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Remediation of Acid Rock Drainage by Regenerable Natural Clinoptilolite

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Abstract Clinoptilolite is investigated as a possible regenerable sorbent for acid rock drainage based on its adsorption capacity for Zn, adsorption kinetics, effect of pH, and regeneration performance. Adsorption of Zn ions depends on the initial concentration and pH. Adsorption/Desorption of Zn reached 75% of capacity after 1–2 h. Desorption depended on pH, with an optimum range of 2.5 to 4.0. The rank of desorption effectiveness was EDTA>NaCl>$NaNO_3$> NaOAc>$NaHCO_3$>Na_2CO_3>NaOH>$Ca(OH)_2$. For cyclic absorption/desorption, adsorption remained satisfactory for six to nine regenerations with EDTA and NaCl, respectively. The crystallinity and morphology of clinoptilolite remained intact following 10 regeneration cycles. Clinoptilolite appears to be promising for ARD leachate treatment, with significant potential advantages relative to current treatment systems.

Keywords zinc · acid drainage · remediation · clinoptilolite · sorbent regeneration

1 Introduction

Acid rock drainage (ARD) is one of the most serious environmental problems faced by the mining industry worldwide. The environmental damage is devastating (D. Banks, Younger, Arneson, Iversen, & S. Banks, 1997; García, Morena, Ballester, Blázquez, & González, 2001) and adversely affecting highways (Li, 2005). ARD encompasses heavy metals and inorganic compounds at concentrations well above allowable limits in water quality guidelines for the protection of aquatic life. The low pH and high metal concentrations threaten fragile aquatic life forms. Dissolved metals like copper, zinc and cadmium can be toxic to flora and fauna.

Several remediation techniques have been developed to reduce effluent acidity and sulfur, and to immobilize heavy metal ions. These include alkalinity addition (Bellaloui, Chtaini, Ballivy, & Narasiah, 1999; Bernier, 2005; Duchesne & Doye, 2005; Kongolo, Benzaazoua, de Donato, Drouet, & Barrès, 2004; Xenidis, Mylona, & Paspaliaris, 2000), bioremediation (García et al., 2001; Lindow & Borden, 2005), passivation (Belzile, Maki, Chen, & Goldsack, 1997)

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which involves coating the individual particles with an oxidation preventive substance such as acetylacetone, sodium silicate, lignin, and oxalic acid, passive systems and effluent treatment (Burgess & Stuetz, 2002). However, no remediation scheme has been cost-effective for all mine locations. Most remediation techniques generate additional solid waste for disposal.

Zeolites have been intensively studied in recent decades for catalysis, ion exchange, adsorption, molecular sieves, dehydration and rehydration. Applications include petroleum refining, pollution control, energy conservation, agriculture, aquaculture, mining, and metallurgy (Mumpton, 1981). A locally available and inexpensive soil—mineral zeolite-clinoptilolite—has high metal-adsorption capacity and significant buffering capacity (Lai, 2005; Li, 2002, 2005; Li, Chen, & Grace, 2005). It could have potential as a sorbent for ARD, especially if the clinoptilolite could be regenerated on site.

Thirty-nine naturally occurring zeolites have been studied (Bernal & Lopez Real, 1993), with clinoptilolite being one of the most abundant. Its relatively low cost, cation exchange capacity, and selectivity of cations have led to its use in waste water treatment (Baykal, 1998; Komarowski & Yu, 1997; Lahav & Green, 1998; Nguyen & Tanner, 1998; Veigh & Weatherley, 1999), agriculture and aquaculture (Kithome, Paul, Lavkulich, & Bomke, 1999a; Kithome, Paul, Lavkulich, & Bomke, 1999b; Milan et al., 1997); radioactivity treatment (Faghihian, Ghannadi Maraeh, & Kazemian, 1999); and adsorption of heavy metal ions Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+} and Mn^{2+} (Malliou, Loizidou, & Spyrellis, 1994; Ouki & Kavannagh, 1997; Yuan, Seyama, Soma, Theng, & Tanaka, 1999). Clinoptilolite has been found (Lai, 2005; Li, 2002, 2005; Li et al., 2005) to have high adsorption capacity for Cu, Zn and Al from artificial solutions and natural ARD (pH 3.3). It is chemically stable in acidic environments with pH>2.0. Clinoptilolite has the highest Si/Al molar ratio (4.3–5.3) among its group of zeolites (Beck, 1996) and is less easily destroyed by losing Al at low pH than other zeolites (Boles et al., 1977).

Previous studies have emphasized the removal of heavy metals using zeolite. Little research (Erwe, Mavrov, & Chmiel, 2003) has been conducted to investigate regeneration techniques for the contaminated zeolite by which the adsorbed contaminants can be removed at high concentrations and the sorbent restored to a state where it can be reused. Greater understanding of desorption of heavy metals is needed to assess possible regeneration. The goal of this project was to explore clinoptilolite as a potential ARD sorbent. The objectives were to (1) determine the adsorptivity of clinoptilolite for Zn and the effect of pH; (2) examine adsorption and desorption kinetics of heavy metals; (3) explore possible extraction chemicals for removing heavy metals from loaded clinoptilolite; and (4) assess regeneration of contaminated clinoptilolite in multiple adsorption/desorption cycles. The results provide information for the design of a more sustainable cost-effective system for on-site ARD treatment.

2 Materials and Methods

The clinoptilolite was provided by Canmark International Resources from Sunday Creek, near Princeton, B.C. Physical and chemical characteristics are shown in Table I. Acid rock drainage from the Britannia Mines near Squamish, British Columbia was used to study adsorption and desorption of clinoptilolite. Acid rock drainage from Highway 97C, (Coquihalla Merritt-to-Peachland connector), B.C. (designated as HW97C ARD) was employed for detailed adsorption, desorption, and regeneration experiments.

The batch equilibrium test technique (US EPA, 1987) was used to investigate Zn^{2+} and Cu^{2+} adsorption characteristics. The solution/solid ratio was 10:1 (by weight) as recommended in the standard EPA procedures and shaken for 24 h to achieve chemical equilibrium.

The adsorption kinetics of clinoptilolite were determined via the same procedures as for the batch equilibrium test, with nine different durations from 10 to 1,440 min, for HW97C ARD to which 100 ppm Zn had been added. The desorption kinetic tests followed the same procedure as the adsorption kinetic tests. The samples were spiked with 690 mg Zn/kg clinoptilolite and were submitted for desorption with 20 g/l NaCl extractant solution.

Sodium chloride (NaCl), carbonate ($NaCO_3$), bicarbonate ($NaHCO_3$), hydroxide (NaOH), acetate (NaOAc) and disodium ethylenediaminetetraacetic acid (EDTA) were tested as possible extractants from clinoptilolite samples spiked with Zn^{2+} and Cu^{2+} (extractant test program using Britannia Mine ARD is

Table I Physiochemical characterization of the clinoptilolite (Lai, 2005)

Physicochemical properties	
pH (1:1 soil:deionized distilled water ratio)	7.6
pH (1:2 soil:0.01 M $CaCl_2$ ratio)	8.3
CEC (cmol/kg or meq/100 g)	121
Exchangeable cations (cmol/kg or meq/100 g)	
Ca^{2+}	46
Na^{+}	44
Mg^{2+}	2.76
K^{+}	24.3
NH_4^{+}	10.3
Base saturation (%)	183
Specific surface area (m^2/g)	64
Carbonate content (% by weight)	1.54

summarized in Table II). Each Zn ion-spiked sample was washed with an extractant solution for 1 h, with shaking, to reach equilibration. The most effective extractant solutions were selected and then optimized for their pH, concentration, buffer and H^+ (see Tables III, IV, and V).

EDTA at a concentration of 4 g/l at pH 3 and 30 g/l NaCl at pH 3 were selected as extractant solutions for regeneration of clinoptilolite spiked with 280 mg Zn concentration/kg clinoptilolite, in cyclic sorption/regeneration studies. One-hour contact was chosen for each cycle, based on the adsorption and desorption tests. All tests were performed in duplicate at 25±2 °C. The pH of each equilibrated solution was measured by an Orion model 420-A pH meter. The Zn concentration in the supernatant was determined by a Video 22 Thermo Jarrell Ash aa/ae Spectrophotometer-Model 957.

The concentrations of adsorbed or desorbed metal were obtained from the differences between their initial and final concentrations in the supernatant. The amount of each metal desorbed from the clinoptilolite (in mg/kg soil) was calculated from:

$$q = \frac{VC}{M} \qquad (1)$$

where C was the final solution concentration (mg/l), V the solution volume (l), and M the sorbent mass (kg).

Acid digestion was conducted according to the procedures described by Li (1999) on samples after the 10th desorption period. This allowed the heavy metals still attached to the contaminated clinoptilolite after desorption to be determined to eliminate discrepancies from the desorption residuals. Mass balances on the metals in the supernatant and contaminated clinoptilolite were calculated to check the accuracy of the determinations.

Clinoptilolite was prepared at random orientations for X-ray difftraction (XRD) scanning. The powder was mounted on the square concavity of a glass slide and set up on the XRD stage. The scanning was at a controlled room temperature of 22°C using a Rigaku RINT 2000 X-ray diffractometer with CuKα radiation, at 40 kV and 30 mA based on the 2°θ/θ method with a scan speed of 1°/min. For Scanning Electron Microscopy (SEM), dry thin dispersed clinoptilolite powder was pressed onto a carbon-typed 10-mm Φ aluminium stub. This sample was then carbon-coated with 2-nm thickness using TB500-Carbon Flash Evaporation system EMSCOPE with string×1 filament type at a 3-A outgas current. The image was observed by SEM (JEOL JSM-5200LV) with an energy dispersive sample on an X-ray spectrometer (Philips-ECX PV 9800STD). For Transmission Electron Microscopy (TEM), clinoptilolite was dispersed in a droplet of distilled waster, and then a copper microgrid was

Table II Summary of selection of extractant test program using Britannia Mine ARD

Extractant	NaCl	NaOH	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$	NaCl				$NaNO_3$				EDTA			
pH	11	12.7	12.3	11.3	8.2	6.1	8.0	6.0	8.0	5.3	5.0	5.7	8.4	4.7	6.9	4.5	6.9
Concentration (g/l)	10					10	10	20	20	10	10	20	20	2.5	2.5	5.0	5.0
Desorption time (h)	24					1											
Cu/Zn concentration adsorbed onto C (mg/kg C)	2,350/1,600					350/310											

Contaminant solution pH 3.8.

Table III Test program conditions for desorption of metals from clinoptilolite contaminated with Zn from a pH 3.5 ARD solution; NaCl as extractant

Parameter	Desorption kinetics	Concentration effect	pH effect	H^+ ion effect
Extractant	NaCl	NaCl	NaCl	HCl
pH	3	3	2, 3, 4, 5, 7	2, 3, 4, 5
Concentration (g/l)	20	5, 10, 20, 40, 60	30	NaCl (0)
Desorption time (min)	10, 20, 40, 80, 160, 300, 600, 1,200, 1,440	60	60	60
Spiked Zn concentration onto C (mg/kg C) [a]	250	250	250	250

[a] C denotes Clinoptilolite.

carefully placed on top of the droplet. After 1 min the TEM grid was removed for drying. TEM images of clinoptilolite were taken by a JEOL JEM-2000Ex Electron Microscope at a 200 kV accelerated voltage.

3 Results and Discussion

3.1 Adsorption capacity, adsorption/desorption kinetics

Previous work (Lai, 2005; Li, 2002, 2005) indicated that clinoptilolite has a high metal adsorption capacity at different pHs, when the acidity was augmented by HNO_3 with Britannia Mine ARD as the background solution. Zn is of major concern along HW97C. Its adsorption isotherm, Figure 1 (in which C denotes clinoptilolite), further demonstrates that clinoptilolite has the ability to retain Zn ions and that the amount adsorbed is a function of the initial Zn concentration, in agreement with previous findings (Curkovic, Cerian-Stefanovic, & Filipan, 1997; Langella, Pansini, Loizidou, & Grigoropoulou, 2001).

The kinetics of clinoptilolite adsorption are important with respect to whether this material could be suitable as a reactive bed or barrier material. Kinetic tests were carried out with a solution containing both Cu and Zn in natural ARD (pH 3.9) from Britannia Mine. Figure 2 shows the Cu and Zn adsorption as functions of time in a stirred-batch system where the initial Cu and Zn concentrations were 131 and 137 mg/l, respectively. The results indicate that adsorption was almost complete within 120 min, in agreement with a previous study (Lai, 2005) which reported that sorption of heavy metals by natural zeolite was essentially complete after shaking for 1–2 h. In view of these findings, all subsequent adsorption periods were 1 h.

The affinity of clinoptilolite for heavy metals is based on physical adsorption (Curkovic et al., 1997). Adsorption has been found to occur by ion exchange and to be reversible. Figure 3 presents desorption kinetic results for extraction by a 20-g/l NaCl solution at pH 3.0. The samples were spiked with 250 mg Zn/kg C, with Highway 97C ARD as the background

Table IV Test program conditions for desorption of metals from clinoptilolite contaminated with Zn from a pH 3.5 ARD solution; EDTA as extractant

Parameter	Concentration effect	pH effect	Buffer effect	H^+ ion effect
Extractant	EDTA	EDTA	EDTA	EDTA
pH	4	2, 3, 4, 4.7	3	3
Concentration (g/l)	1, 2, 4, 6, 8	4	4	4
Desorption time (h)	1	1	1	1
Buffering solution	–	HOAc	NaOAc–HOAc[b]	HNO_3
Concentration of buffering solution (M)	–	–	0.1, 0.3, 0.5, 0.7, 1	–
Spiked Zn concentration onto C (mg/kg C)	246	246	246	246

[b] OAc designates acetate.

Table V Test program conditions for cyclic tests

Parameter	Cyclic desorption/ adsorption with NaCl	Cyclic desorption/ adsorption with EDTA
Extractant	NaCl	EDTA
pH	3	3
Concentration (g/l)	30	4
Desorption time (h)	1	1
Adsorption time (h)	1	1
Buffering solution	HCl	HNO_3
Spiked Zn concentration onto C (mg/kg C)	280	280
Desorption cycles	10	10
Adsorption cycles	11	11

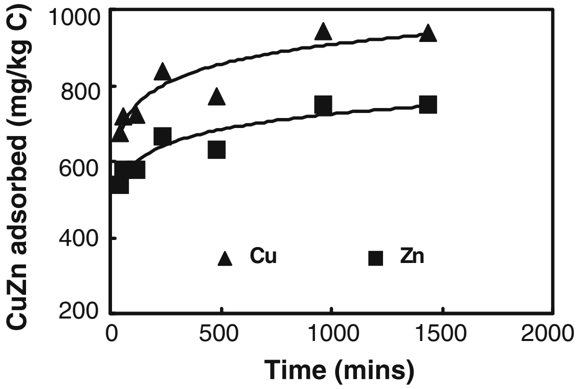


Figure 2 Heavy metal adsorption by clinoptilolite as a function of time. Contaminant solution Cu (131 mg/l) and Zn (137 mg/l) with real ARD (Britannia Mine) background, initial pH 3.8.

matrix. No copper was added, since Cu is not of concern for this ARD.

The results in Figure 3 follow a similar trend as those in Figure 2. Within 24 h, the Zn desorption increased by 34 mg/kg clinoptilolite. Most removal was complete within 80 min, again consistent with the adsorption process. This similarity suggests that the adsorption/desorption processes are nearly reversible, i.e.,

$$M_s^{2+} + 2Na_c^{+} \rightleftharpoons M_c^{2+} + 2Na_s^{+} \qquad (2)$$

where M^{2+} designates the heavy metal ion, and subscripts s and c denote the "solution" and "clinoptilolite" phases. The exchanging groups responsible for the desorptive capacity of zeolite are known to be dispersed randomly in aqueous solution throughout the pores and capillaries of the zeolite (Kithome, Paul, Lavkulich, & Bomke, 1998). Given the importance of being able to cycle rapidly between adsorption and desorption, the desorption time was limited to 1 h in subsequent experiments.

3.2 pH effect on adsorption

Three initial Zn^{2+} concentrations—93, 735, 1,290 ppm—were tested to investigate the effect of pH between 1.0 and 5.0 on adsorption. The results in Figure 2 and the adsorption isotherm in Figure 4 confirm that the adsorption is affected by the original Zn concentration, possibly because most sorption is due to physical sorption at low pH, with H^+ ions

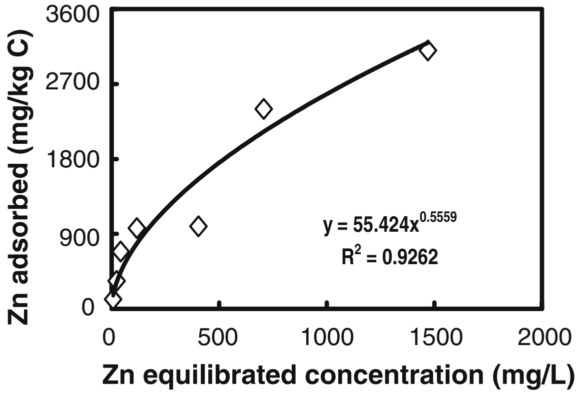


Figure 1 Adsorption of Zn ions on clinoptilolite with HW97C ARD (pH 3.5) after 24 h equilibration.

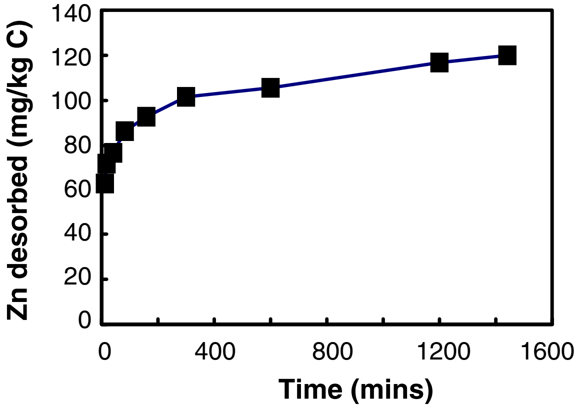


Figure 3 Heavy metal removal with time in NaCl solution of concentration 20 g/l, pH 3.0.

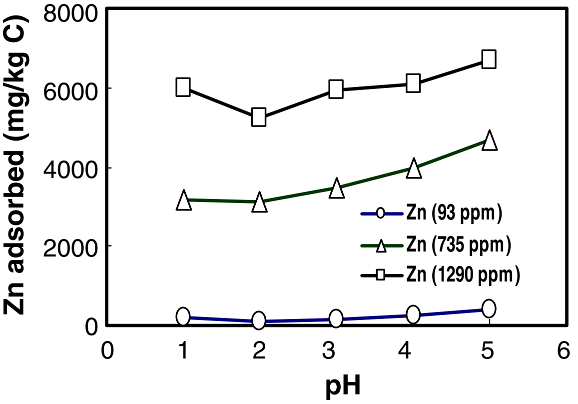


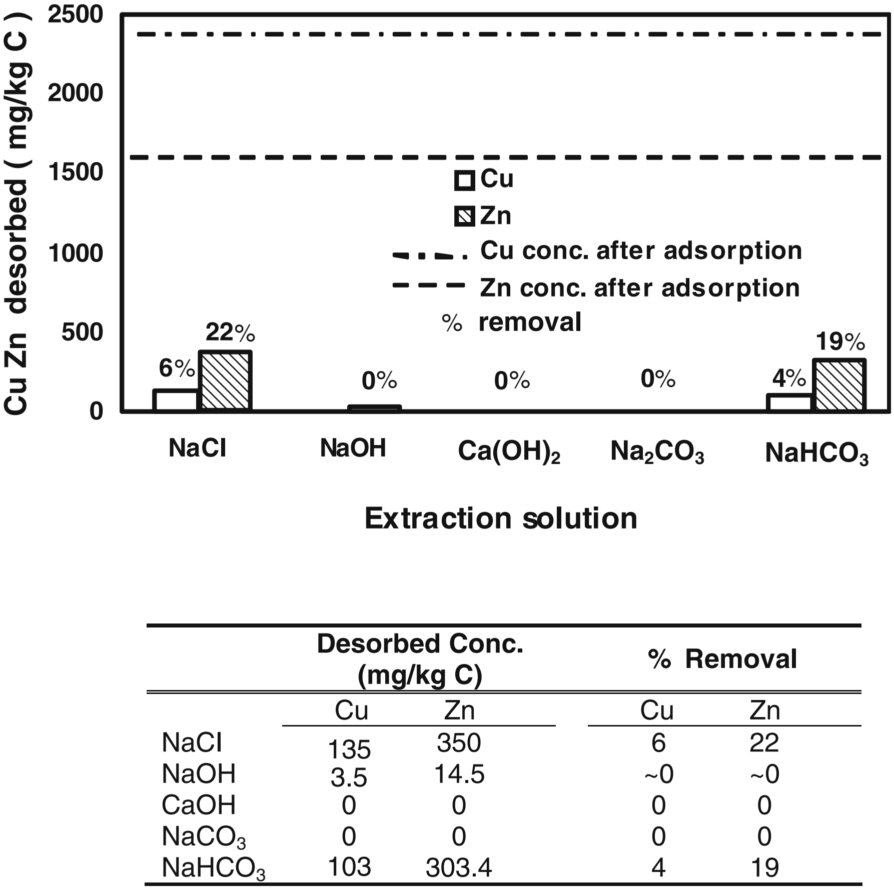
Figure 4 pH and concentration effect on adsorption of Zn ions on clinoptilolite with HW 97C ARD as background solution.

competing with Zn^{2+} ions for adsorption sites. The efficiency of adsorption of Zn was higher for pH≥3, possibly due to fewer H^+ ions being available at high pH, providing less competition with Zn^{2+} for the limited number of adsorption sites on the clinoptilolite surface.

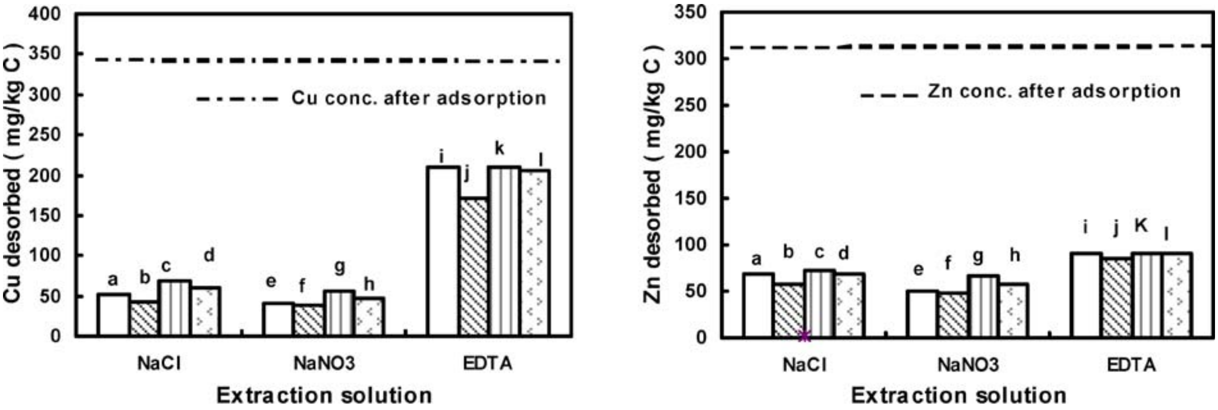
3.3 Efficiency of various extractant solutions

Desorption efficiencies for Cu and Zn from contaminated clinoptilolite using extractant solutions containing NaCl, NaOH, $Ca(OH)_2$, Na_2CO_3, and Na_2HCO_3 at alkaline pHs are compared in Figure 5. These samples were contaminated with Britannia mine ARD, with extra Cu and Zn added to bring each of their concentrations to 1,000 ppm (Table II shows the actual concentrations). The Cu and Zn retained in clinoptilolite were 2,350 and 1,600 mg/kg, confirming the finding of Lai (2005) that the selectivity for Cu^{2+} > that of Zn^{2+}. The results at alkaline pH indicate that all extractants removed less than 25% of the metals. NaCl had the highest removal of Cu and Zn from metal-loaded clinoptilolite (6% removal for Cu and 22% for Zn) of the various

Figure 5 Comparison of desorption efficiency for Cu and Zn from contaminated clinoptilolite using NaCl, NaOH, $Ca(OH)_2$, $NaCO_3$ and $NaHCO_3$ in extractant solutions at a concentration of 10 g/l in each case.



	Desorbed Conc. (mg/kg C)		% Removal	
	Cu	Zn	Cu	Zn
NaCl	135	350	6	22
NaOH	3.5	14.5	~0	~0
CaOH	0	0	0	0
$NaCO_3$	0	0	0	0
$NaHCO_3$	103	303.4	4	19



Symbol	Extractant	Conc. (g/L)	pH	% Removal Cu	% Removal Zn
a	NaCl	10	6.1	14	22
b	NaCl	10	8.0	12	18
c	NaCl	20	6.1	20	24
d	NaCl	20	8.0	17	22
e	$NaNO_3$	10	5.6	11	16
f	$NaNO_3$	10	8.2	11	16
g	$NaNO_3$	20	5.6	16	22
h	$NaNO_3$	20	8.2	14	19
I	EDTA	2.5	4.7	60	29
j	EDTA	2.5	6.9	49	27
k	EDTA	5	4.7	60	29
l	EDTA	5	6.9	58	29

Figure 6 Comparison of desorption efficiency for Cu and Zn from contaminated clinoptilolite using NaCl, Na_2NO_3 and EDTA extractant solutions at various pHs and concentrations.

extractants, followed by $NaHCO_3$. There was insignificant Zn and Cu removal using the Na_2CO_3, NaOH and $Ca(OH)_2$ extractant solutions.

Figure 6 compares the effectiveness of removing adsorbed Cu and Zn from clinoptilolite by NaCl, $NaCO_3$ and EDTA extractant solutions at various pHs and concentrations. The tested samples were contaminated with Britannia mine ARD, where the Cu and Zn were artificially increased to a design concentration of 100 ppm each (see Table II). These more realistic concentrations were used in all subsequent tests. Figure 6 shows that EDTA removed 60% of the copper and 29% of the zinc from the contaminated clinoptilolite. There was some influence of the EDTA concentration (2.5 vs. 5.0 g/l) on the removal. Whereas the NaCl solution desorbed more Cu and Zn from the contaminated clinoptilolite at pH 6.1 than at pH 8.1, varying the NaCl concentration (10 vs. 20 g/l) had little effect. At high Na concentration and low pH, there were more Na^+ and H^+ ions in the solution. This promoted ion exchange for the Zn and Cu from the clinoptilolite. $NaNO_3$ had a slightly lower removal efficiency than NaCl, but it had the same trend with respect to pH and concentration. The results show that the concentration, extractant chemical and pH all affected the removal efficiency from metal-loaded clinoptilolite. EDTA was the most effective extractant among the extractants tested.

3.4 Optimization of extraction solutions—EDTA and NaCl

Preliminary experiments conducted to find the most suitable extraction chemicals and optimum conditions using Britannia Mine ARD indicate that the order of desorption effectiveness is: $EDTA > NaCl > NaNO_3 > NaOAc > NaHCO_3 > Na_2CO_3 > NaOH > Ca(OH)_2$. These preliminary tests also showed that the concentrations and pHs of the extractants can play major roles. Desorption of Zn and Cu from clinoptilolite was found to depend on pH, with an optimum range of 2.5 to 4.0.

3.4.1 EDTA Extraction Solution

As noted above, EDTA was the most effective extractant for blackflushing metal-loaded clinoptilolite. The reaction of metal with EDTA can be expressed as:

$$M^{2+} + H_2Y \rightleftharpoons M^{2+}Y^{2-} + 2H^+ \qquad (3)$$

where M^{2+} designates the heavy metal ion, and H_2Y^{2-} represents EDTA. The fully deprotonated form of EDTA binds to the metal ion. The equilibrium constants for metals are very large ($10^{18.8}$ for Cu^{2+} and $10^{16.5}$ for Zn^{2+}) (http://tardiscsudhedu/fromero/chemistry/complex). Hence the reactions shift to the right. This process is pH-dependent (http://tardiscsudhedu/fromero/chemistry/complex). The optimization for EDTA extraction solution (including concentration, pH, buffering and H^+ ion effects) is summarized in Figure 7a–d.

EDTA concentrations of 1, 2, 4, 6, and 8 g/l at pH 4.0 were tested for their influence on the desorption efficiency. Figure 7a shows that 121 mg of Zn/kg clinoptilolite and 131 mg of Zn/kg clinoptilolite were desorbed by EDTA at concentrations of 4 and 8 g/l, respectively. As EDTA tends to complex metal ions in 1:1 metal-to-EDTA complexes, higher extraction solution concentrations do not significantly increase Zn desorption. Hence, the EDTA concentration was chosen as 4 g/l.

The effect of pH on Zn desorption from clinoptilolite with EDTA in the extraction solution was investigated at pH adjusted by HOAc to 2.0, 3.0, 4.0 and 4.7. A maximum desorption of 142 mg of Zn/kg clinoptilolite was obtained for pH 3 (Figure 7b). EDTA contributed to the greater selectivity for heavy metal cations. At high pH, metal ions tend to precipitate, preventing formation of a complex, lowering the rate of desorption and reducing the ability to be exchanged. At much lower pH, the EDTA-Metal complexes tended to dissolve, increasing the concentration of cations, causing the desorption to be reversible. In the desorption process, any increases of hydrogen ions might cause the metal

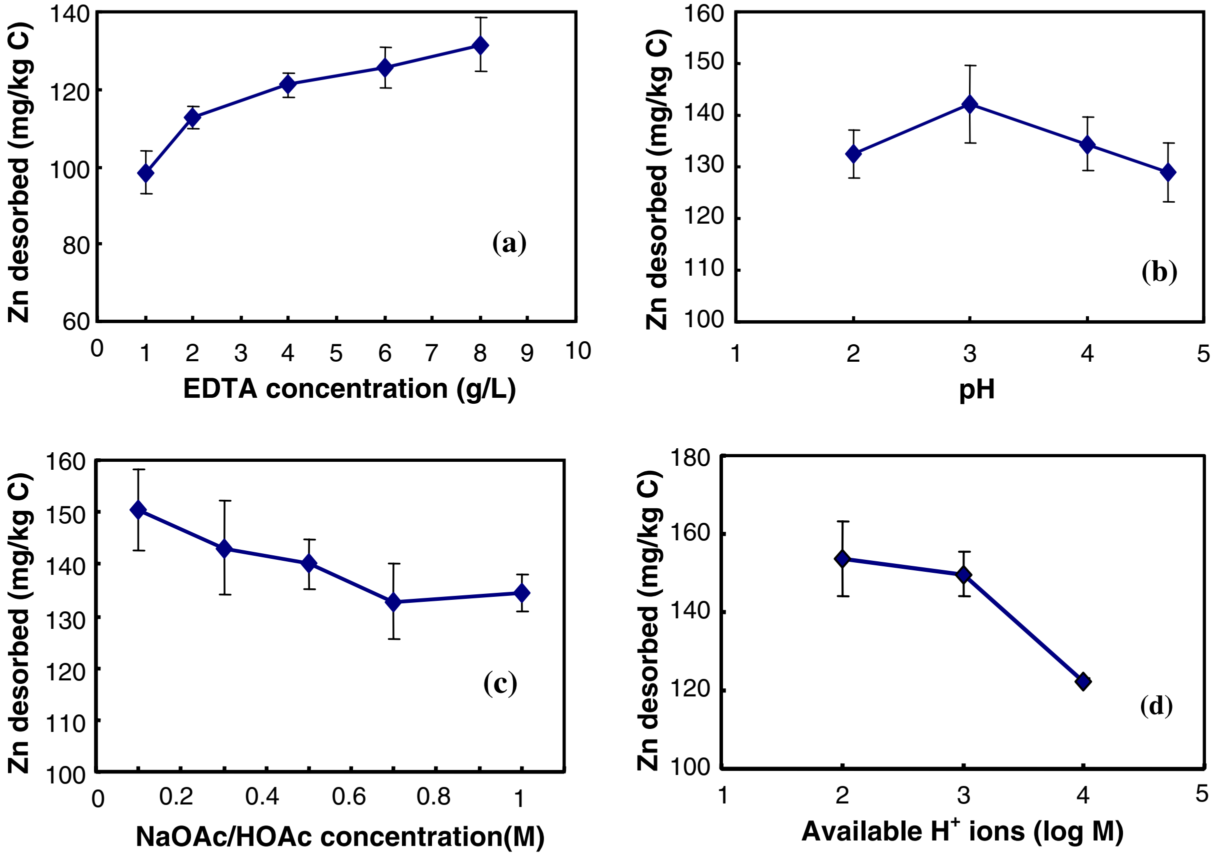


Figure 7 Optimization of EDTA for Zn removal from loaded clinoptilolite: (a) EDTA concentration effects at pH 4, (b) effect of concentration 4 g/l, with pH adjusted by HOAc, (c) effect of concentration of buffer (NaOAc–HOAc) with an EDTA concentration of 4 g/l at pH 3, (d) H^+ ion effects at a EDTA concentration of 4 g/l, with pH adjusted by HNO_3.

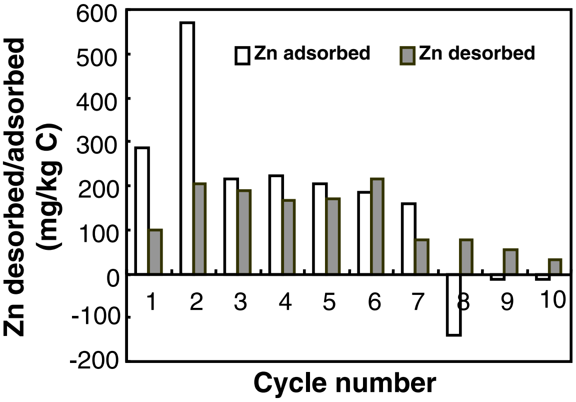


Figure 8 Comparison of individual adsorption/desorption in cyclic system with EDTA. Extractant solution EDTA of concentration 4 g/l, pH 3.0, contaminant solution in 1:10 (solid:water) ratio, initial pH 3.5 and initial Zn concentration 86 mg/l.

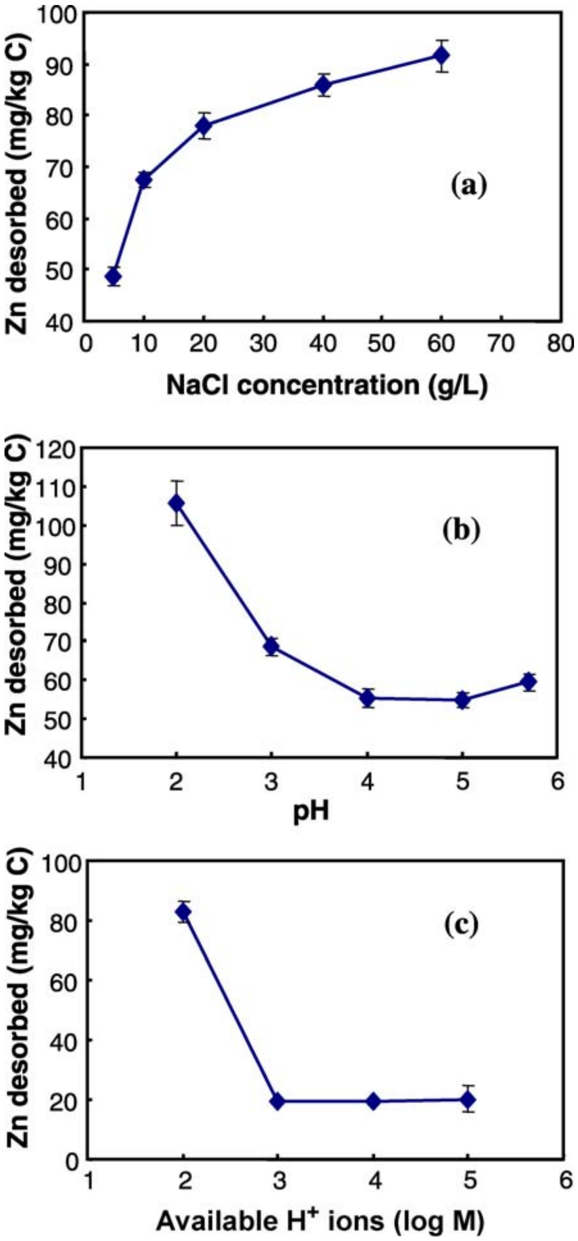


Figure 9 Optimization of NaCl extraction for removal of Zn from loaded clinoplilolite: (a) concentration effect of NaCl at pH 3 (pH was adjusted by HCl); (b) effect of pH at concentration 30 g/l NaCl, with pH adjusted by HCl; (c) H^+ ion effects with HCl as the only source of H^+ ions.

complex to dissociate (http://tardiscsudhedu/fromero/chemistry/complex). Therefore, a buffer was employed to maintain constant pH and prevent the formation of metal hydroxides. Furthermore, the formation of hydrogen ions as a reaction product would cause the solution pH to decrease and the desired reaction to cease or even reverse, unless the solution is buffered. NaOAc–HOAc buffer solutions at different concentrations were examined to find the effects of the buffer on Zn removal from contaminated clinoptilolite in a 4 g/l aqueous EDTA extraction solution at pH 3. Figure 7c indicates that the Zn removal efficiency decreased with increasing buffer solution concentration, in agreement with our preliminary experimental results. The greatest Zn removal was 150 mg/kg of clinoptilolite at a buffer concentration of 0.1 M. A higher concentration did not produce greater removal, contrary to a previous finding (R. S. Li & L. Y. Li, 2000).

The effect of H^+ on heavy metal desorption in an EDTA extraction solution was investigated by employing HNO_3 at pHs of 2, 3 and 4 with an EDTA concentration of 4 g/l. Figure 7d portrays a decrease of desorption with increasing pH. Compared to Figure 7b in which HOAc was used to adjust pH, the desorption of Zn from clinoptilolite was similar (149 vs. 142 mg/kg clinoptilolite, Figure 7b and d). The performance was also nearly the same as for the buffered EDTA extraction solution at low NaOAc concentration. This finding might be due to: (1) The high concentration of H^+ may cause the soil edge to break down, liberating aluminum, which has a much higher replacing power because of its high valence and low ionic radius (Yong, Mohamed, & Warkentin, 1992); Al^{3+} ions would then replace absorbed copper and zinc ions. (2) Free H^+ ions can dissolve metal–organic compounds, complex and hydrous oxides,

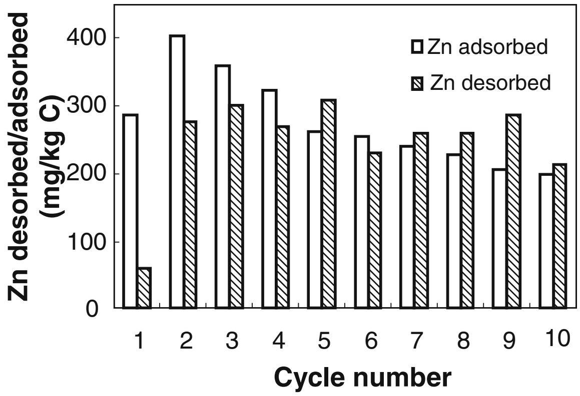


Figure 10 Comparison of adsorption/desorption in successive cycles with NaCl. NaCl concentration 30 g/l, pH 3, extraction solution pH adjusted by HCl, contaminant solution initial pH 3.5, Zn concentration 86 mg/l.

releasing Cu^{2+} and Zn^{2+} ions (R. S. Li & L. Y. Li, 2000). This result is consistent with the preliminary tests. Therefore, HNO_3 was chosen to adjust the pH to a desired value of 3, simplifying the procedure.

3.4.1.1 Cyclic desorption/adsorption of Zn with EDTA

Results of a cyclic desorption/adsorption test with an EDTA concentration of 4 g/L at pH 3.0 appear in Figure 8, with desorption and adsorption times both 1 h. There were 11 adsorption and ten desorption periods. After the first regeneration, desorption and adsorption increased significantly, with a removal of 202 mg Zn/kg clinoptilolite and an adsorbed mass ratio of 569 mg Zn/kg clinoptilolite in the second cycle. After the second cycle, the desorption and adsorption decreased slowly, but perceptibly, with each successive cycle. By the seventh cycle, the adsorption was only 158 mg Zn/kg clinoptilolite, indicating that the sorptive capacity was nearing exhaustion. Figure 8 indicates that desorption of Zn exceeded adsorption after three cycles. It also shows negative adsorption after seven cycles, probably due to a change in surface charge or structure of the clinoptilolite.

Table VI Comparison of NaCl and EDTA extractants

Extractant	NaCl	EDTA
Adsorption/Desorption ability after regeneration (mg Zn/kg C)	250–300	~200
Regeneration cycles	10	6
Cost ($/kg)	0.12–0.18[a]	2–3[b]
Impacts on environment	–	Extract metals

[a] Source: Canadian Tire.

[b] http://protex.en.akubaba.com/offerdetail/50687858/sell_EDTA_EDTA2Na.Htmla-inc.com

Table VII Summary of mass balance results for cyclic desorption/adsorption systems

Extractant	NaCl	EDTA
A. Total desorbed ($\sum m_d$), (mg/kg clinoptilolite)	2,457	1,275
B. Total adsorbed ($\sum m_a$), (mg/kg clinoptilolite)	2,757	1,672
C. Retained on clinoptilolite ($\sum m_a - \sum m_d$) = m_r (mg/kg clinoptilolite)	480	414
D. Difference (mg/kg soil)=B−A−C	−180	−17
E. Difference (%)=(−D/B)×100%	6.5%	~1%

3.4.2 NaCl Extraction Solutions

Test results for NaCl extraction solutions are summarized in Figure 9 for pH 3 with different concentrations of NaCl. Figure 9a shows that the Zn desorption changed little after the NaCl concentration exceeded 20 g/l, so 30 g/l was chosen as the NaCl concentration. The influence of pH on the desorption in NaCl extraction solution was investigated with initial pHs of 2, 3, 4, 5 and 5.7, varied by adjusting the concentration of HCl. The highest desorption mass ratio of 105 mg Zn desorbed/kg clinoptilolite corresponds to a pH of 2. Figure 9b shows that the desorption improved at low pH. The mechanism of desorption is ion exchange. Heavy metal ions are more soluble at lower pH, thus promoting ion exchange and increasing desorption. At pH <2.5, clinoptilolite tends to leach ions from its structure (Lai, 2005; Li, 2005). It is impractical to apply such low pHs in *in-situ* environmental treatment.

The effects of H^+ ion on the desorption process were investigated at various pHs using HCl to adjust the acidity to the designated pHs. Figure 9c indicates that desorption decreases with increasing pH. Desorption of 83 mg of Zn/kg C was observed at pH 2, somewhat less than the 105 mg of Zn/kg in Figure 9c at the same pH with NaCl. In the desorption process, the main exchange ion is Na^+. Hence, sodium ions assist the desorption.

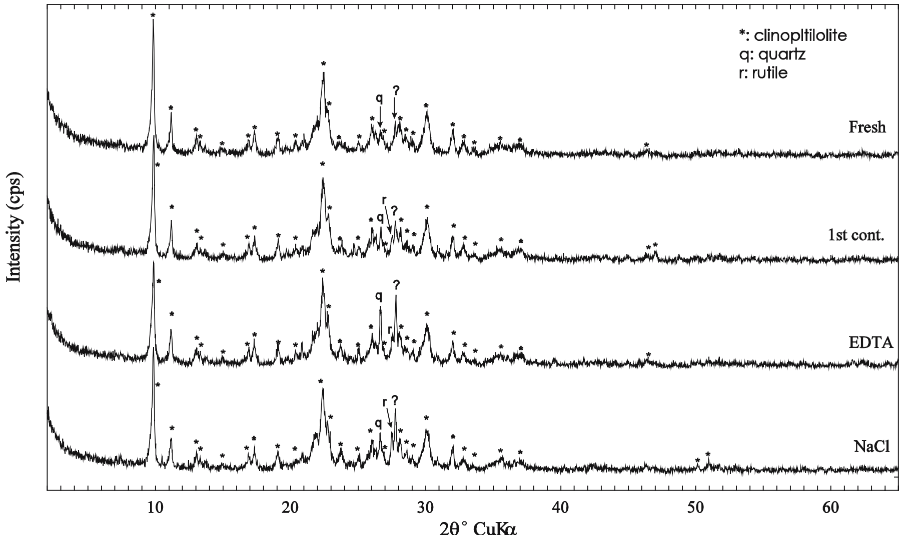


Figure 11 X-ray diffraction patterns of clinoptilolite at four different conditions: (a) fresh (nontreated); (b) after first contamination, i.e., after Zn adsorption; (c) after 10 cycles of adsorption/desorption with EDTA; and (d) after 10 cycles of adsorption/desorption with NaCl.

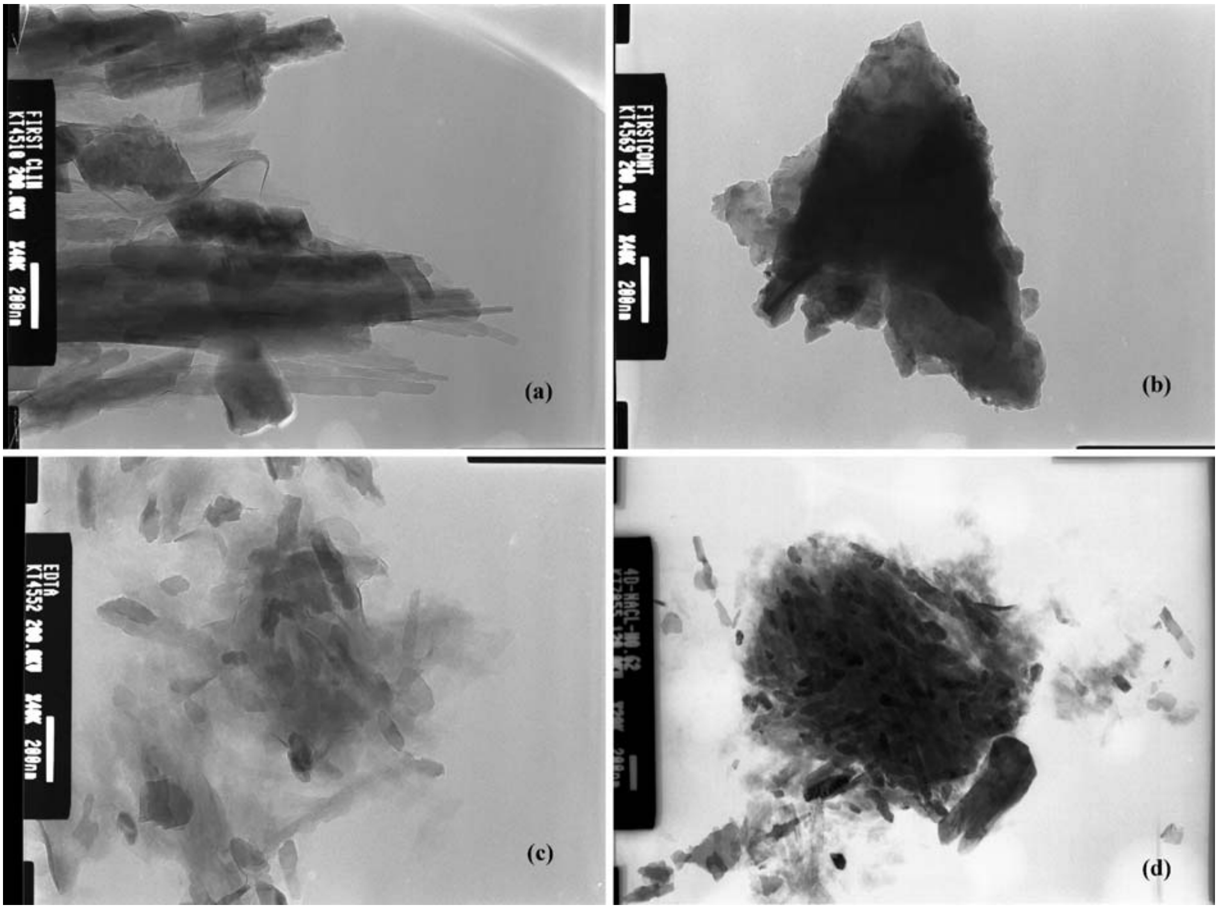


Figure 12 Transmission electron microscopy (TEM) images of clinoptilolite: (a) untreated, (b) after first contamination, i.e., after Zn adsorption, (c) after 10 cycles of adsorption/desorption with EDTA, (d) after 10 cycles of adsorption/desorption with NaCl.

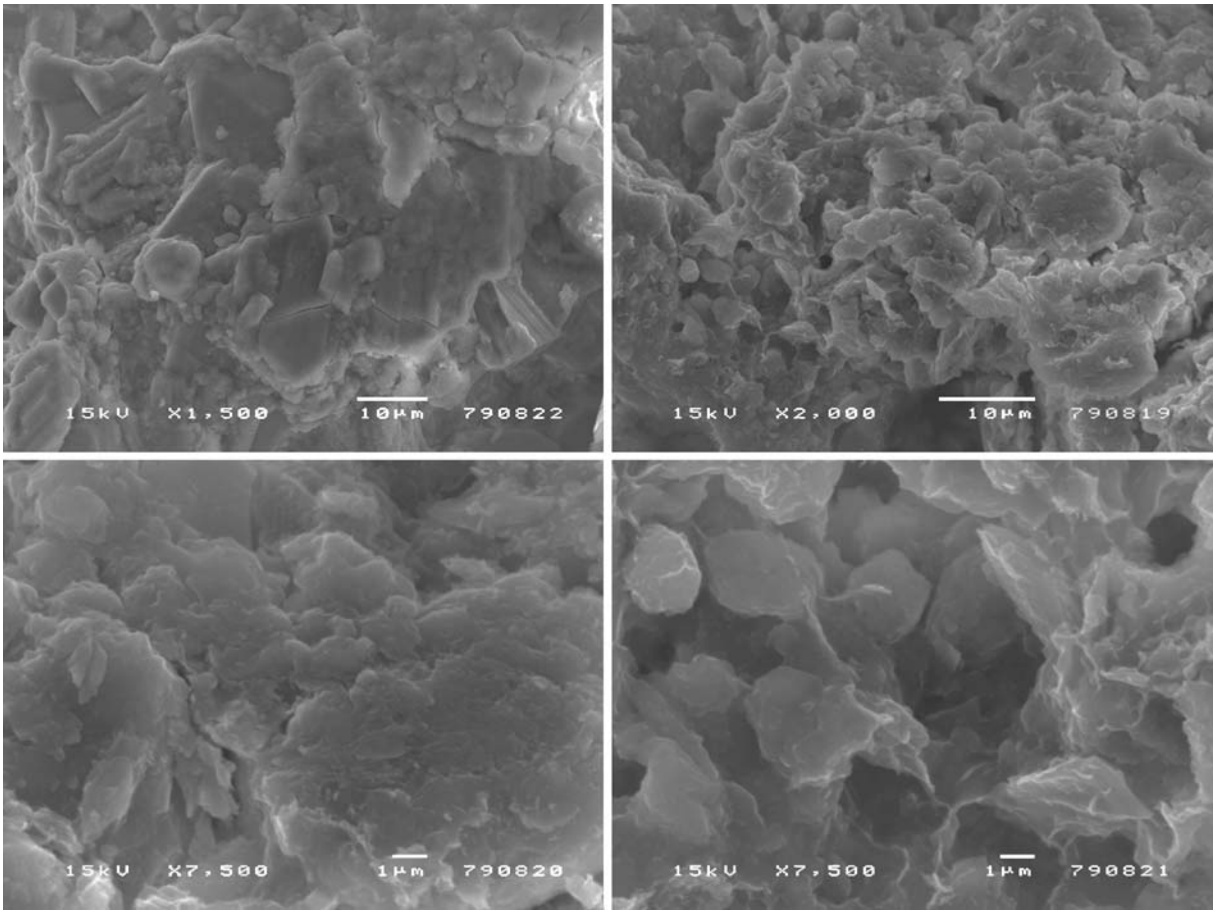


Figure 13 Scanning electron microscopy images of non-treated clinoptilolite.

3.4.2.1 Cyclic desorption/adsorption of Zn with NaCl Results of a cyclic desorption/adsorption test with a NaCl concentration of 30 g/l at pH 3.0 are shown in Figure 10. There were eleven adsorption and ten desorption periods, the same as for the EDTA cyclic desorption/adsorption trials. After the first regeneration, desorption and adsorption increased significantly, with 278 mg Zn removed per kg clinoptilolite and an adsorbed mass ratio of 405 mg Zn/kg clinoptilolite in the second cycle. Beyond the second cycle, the desorption remained relatively constant within the range 250 to 300 mg Zn/kg clinoptilolite. Adsorption decreased slowly, but perceptibly, with each successive cycle. By the eleventh cycle, adsorption was only 140 mg Zn/kg clinoptilolite, indicating that the sorptive capacity of the clinoptilolite was nearing exhaustion. Figure 10 indicates that desorption exceeded adsorption after seven cycles, but it did not show a negative adsorption like EDTA. The fact that the desorption exceeded the adsorption after the seventh cycle probably reflects a change in clinoptilolite surface charge or structure. The effective lifetime of the sorbent appears to be ~10 cycles for the conditions investigated. Further study is needed to examine the lifetime of the zeolite over broader ranges of conditions.

Table VI summarizes the NaCl and EDTA extraction results in terms of regeneration cycles, cost and environmental impact. Figures 8 and 10 show that the NaCl performed better than the EDTA solution after the second cycle. NaCl surpassed EDTA in the regeneration of zeolite and is less costly. Clinoptilolite pretreatment using 1 M NaCl solution is recommended. For natural clinoptilolite, the adsorption sites are various ions such as Mn, K and Mg. The NaCl treatment homogenizes the

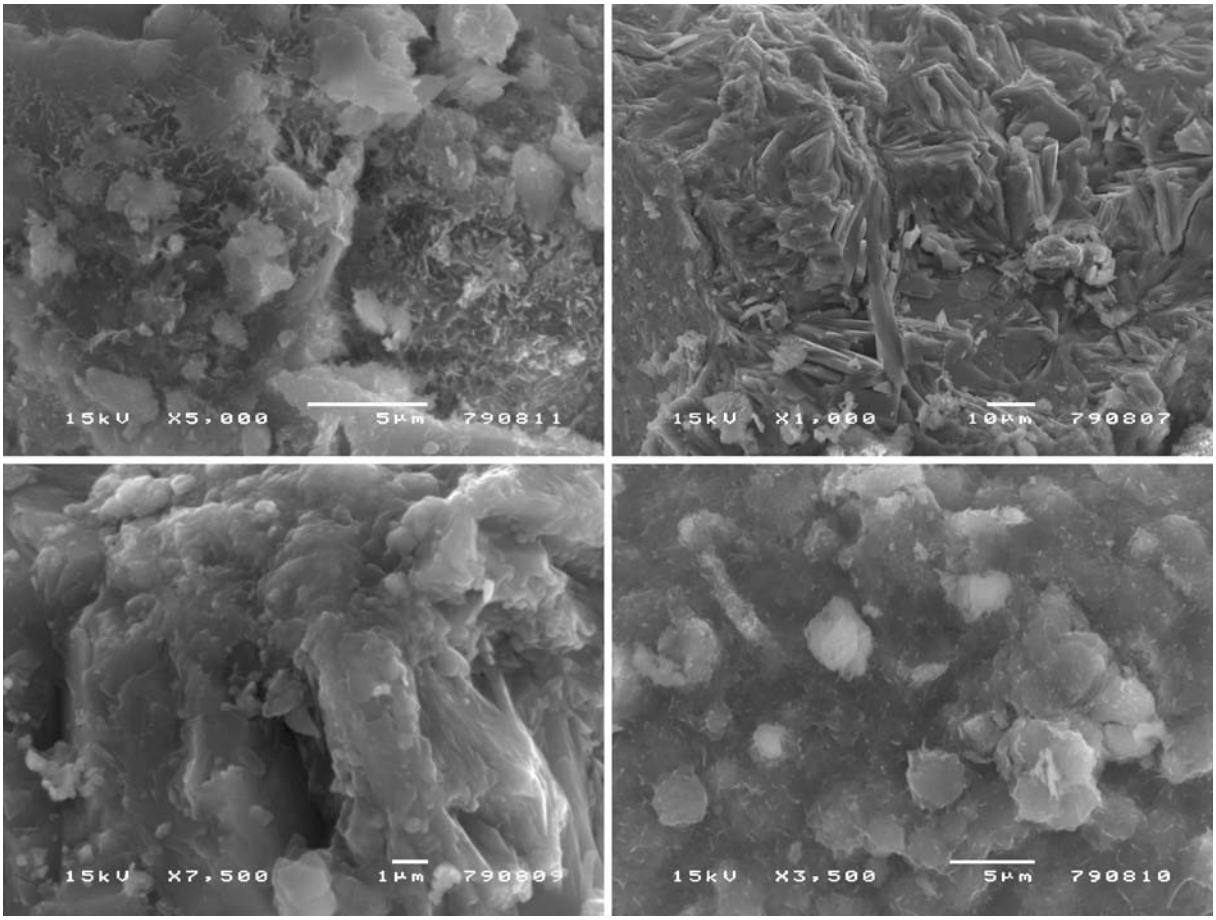


Figure 14 Scanning electron microscopy images of clinoptilolite after first contamination, i.e., after Zn adsorption.

adsorption site, as seen in the regeneration test where the second adsorption of Zn ions improved greatly after initial desorption by NaCl.

3.4.3 Mass Balance in Cyclic Adsorption/Desorption Systems

A mass balance after each desorption cycle gives

$$m_d + m_r = m_a \tag{4}$$

where m_d is the heavy metal desorbed, m_r the heavy metal retained on the soil, and m_a the heavy metal adsorbed (all in mg/kg clinoptilolite). The amounts adsorbed and desorbed were determined in batch adsorption/desorption tests; m_r was measured by total digestion.

The mass balance after 10 cycles using EDTA for clinoptilolite regeneration should give $\left(\sum m_a - \sum m_d\right) = m_r$, i.e., the amount retained should equal the summation of the amounts absorbed over these cycles minus the summation of amounts desorbed over the same cycles. The $\sum m_d$ value is 1,275 mg/kg clinoptilolite, whereas m_r from acid digestion of the samples after desorption in the tenth cycle is 414 mg/kg clinoptilolite, and $\sum m_a$ is 1,672 mg/kg clinoptilolite. The difference is only 17 mg/kg clinoptilolite for the EDTA system at pH 3.0. The overall discrepancy (~1%) is small enough that the results are consistent with respect to the overall mass balance. The discrepancy is larger (6.5%), but still acceptable, for the aqueous NaCl solution extraction (Table VII).

3.5 Morphology changes

Clinoptilolite samples were examined before and after cyclic adsorption/desorption tests by XRD, SEM and TEM. The samples were: (1) nontreated clinoptilolite,

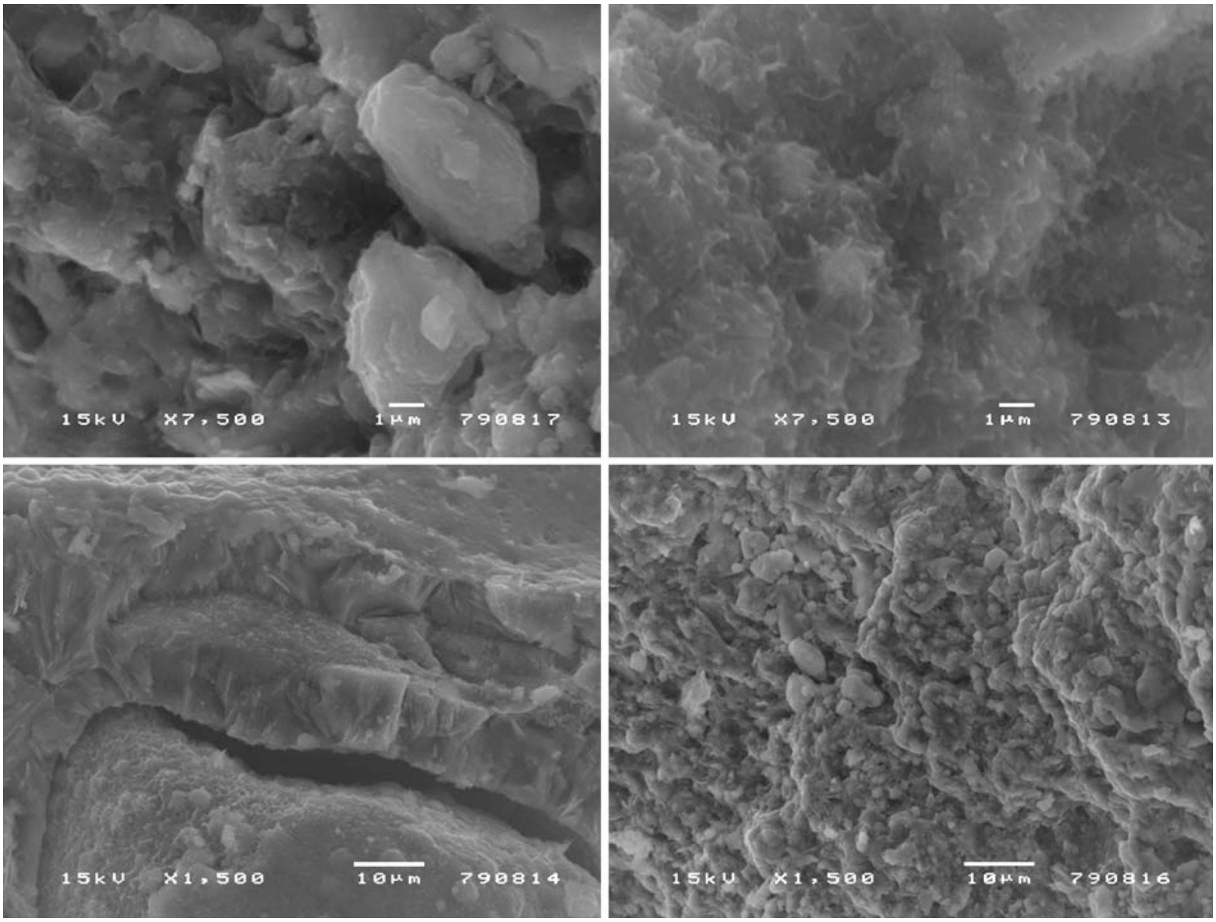


Figure 15 Scanning electron microscopy images of clinoptilolite after 10 cycles of adsorption/desorption with EDTA.

(2) first cycle contaminated clinoptilolite, (3) after 10.5 cycles, regeneration using EDTA, and (4) after 10.5 cycles, regeneration using NaCl.

XRD patterns for nontreated clinoptilolite, initial contamination, and after 10.5 cycles, regeneration using both EDTA and NaCl, appear in Figure 11. These indicate that the framework of clinoptilolite was not altered by cyclic adsorption/desorption. However, the peak intensity of clinoptilolite after treatment seems to have decreased slightly, possibly due to leaching of Al^{3+}. The cyclic adsorption/desorption results (Figures 8 and 10) indicate that the adsorption capacity was reduced drastically by the 7th cycle of EDTA regeneration and by the 11th cycle for NaCl regeneration. However, the XRD results show that the decreased capacity was not due to any change of integrity of the clinoptilolite. Instead it may have been due to changes in surface properties. Further research is needed to explain the decrease in sorption/regeneration ability.

For SEM results, see Figures 13 to 16 (Supporting Information, SI). TEM images of fresh clinoptilolite, after the 1st adsorption, and after cyclic regeneration by EDTA and NaCl solutions appear in Figure 12. Fresh clinoptilolite has a flaky appearance with sharp edges with fine materials attached, likely amorphous (Figure 12a). Aggregation of particles can be observed for the 1st contamination clinoptilolite samples (Figure 12b); no clear shape of the particles can be identified due to the high density and thickness of the aggregates. Mixed morphology is observed with EDTA-treated samples (Figure 12c). Aggregates are seen, some retaining their original appearance. There are also smaller particles. Regenerated particles have smoother edges than untreated ones. Figure 9d shows that there are no thinner particles of the kind observed

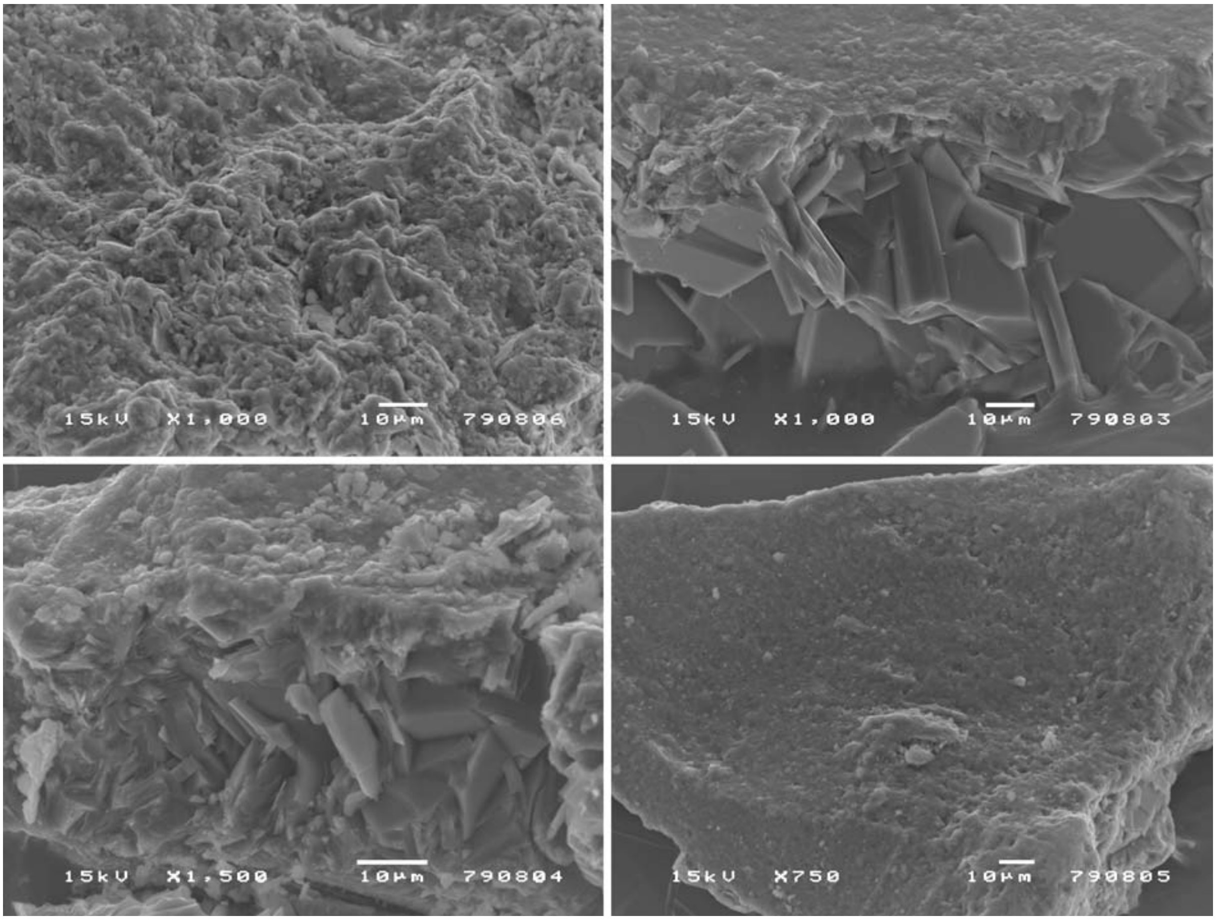


Figure 16 Scanning electron microscopy images of clinoptilolite after 10 cycles of adsorption/desorption with NaCl.

after clinoptilolite was treated with NaCl. Generally, clinoptilolite particles have a high electrical density, i.e., they are thicker than originally, larger in size and mostly rounded.

In our tests, net absorption of Zn became negative after seven cycles for EDTA regeneration, whereas it remained positive, but was drastically reduced, after 10 cycles for NaCl regeneration. This may indicate that zinc is being displaced by more tightly held species. The sorption/regeneration treatment appears to change the surface properties of the clinoptilolite as demonstrated by the SEM and TEM images. EDX (X-ray Electron Dispersion) with SEM and electron diffraction pattern with TEM may help in the future to determine the Al/Si ratio for different treatment conditions to determine the extent to which the clinoptilolite has been altered. Further tests are needed to determine whether the clinoptilolite can be completely regenerated at this stage. XRD and TEM could be useful to examine the crystallinity and morphology after treatment.

4 Conclusions and Recommendations

- Clinoptilolite was able to remove metal cations from Britannia Mine and Highway 97C ARD. Batch equilibrium adsorption tests showed that the ability to adsorb metal ions was related to the metal concentrations and the pH of the extracting solution.
- Desorption of Zn and Cu from clinoptilolite was found to depend on pH, with an optimum pH range of 2.5 to 4.0.
- The rank of desorption effectiveness was EDTA> $NaCl > NaNO_3 > NaOAc > NaHCO_3 > Na_2CO_3 >$ $NaOH > Ca(OH)_2$.

- In cyclic absorption/desorption tests, the adsorption by clinoptilolite fell slowly, but remained viable for six regenerations with EDTA present, whereas adsorption by clinoptilolite fell slowly, but remained viable for 10 regenerations using NaCl.
- Clinoptilolite samples at different stages of cyclic sorption/regeneration observed by XRD have similar XRD patterns, implying that the framework of clinoptilolite is not altered by cyclic adsorption/desorption.
- Clinoptilolite samples at different stage of cyclic sorption/regeneration observed by SEM and TEM indicate that after treatment the clinoptilolite forms dense aggregates. As well, sharp corners and amorphous-like materials disappeared.
- Clinoptilolite appears to be a promising agent for ARD leachate treatment.
- Clinoptilolite pretreatment using a 1 M NaCl solution is recommended. For natural clinoptilolite, the adsorption sites are various ions such as Mn, K and Mg. The NaCl treatment homogenizes the adsorption sites, as seen in the regeneration test where the 2nd adsorption of Zn ions improved greatly after the initial desorption by NaCl.
- In the present tests, the net absorption of Zn became negative after seven cycles for EDTA regeneration, whereas the net absorption of Zn remained positive, but was drastically reduced after 10 cycles for a NaCl solution. Further tests are needed to determine whether it is possible to completely regenerate the clinoptilolite at this stage.

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Appendix

Supporting Information

SEM Results:

Under SEM (Figures 13, 14, 15 and 16), the non-treated (fresh) clinoptilolite looks flaky and granular (Figure 13). After the initial adsorption and EDTA cyclic regeneration, the sorbent appears to be more flaky than the fresh clinoptilolite (Figures 14 and 15). However, the clinoptilolite is more crystallized after the NaCl cyclic regeneration (Figure 16).

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