried out until the concentration in the eluent was <0.5 mg/L. Although it was expected that all the loaded copper would be removed, only 87 and 86% of the copper loaded in the last cycle was eluted from sodium chloride and sea water elution columns, respectively. Thus, a total of 191 and 218 mg/L copper were not eluted from the sodium chloride and sea water columns, respectively.

A subsequent washing with distilled water and screen assay of the salt water zeolite column material showed that the zeolite had been slaking during the loading and elution cycles. Screen assay results showed that 31.2% of the material was passing 40 mesh compared to the initial material which was 100% between 20 and 40 mesh. Flow restrictions observed early in the test work were initially attributed to precipitant in the ARD water which was thereafter filtered out; however, the major contributor to flow restriction was more likely due to the slaking that was occurring. The increased loading capacity was probably due to the increased zeolite surface area caused by slaking, and the poor copper elution results may have been caused by flow restrictions which prevented contact of loaded zeolite with eluent. Nevertheless the copper loading and elution rates were very similar for both the 3% sodium chloride and sea water columns indicating that sea water is an effective eluent for regeneration of zeolite.

The second column test, conducted with the Pine Valley phillipsite through one loading/elution

cycle, was to estimate the quantity of zeolite for full scale treatment of Britannia ARD water. Fifty grams of sea water washed phillipsite was poured into the column as a slurry and loaded with ARD water and subsequently eluted with sea water. A total of 20.5 L of ARD water were required to totally load the column with 760 mg Cu/kg zeolite. The subsequent elution volume was 2 L before the elution effluent concentration was <0.5 mg/L. Sea water elution was able to remove 95% of the copper loaded. Flow was maintained throughout the test, and visual observation of the zeolite when discharged from the column showed no apparent slaking.

## CONCLUSIONS AND RECOMMENDATIONS

Column tests on Allenby AZ-5 zeolite, employed through 3 cycles of loading and elution to compare sea water and 3% sodium chloride solution elution showed that sea water containing 1.9% sodium chloride was as effective an eluent as 3% sodium chloride solution. Zeolite sample AZ-5 from the Allenby deposit would be unsuitable for the water treatment of Britannia ARD due to slaking. Calcining and/or acid washing may solve this problem.

Phillipsite was found to be the best zeolite for copper uptake. Column loading and elution tests showed that 95% of the 760 mg Cu/kg zeolite could be eluted with sea water. Using the elution figure of 720 mg/kg for the loading capacity, the quantity of zeolite required to treat the Britannia ARD water can be determined. Information obtained from Steffen, Roberston and Kirsten (BC) Incorporated on the Britannia water drainage system indicated that the average annual flow rate to the can plant was 518 L/h with an average copper concentration of 18 mg/L.

Thus the average quantity of copper in effluent per day is:

$$518\text{m}^3/\text{h} \times 1000\text{L}/\text{m}^3 \times 24\text{h}/\text{day} \times 18\text{ mg Cu}/\text{L} \times 1\text{g}/1000\text{mg} = 224,000\text{ g Cu}/\text{day}$$

Zeolite required to load one days copper is:

$$224,000\text{ g Cu}/\text{day} \times 1\text{ kg}/720\text{ mg Cu loaded} \times 1000\text{ mg}/\text{g} \times 1\text{ tonne}/1000\text{ kg} = 311\text{ tonnes}.$$

Thus, 311 tonnes of Pine Valley phillipsite are required. With a bulk density of 0.670 tonnes/m<sup>3</sup> (Zamzow 1991), a tankage volume of (311 tonnes/0.670 tonnes/m<sup>3</sup>) 464 m<sup>3</sup> is required.

The cost of zeolite, excluding shipping, is approximately \$400 US/tonne. The cost of the treatment plant, operation and maintenance should be offset by the value of the copper which would be more efficiently recovered. Less zeolite could be used depending on the elution frequency. However, the flow rate and copper concentration are average values, and unless surge tanks are installed to equalize flow, additional zeolite should be available.

The envisaged process would include 5 to 10 chambers containing zeolite connected in series. The ARD water would be filtered to remove iron precipitants so that plugging of the zeolite does not occur. The system would be fully automated. As the first chamber becomes completely loaded with copper, it would be removed from the circuit and sea water introduced to elute copper and regenerate the zeolite. The eluted chamber would then be placed back in the circuit and become the column through which the final effluent would flow. Each chamber would be eluted in turn as it became loaded. Sea water from the elution step would be recycled until the copper concentration in the eluent was maximized. Only then would the copper loaded sea water be transferred to the can plant for copper removal. Effluent from the can plant would be discharged to the receiving waters without further treatment. Can plant effluent which would

contain ~10 mg/L copper could not be re-treated with zeolite due to the high sodium and iron concentration. However, it is expected that the zeolite/can plant process would remove 90 to 95% of the copper.

Further work is required to address variables that were not included in this study. These include:

- maximum feed flow rates
- regeneration flow rate
- maximum eluent copper concentration
- temperature effects
- effect of repeated loading/elution cycles

Some of the variables can be addressed in laboratory scale tests; however, a small pilot study conducted at the site would be required for the final design.

A program should be set up to investigate all zeolite deposits in B.C. These should be analyzed for whole rock analysis and x-ray diffraction to identify the mineral type. Standard zeolites can be obtained from Mr. Fred Mumpton Department of the Earth Sciences, SUNY-College at Brockport, Brockport, New York 14420, USA, to aid in identification. The effects of pretreatment such as acid washing and calcining should be included. Other potential applications for zeolite such as odour control, ammonia removal and soil nutrient retention should also be investigated.

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**TABLE 1**  
**Properties of Zeolite Samples**

Sample	Mineral Type	Size Fraction (Mesh)	CEC (meq/100g)	Si/Al Ratio	CO <sub>2</sub> (%)
Allenby Deposit					
-AZ5	Clinoptilolite	20-40	77	5.35	<0.2
-AZ8	Clinoptilolite	20-40	82	13.46	-
-AZ10	Clinoptilolite	20-40	80	16.08	-
Pine Valley, NV	Phillipsite	20-65	*273	3.6	-
Barstow, CA.	Clinoptilolite	20-65	*131	5.1	-
Death Valley, CA.	Clinoptilolite	20-65	*113	5.4	-
New World Mines	Clinoptilolite	20-40	-	4.47	-

\*Cation Exchange Capacity for copper.

**TABLE 2** **Britannia Mine ARD and Sea Water Quality**

Parameter	Britannia ARD	Sea Water
pH	3.59	7.74
Eh (millivolts)	600	-
Acidity (mg CaCO <sub>3</sub> /L)	180	-
Alkalinity (mg CaCO <sub>3</sub> /L)	< 1	-
Redox Potential (millivolts)	560	-
Conductance (umhos/cm <sup>2</sup> )	2,050	36,300
Sulphate (mg SO <sub>4</sub> /L)	1,730	-
Copper (mg/L)	13.4	-
Zinc (mg/L)	26	-
Iron (mg/L)	1.06	-
Magnesium (mg/L)	77	927
Sodium (mg/L)	6.9	7,500
Calcium (mg/L)	397	297
Potassium (mg/L)	4.8	138



TABLE 3  
Results of Shake Flask Tests

Zeolite	g of Zeolite per 100 mL of ARD	pH	Cu (mg/L)	*Cu Loading (mg/kg)	Zn (mg/L)	*Zn Loading (mg/kg)	Fe (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Ca (mg/L)
ARD Water	0	3.59	13.4	-	26	-	1.06	77	48	6.9	397
Allenby AZ-5	2	3.73	10.6	140	23	150	0.12	73	11	60	373
AZ-8	2	3.73	11.8	80	23	150	0.20	73	15	41	400
AZ-10	2	3.73	11.2	110	23	150	0.20	75	12	60	384
NWM	5	4.00	9.5	78	16	200	-	-	-	-	-
Death Valley	5	4.72	3.6	196	11	300	<0.05	63	21	395	188
Barstow	5	4.55	4.2	184	14	240	<0.05	70	8.4	387	184
Pine Valley	5	5.02	1.6	236	13	260	<0.05	90	8.6	397	278

\*mg Cu/kg X 0.00315 = meq Cu/100 g, and  
mg Zn/kg X 0.00306 = meq Zn/100 g

TABLE 4  
Percent Removal of Iron, Copper, Zinc and Calcium from Britannia ARD

Zeolite	Percent Removal			
	Iron	Copper	Zinc	Calcium
Allenby AZ-5	88.7	20.9	11.5	6.0
AZ-8	81.1	11.9	11.5	0
AZ-10	81.1	16.4	11.5	3.2
Death Valley	>95	73.1	57.6	52.6
Barstow	>95	68.7	46.2	53.6
Pine Valley	>95	88.1	50.0	55.1

TABLE 5  
Summary of Column Tests

Loading/ Elution Cycle	3% Sodium Chloride Elution						Sea Water Elution					
	Load- ing Vol (L)	Cu Loaded (mg/kg)	Equiv. Treat- ed Vol. (L/kg)	Elution Vol. (L)	Cu Eluted (mg/kg)	Percent Eluted (%)	Load- ing Vol (L)	Cu Loaded (mg/kg)	Equiv. Treat- ed Vol. (L/kg)	Elution Vol. (L)	Cu Eluted (mg/kg)	Percent Eluted (%)
Allenby AZ-5												
1	2,350	128	9.6	0.318	70	55	2,300	130	9.7	0.323	71	55
2	6,765	314	23.4	0.570	182	58	6,630	339	25.3	0.569	182	54
3	9,058	272	20.3	2.37	237	87	8,125	244	18.2	2.23	209	86
Phillipsite	-	-	-	-	-	-	20.5	760	57.6	2.0	720	95