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Exploration of remediation of acid rock drainage with clinoptilolite as sorbent in a slurry bubble column for both heavy metal capture and regeneration

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ABSTRACT

Preliminary work was carried out to explore a novel process for high-efficiency high-capacity remediation of acid rock drainage. Zn and other metal ions were adsorbed and desorbed in a laboratory Plexiglas slurry bubble column with natural clinoptilolite particles as sorbent. The results indicate that both adsorption and desorption in this medium have considerable advantages over those in the packed beds and rotating columns, leading to faster batch adsorption and desorption, as well as greater uptake of zinc. The adsorption order of clinoptilolite particles to different metal ions appeared to be Fe > Al > Cu > Zn > Mg > Mn on the basis of normalized concentrations. Smaller particles had significantly higher capacity and rates of the adsorption than larger particles for the same operating conditions.

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1. Introduction

Acid rock drainage (ARD) is one of the most serious environmental problems faced by the mining industry. It also adversely affects many highways. Dissolved metals such as copper, zinc and cadmium can be toxic to fish and animals, and can harm ecosystem health. A number of methods have been explored for the treatment of ARD waste, in particular to reduce acidity and immobilize heavy metal ions. These include alkalinity addition (Bellaloui et al., 1999; Bernier, 2005; Duchesne and Doye, 2005; Kongolo et al., 2004; Xenidis et al., 2000), bioremediation (García et al., 2001; Lindow and Borden, 2005), passivation (Belzile et al., 1997), passive systems and effluent treatment (Burgess and Stuetz, 2002). The most common method in use currently is to add limestone as a neutralization and precipitation agent. However, this is expensive due to the reddish ferric hydroxide/

salts coating on limestone, resulting in rapid loss of effectiveness, thus requiring frequent addition of fresh limestone. The method also generates additional solid waste. Moreover, its performance depends on the pH of the ARD, with no single pH being optimal for all metals found in ARD.

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). Natural zeolite has a relatively low cost, a favorable cation-exchange capacity and a good selectivity for cations. These features have led to its use in waste water treatment (Veigh and Weatherley, 1999; Nguyen and Tanner, 1998; Lahav and Green, 1998; Baykal, 1998; Komarowski and Yu, 1997), agriculture and aquaculture (Kithome et al., 1999a,b; Milan et al., 1997); radioactivity treatment (Faghihian et al., 1999)

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and adsorption of heavy metal ions— Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} , Fe^{2+} and Mn^{2+} (Yuan et al., 1999; Ouki and Kavannah, 1997; Malliou et al., 1994).

Clinoptilolite is one of the most abundant among the 39 identified naturally occurring zeolites (Bernal and Lopez Real, 1993). Early batch adsorption studies at the University of British Columbia, using stationary packed beds (Lai, 2005) and rotating columns (Li, 2005; Li et al., 2005), demonstrated that an inexpensive and locally available clinoptilolite has a high adsorption capacity for copper, zinc and aluminum, with adsorption concentrations of 131, 158 and 215 mg/kg clinoptilolite, respectively. The metals can be removed from the loaded clinoptilolite by backflushing. Clinoptilolite adsorption/desorption of Zn occurred during the first 1–2 h, reaching 75% of capacity, and was independent of pH. For cyclic absorption/desorption, the adsorption by clinoptilolite remained satisfactory for six and nine regenerations with EDTA and NaCl, respectively. Thus, clinoptilolite appears to be a promising agent for ARD leachate treatment, with significant potential cost advantages compared to current treatment systems. However, 1–2 h residence time is longer than one would like, requiring large treatment vessels if a commercial process were to be established.

Three-phase fluidized beds and slurry bubble columns are applied to a number of chemical, biochemical and physical processes involving liquids, solid particles and gases (Ramachandran and Chaudhari, 1983; Fan, 1989). In slurry bubble columns, gas is introduced into a suspension of relatively fine particles dispersed in a liquid. The gas bubbles result in vigorous mixing of the slurry. Mixing could also be achieved by vigorous stirring in a single stirred tank or in a series of mixed vessels, but this would require additional capital and operating costs. Fixed beds have the advantage of giving little axial dispersion, i.e. they operate close to plug flow. However, the vigorous relative motion and relatively small particle sizes in slurry bubble columns result in high rates of external and internal mass and heat transfer, ideal for many processes, including those involving sorbents. An additional advantage over fixed beds for sorption processes is the ease with which the particles can be removed from, and returned to, the column for continuous regeneration of the sorbent.

In this project, we have investigated in a preliminary manner the ability of a slurry bubble column containing clinoptilolite particles to absorb and desorb heavy metals from ARD in order to explore the feasibility of a novel process based on recirculation of clinoptilolite between an absorption column and a desorber/regenerator. Zinc is the principal focus of attention since it is the major concern in the specific site of interest in the current work.

2. Experimental equipment, materials and methodology

The experiments were carried out in a laboratory-scale Plexiglas column of inside diameter 90 mm and height 1.4 m, as shown schematically in Fig. 1. The distributor plate at the base was perforated with 57 evenly spaced holes of 6-mm diameter with a 38 μm mesh screen below to prevent particles from falling through the orifices. The conical plenum chamber below the distributor was filled with plastic

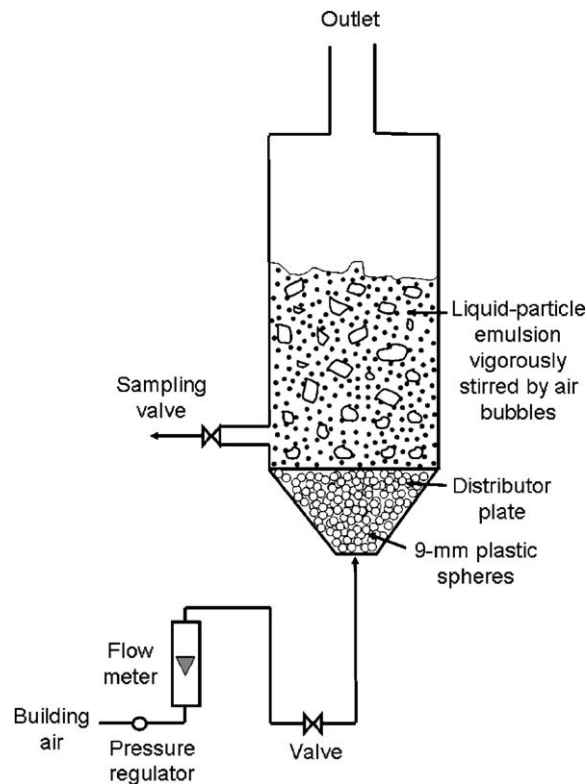


Fig. 1 – Schematic of experimental apparatus.

spheres of diameter 9 mm to provide a uniform flow of gas to the distributor plate.

The liquid used in the experiments was ARD from Highway 97C in British Columbia (Coquihalla Merritt-to-Peachland connector). The pH was 3.2. The concentrations of key metals are shown in Table 1. As zinc is the key contaminant in the ARD, it was the major focus of our preliminary tests.

The sorbent tested in this study consisted of natural clinoptilolite particles from Sunday Creek, near Princeton, BC. These particles were of rounded shape, with a size distribution, determined by sieving, given in Table 2 and a Sauter mean diameter of 695 μm . The density of the particles was 1960 kg/m^3 and the bulk density 1090 kg/m^3 . The BET surface area was 64 m^2/g , whereas the internal porosity was 45%. The mineralogical and chemical composition of the particles, characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF) are shown in Fig. 2 and Table 3.

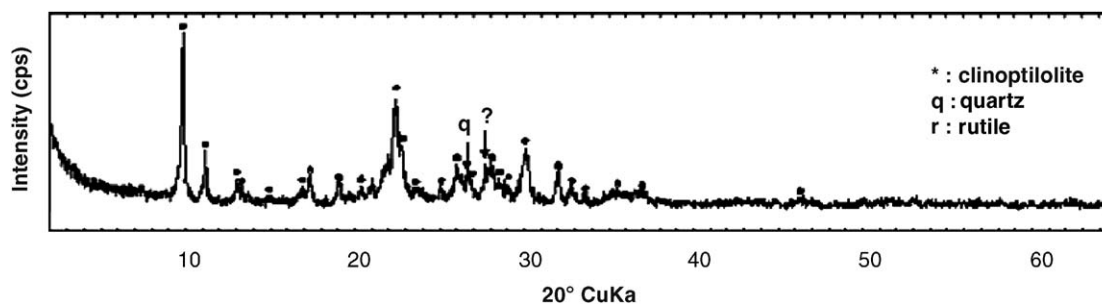
The absorption tests were carried out batchwise, with 2.0 kg ARD and 200 g clinoptilolite first added to the column, and then air flow was initiated from below, metered by a rotameter to mobilize the liquid–solid slurry. The static bed depth was 335 mm. All experiments were carried out at $15 \pm 2^\circ\text{C}$ and at two values of the superficial air velocity, U_g , 0.08 and 0.23 m/s. At the higher velocity, all of the particles were in suspension, whereas a thin layer (approximately 10 mm deep) of coarser particles was immobile on the distributor for the lower gas velocity. Runs were carried out of different durations, and then 1.0 kg of liquid was withdrawn and set aside for analysis. The concentrations of the metals in samples of the liquid at the end of each run were then analyzed using ICP by MAXXAM Analytics Inc.

Table 1 – Concentrations of various metal ions and their changes during adsorption and desorption

Conditions	Ions								
	Zn	Al	Cu	Fe	Si	Na	Mg	Mn	Ca
Concentration in base ARD (ppm)	101.2	22.6	0.17	0.82	44.2	181	52.3	10.7	204
Concentration during adsorption ($U_g = 0.23$ m/s, 30 min) (ppm)	69.7	4.4	0.06	0.01	42.8	266	40.1	9.2	213
Reduction in concentration due to adsorption ($U_g = 0.23$ m/s, 30 min) (ppm)	31.5	18.2	0.11	0.81	1.4	–85	12.2	1.3	–9
Concentration during desorption ($U_g = 0.23$ m/s, 30 min) (ppm)	17.7	5.39	0.06	0.1	1.75	7660	9.3	2.4	101
Ratio of metal amounts desorbed/adsorbed on the particles (%)	56	30	55	12	125		76	185	

Table 2 – Particle size distribution of clinoptilolite particles

Size (μm)	< 125	125–300	300–425	425–500	500–710	710–850	850–1400	1400–2000	> 2000
Percent (%)	2.40	1.86	4.88	6.99	15.71	10.73	31.08	21.7	4.63

**Fig. 2 – X-ray diffraction pattern of clinoptilolite.****Table 3 – Major elements in the clinoptilolite sample by X-ray fluorescence (XRF)**

Element	Unit	Clinoptilolite ore ^a (XRF)
SiO ₂	%	66.53
Al ₂ O ₃	%	12.30
Fe ₂ O ₃	%	2.41
MgO	%	0.72
CaO	%	2.08
Na ₂ O	%	3.38
K ₂ O	%	2.27
TiO ₂	%	0.25
P ₂ O ₅	%	0.05
MnO	%	0.05
Cr ₂ O ₃	%	n/a
Ba	ppm	1633
Ni	ppm	n/a
Sc	ppm	n/a
LOI	%	n/a
TOT/C	%	n/a
TOT/S	%	n/a
SUM	%	90.21

^a XRF result was provided by Canmark Resources Inc. on the ore body.

All the particles used for the desorption tests were obtained from several repeated runs of 60 min absorption. The liquid was drained and the particles were washed twice with distilled water. A desorption test was then undertaken by returning the 200 g of used clinoptilolite particles to the column with 2.0 kg of an aqueous NaCl solution (in which 20 g of NaCl had been dissolved per liter of distilled water). The suspension was re-suspended by a flow of air at the same temperature and superficial velocities as in the absorption tests for pre-specified time periods (15, 30, 45, 60 and 120 min) to determine the rate of desorption as a function of time. The particles were then removed, and the column was washed with water. The operation was then repeated with another 200 g of used clinoptilolite particles for another desorption period.

3. Results and discussion

3.1. Adsorption tests

Fig. 3 shows the Zn adsorption as a function of the adsorption time for two superficial air velocities. Adsorption is seen to

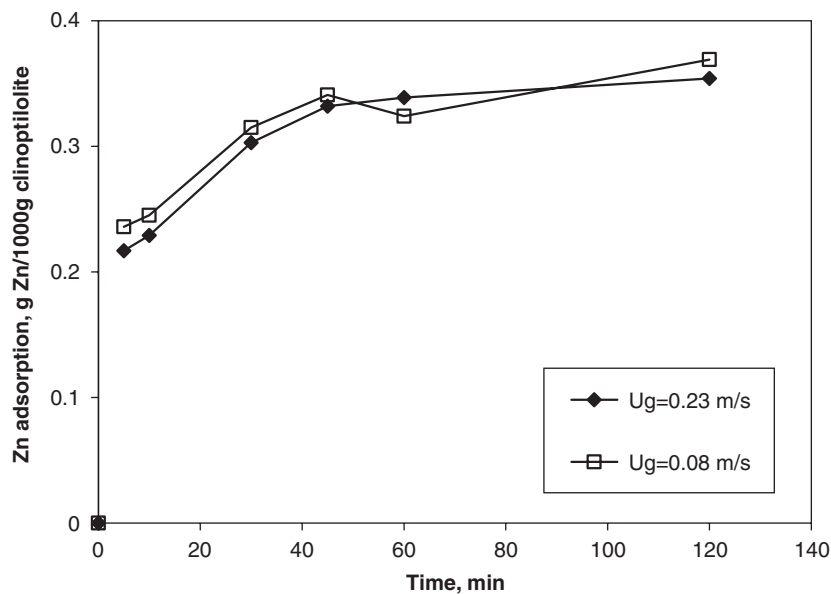


Fig. 3 – Zn adsorption at different times and superficial gas velocities.

have occurred very quickly during the first 10 min. The adsorption rate then decelerated, with 0.28 g of Zn removed per kg clinoptilolite, equivalent to approximately 30% of the Zn removed from the liquid (100 ppm Zn) after about 30 min. The Zn uptake changed little over the subsequent 100 min, reaching what appeared to be a near-saturation value of ~ 0.35 g of zinc per kg clinoptilolite sorbent. Thus, the practical adsorption time for the slurry bubble column system appears to be 30 min or less, much less than the 1–2 h observed previously in a fixed bed absorber of the same type and size of particles (Li, 2005; Li et al., 2005). The faster uptake indicates that the external mass transfer resistance played a strong role in the previous tests and that the vigorous stirring of the sorbent can significantly reduce the time needed for absorption, and hence the residence time needed for adsorption of metals from ARD. This occurs due to the smaller size of the sorbent particles (hence giving them more surface area and shorter paths for internal diffusion), coupled with turbulence (evident by visual observation, for example, from the frequent bubble splitting and coalescence) enhancing external mass transfer to the particles.

As shown in Fig. 3, for the range of operating conditions investigated, the superficial gas velocity had little effect on the adsorption of Zn. The higher velocity appeared to lead to a slight reduction in the adsorption of Zn. Because a lower gas velocity also requires less bed expansion, results in less entrainment of liquid and particles, and consumes less energy, our preliminary test results suggest that the adsorption can be carried out at lower gas velocities for more economical operation.

3.2. Desorption tests

Fig. 4 shows experimental desorption results for the spent clinoptilolite. As for the adsorption, desorption occurred very quickly in the early stages of the operation. The Zn concentration in the NaCl-distilled water liquid phase

increased to 14 ppm during the first 10 min. After 30 min, the Zn concentration in the liquid was almost constant, indicating approach to equilibrium.

The test results can be compared to previous ones obtained in end-over-end rotating tubes (Li et al., 2005) with the same particles, same liquid and same ratio of liquid mass to particle mass. As seen in Fig. 4, both processes showed quick desorption of Zn during the first 10 min. The slurry bubble column desorption appeared to reach equilibrium after 30 min, whereas the desorption continued slowly over 1 day for the rotating column. More important, after 30 min the Zn concentration reached 18 ppm in the desorption liquid for the slurry bubble column process, whereas it was less than 8 ppm for the rotating tubes. Our results indicate that both the adsorption and desorption were much quicker in our column than in either rotating tubes or packed beds. In addition, the clinoptilolite particles absorbed more Zn from the ARD and desorbed Zn more quickly in the slurry bubble column, presumably due to the improved external mass transfer.

3.3. Other metal ions

Fig. 5 shows the changes of the concentrations of several other metal ions during the adsorption tests for the two gas velocities studied. The plotted concentrations are normalized by dividing by the concentrations of the metal ions in the base ARD. The changes of metal ion concentrations differ considerably for the different metals. Metals such as Fe, Cu, Al, Zn, Mg and Mn were well adsorbed, whereas the concentrations of Si and Ca were stable, indicating insensitivity to the clinoptilolite. In contrast, the concentration of Na increased during the adsorption, particularly during the first 5 min, indicating that Na ions were leached from the clinoptilolite particles.

The concentration of Fe ions decreased sharply and considerably in the first 5 min, approaching zero. The Al and Cu ions also showed significant adsorption. The adsorption

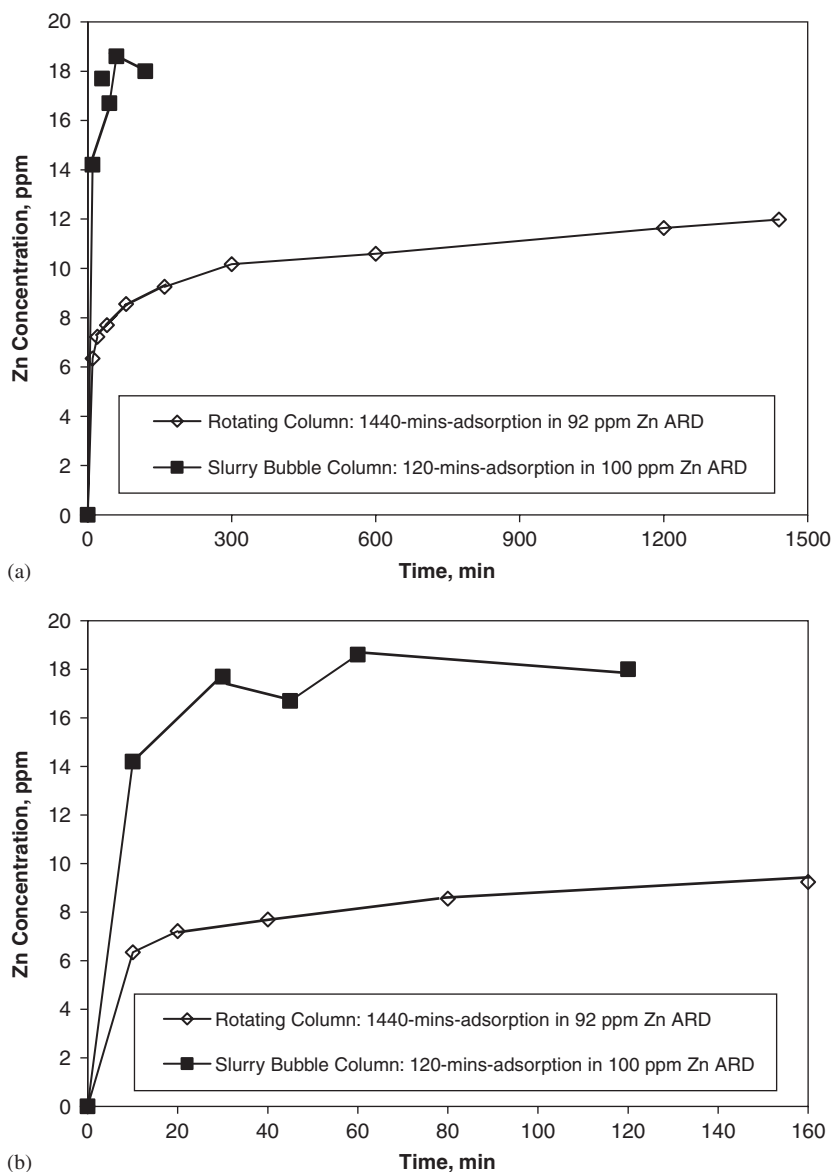


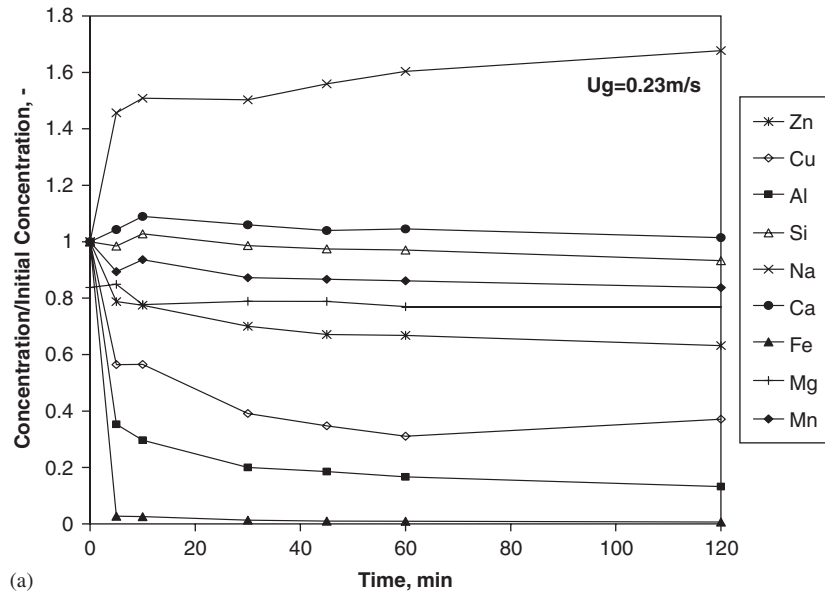
Fig. 4 – Comparison of slurry bubble column adsorption and rotating tube adsorption (rotation speed: 20 rpm) (with the same ratio of liquid mass to particle mass for the two series of tests).

order of clinoptilolite particles to metal ions appeared to be $Fe > Al > Cu > Zn > Mg > Mn$ on the basis of normalized concentrations. It was also found that the concentrations of metal ions varied only slightly after the initial 30 min. Table 1 reports the concentrations of the metal ions after 30 min of adsorption at a superficial gas velocity of 0.23 m/s. The results suggest that a residence time of 30 min is ample for adsorption, a finding that is important for the design of a continuous adsorption system.

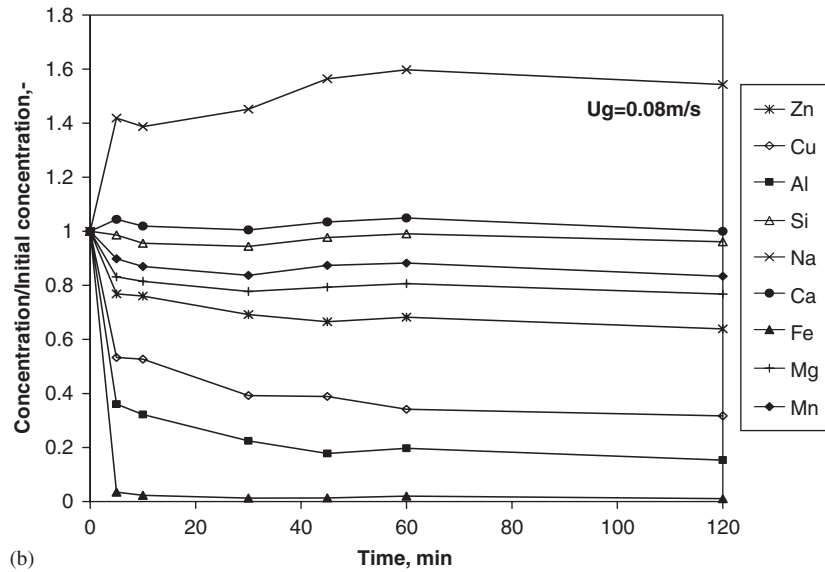
The ion adsorption may be explained by the categories in the Periodic Table. All transitional elements have d-orbitals available for bonding, so they have variable charges. For example, Fe and Mn have higher charges than Zn and Cu. The others are not transitional elements. Ca, Mg are relatively large ions and have a charge of 2, whereas Al and Si are relatively small ions and have a charge of +3 and +4. This

explains the results shown in Fig. 5. Because clinoptilolite has a molecular sieve structure, the adsorption of ions is dependent on the size of the ion and whether it can fit in the clinoptilolite channel, as well as the charge and concentration of ions.

Fig. 6 shows the apparent concentrations of the key metal ions during desorption. The concentrations of the metal ions increased quickly in the first 5 min, then levelled off and approached constant values after 30 min. It was observed that all of the metal ions analyzed could be leached during the desorption, but to different extents. As for adsorption, the various metal ions behaved differently during desorption. Ca ions reached the highest concentrations in the liquid (100 ppm at 30 min), followed by Zn (18 ppm), Mg (9 ppm), Al (5.5 ppm), Mn (2.5 ppm), Si (1.8 ppm), Ba (1.2 ppm), Fe (0.1 ppm) and Cu (0.06 ppm).



(a)



(b)

Fig. 5 – Change of concentration of other metals in ARD (normalized by each corresponding initial concentration) with adsorption time.

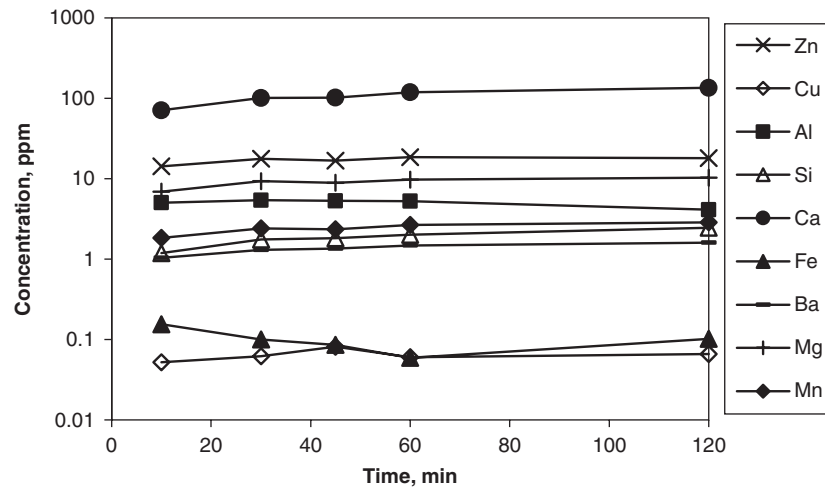


Fig. 6 – Change of concentration of metals in liquid with desorption time for $U_g = 0.23 \text{ m/s}$.

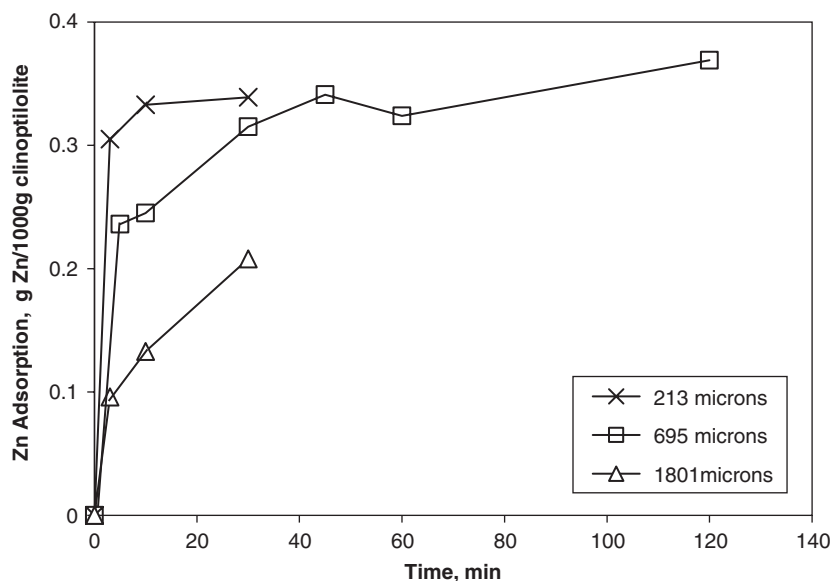


Fig. 7 – Zn adsorption for different size clinoptilolite particle sizes and adsorption times for $U_g = 0.08$ m/s.

3.4. Effects of particle size

Clinoptilolite particles of three different size ranges were tested to study the effects of particle size on Zn adsorption. The first sample consisted of the original particles with a wide size distribution as shown in Table 1. Smaller particles with an average size of 213 μm were prepared by sieving, including only particles $<500\mu\text{m}$ from the original distribution, whereas larger particles with an average size of 1801 μm were obtained by retaining the $>1400\mu\text{m}$ particles.

As shown in Fig. 7, both the rate and capacity of the adsorption depended strongly on particle size. Smaller particles adsorbed significantly more Zn ions than the larger particles for the same conditions, because small particles have more surface area and shorter pores. It was also observed that the adsorption was quicker for the smaller particles. During the first 3 min, about 0.3 g Zn/kg clinoptilolite was adsorbed by the smaller clinoptilolite particles, whereas the larger particles adsorbed about 0.1 g Zn/kg clinoptilolite during the same period. The effect of increasing particle size is probably due to the decrease in external and internal mass transfer as particles become larger. The airflow rate was sufficient to suspend even the largest particles in our experiments, so that immobilization of particles was not an explanation.

4. Conclusions and recommendations

- Both the adsorption and desorption for ARD remediation using clinoptilolite in a slurry bubble column approached equilibrium after ~ 30 min, significantly faster than in rotating tubes and packed beds.
- Adsorption and desorption of various metal ions both occurred very quickly (within 10 min).
- The clinoptilolite particles appear to adsorb more Zn in the slurry bubble column, leading to greater reduction in ARD, probably due to improved liquid-to-particle transfer.

- A continuous slurry bubble column or three-phase fluidized bed adsorption/desorption process therefore has potential to considerably reduce residence times, increasing the treatment capacity for ARD remediation.
- The superficial gas velocity had very little effect on the adsorption (desorption) processes for the range of conditions studied indicating that it should be possible to use a low gas velocity for practical operations.
- The adsorption of clinoptilolite particles differed for various metal ions, with a normalized order of $\text{Fe} > \text{Al} > \text{Cu} > \text{Zn} > \text{Mg} > \text{Mn}$. Si and Ca ions were not sensitive to the clinoptilolite particles.
- Smaller particles showed significantly higher capacity and rates of the adsorption than larger particles for the same operating conditions.
- More tests are needed to determine the optimum particle size distribution and gas velocity for ARD remediation in slurry bubble columns considering both adsorption efficiency and separation of the clinoptilolite particles.
- The zeolite particles can be readily removed from the liquid by filtration or by a hydrocyclone.

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