

Removal of Selected Radionuclides and Metal Contaminants by Natural Zeolites from Liquid Effluents

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Abstract

Investigations have been conducted for potential applications of two natural zeolites (clinoptilolite and chabazite) obtained from ZEOX Corporation, for removal of key radionuclides (Cs, Co and Sr) and common metals contaminants (Cu, Zn) found in active liquid waste stream from nuclear operations. The low cost and easy availability makes these zeolites attractive for a wide range of industrial applications. Experiments have been conducted in shaker flask and a 4" diameter column using dilute solutions of the selected metal ions. The shaker flask experiments provided selectivity sequence for the two zeolites. Superior sorption capacity of chabazite particles has been attributed to combination of its higher pore volume and high alumina to silica ratio. The selectivity sequence is discussed based on hydrated radius and free energy of hydration of the ions. The sorbent dosage required to achieve desired removal of the contaminants is obtained from batch experiments and compared in the column tests. The measurements in column also included hydraulic behavior of the bed of zeolite particles and slurring out of the spent bed. The spent zeolite generated from the treatment allows stabilization of the contaminants in modified cements or ceramic formulations for long-term management of the waste.

Key words: Radionuclides; Metal contaminants; Natural zeolites; Chabazite; Clinoptilolite; Column hydraulics, effluent treatment

1. Introduction

A number of industrial operations generate wastewaters which may have unacceptable levels of metal contaminants (Hui et al., 2005). The treated water is expected to meet drinking water and toxicity standards which are becoming stricter. The problem is particularly challenging in nuclear facilities due to the presence of radionuclide in addition to low concentration of toxic metals in the effluent waters. Heavy metals are a serious health and environmental concern, and since they are not biodegradable, there is potential for accumulation in living organisms and causing a number of different diseases and disorders. For this reason, the research concerning their removal from wastewater is increasing. Many different methods can be used for removal of heavy metals from water. These methods include precipitation, ion exchange, phytoextraction, reverse osmosis, electrodialysis, vacuum evaporation, solvent extraction and carbon adsorption (Erdem et al., 2004; Alvarez-Ayuso, Garcia-Sanchez et al., 2003; Semmens and Martin 1988). Adsorption and ion-exchange work rather well and are commonly used because of their ease of use and simple and robust design. The challenge is that adsorbents such as activated carbon and ion-exchange resins are rather expensive and are not feasible for use in small scale operations or in developing countries where resources may be limited. Using an expensive adsorbent is also not feasible when it cannot be regenerated, as in the nuclear industry. Adsorbents used to clean nuclear wastewater generally have to be stored for many years before they are no longer hazardous and are safe for disposal by traditional means. For these reasons, there has recently been a push to find efficient and low-cost adsorbents. Some of the materials considered include peat moss, clay, dead biomass and, of course, natural zeolites (Babel and Kurniawan 2003; Baily et al., 1999).

Zeolites are very attractive for use as adsorbents for heavy metals for many reasons. They are naturally occurring and abundant in nature, and their physical properties make them highly efficient sorbents. Adsorption capacity of natural zeolites is comparable to organic ion exchange resins for most applications and their cost together with resistance to degradation make them very attractive for removal of contaminants from wastewater (Ouki et al., 1994). Zeolites have been extensively studied because of their unique properties, and wide range of applications. The first zeolite was discovered in 1756 and since then, they have been the object of intense research. Originally zeolites were thought to be only found in small deposits in basaltic and volcanic rocks, which prevented them from becoming widely used. Eventually it was discovered that zeolites actually exist in very large deposits in sedimentary rock, which were ideal for mining these very useful materials. Union Carbide commercialized the first synthetic zeolite in 1954 for use in separation and purification applications. Since then, both natural and synthetic zeolites have been found to be useful in a wide range of applications. Some of these include adsorption, separation processes, catalysis, detergents, wastewater treatment, treatment of nuclear waste, additives for animal feed and soil improvement (Van Bekkum et al., 1991). The wastewater streams to be treated by these sorbents are generally expected to have very low concentrations of suspended impurities such as oil and solid particulates. For high concentrations of these impurities, pretreatment steps would be required to avoid fouling. The objective of this study was to investigate the heavy metal adsorption behavior of the selected natural zeolites (clinoptilolite and chabazite) by performing both batch and column studies. The selected radionuclides (Cs,

Co and Sr) and metals contaminants (Cu, Zn) are commonly found in active liquid waste effluent from nuclear operations.

2. Experimental

The adsorption experiments were conducted in batch mode in small flasks (200 cc) placed on a shaker and in semi-continuous mode in a 0.1 m ID (4") acrylic column. The column consisted of four sections, which could be moved around as needed. The bottom section of the column served as the calming section, and the particle bed was located in the second section of the column. The calming section was separated from the particle bed using a perforated plate distributor. The water flow rate into the column was controlled by rotameters. A schematic of the column setup is shown in Figure 1.

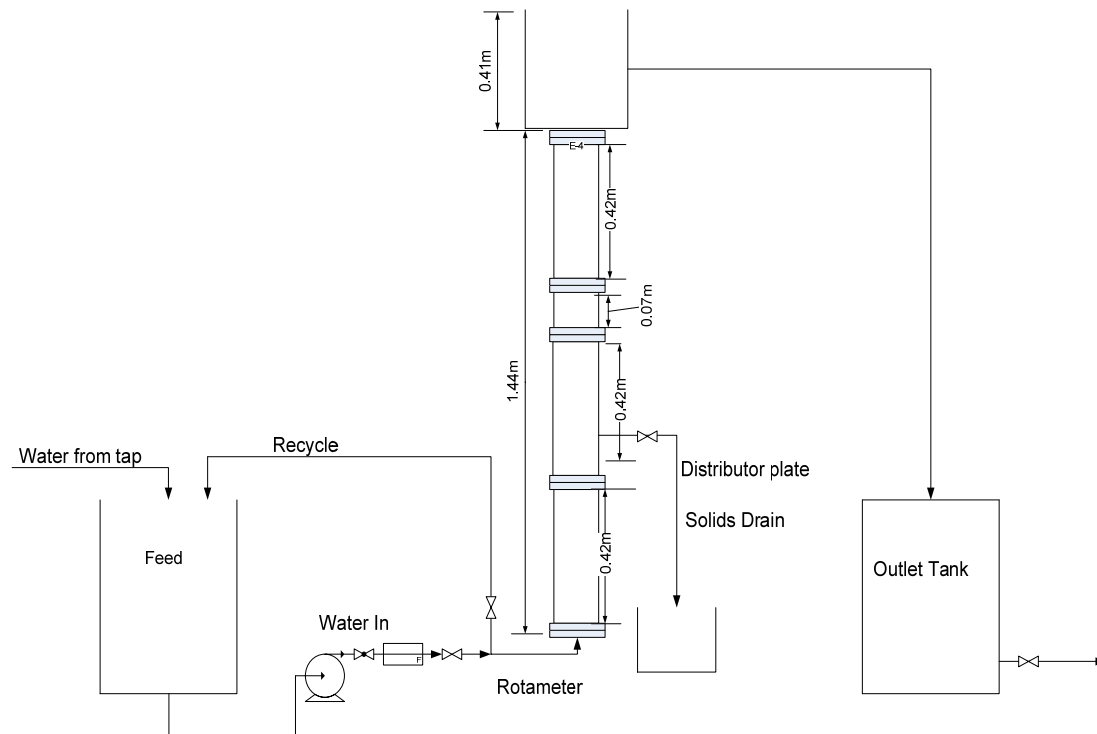


Figure 1. Schematic of the column setup

The two natural zeolites used in this study namely clinoptilolite and chabazite were obtained from ZEOX corporation. Initial characterization of these particles was performed to determine size distribution, pore volume and density. The particles characteristics are summarized in Table 1. Size distribution was determined using Malvern Mastersizer 2000, helium pycnometry determined the skeletal density, and the particle density was calculated using the pore volume obtained from BET analysis. The surface area of the particles was also determined using the BET method.

Table 1: Summary of particle properties

Particle Species	Mean Particle Diameter (μm)	Skeletal Density (kg/m^3)	Particle Density (kg/m^3)	BET Pore Volume (cc/g)	BET Surface Area (m^2/g)	Static Bed Voidage
Clinoptilolite	753	2151	1800	0.205	476.9	0.4
Chabazite	930	2106	1630	0.359	495.2	0.35

The different metal salts used in the study were Zinc Nitrate supplied by J.T. Baker; Copper Nitrate, Cobalt Nitrate and Strontium Nitrate by Alfa Aesar and Cesium Chloride by EMD Chemicals Inc. For shake flask experiments, the prepared metal solutions of known concentration were placed in 125mL flasks and remained on flask shaker for 24hr. The concentration of metals in each of the solutions after 24 hr was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

For the column studies, metal solution was pumped through the particle bed and samples were taken at specific time intervals. Both once through and recirculating flow experiments were performed. In order to prepare the column for the adsorption studies,

the column, and the adsorbent were rinsed with de-ionized water. Rinsing of the zeolite removed fines from the bed which could cause excess pressure drop, or pressure fluctuations. For each column experiment samples of the initial solution in tank and also the initial solution leaving the column were taken. After that, samples of the metal solution were collected on equal time intervals.

3. Results and discussion

3.1 Shaker flask experiments

Figure 2a and b show removal efficiency of different metal ions obtained with the two zeolites. In these experiments, the initial cation concentration was kept constant while weight of adsorbent was varied. The selectivity sequence with clinoptilolite is $Cs > Cu > Sr > Zn > Co$ and with chabazite it is $Cs > Sr > Cu > Zn \sim Co$. It can also be seen that removal efficiency is generally better with chabazite particles. This could be a result of several factors which include framework structure of the zeolite and dimensions of the channel formed by the tetrahedral units which make up the zeolite. These channels must be large enough to allow passage of hydrated metal ions. It has been pointed out that window size that controls access to the pore system is larger in chabazite as compared to clinoptilolite (Ouki and Kavannagh, 1997). Moreover higher Al substitution of Si provides a negative framework favorable to higher ion-exchange capability. The dosage above which there is small change in removal is about half for chabazite (5 g adsorbent/L metal solution) compared to clinoptilolite, indicating higher adsorption capacity for chabazite.

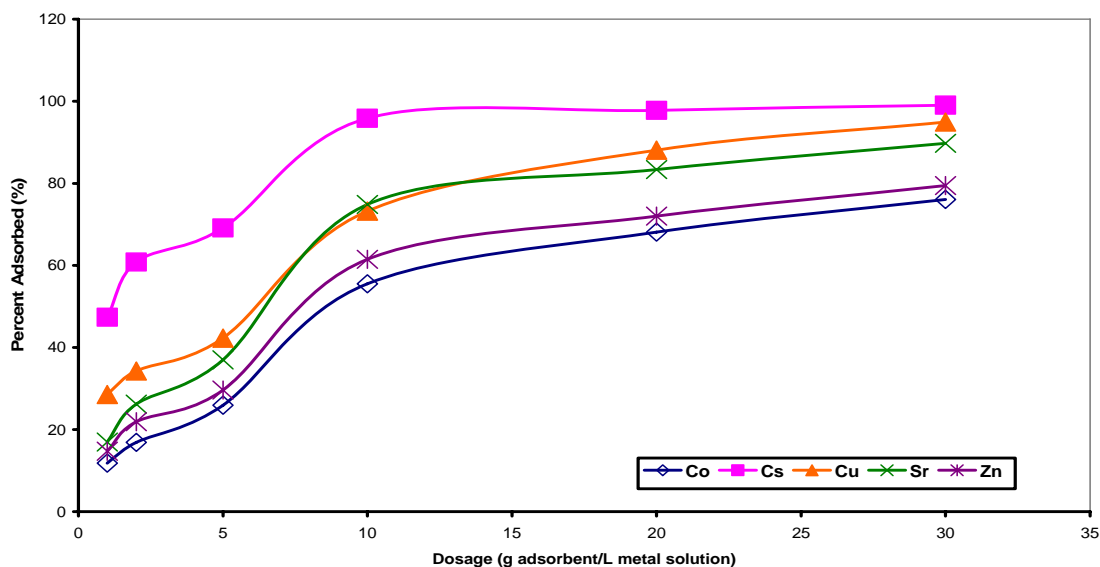


Figure 2a. Percent cation removal obtained with clinoptilolite with increasing adsorbent dosage.

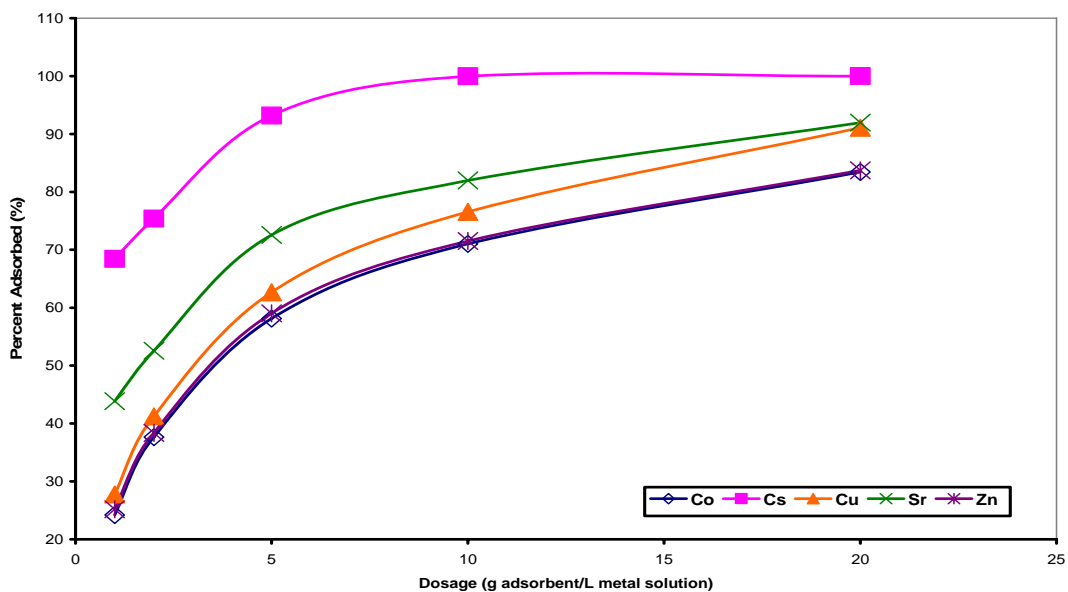


Figure 2b. Cation removal obtained with chabazite for increasing adsorbent dosage

It is also observed that cesium removal was the highest with both zeolites. This can be attributed to low hydrated radius and heat of hydration for cesium ions compared to other cations present (Teppen and Miller, 2005; Mimura and Kanno, 1985). This indicates that removal of other cations can be suppressed in presence of high concentration of cesium in the effluents. It may therefore be more economical to treat the stream first in a bed of low cost clinoptilolite followed by a bed of higher cost chabazite. A few experiments were also conducted in solutions containing binary mixtures of cations. The difference between copper and strontium cations was generally small in the multication solutions studied above. Their adsorption behavior was further studied in solutions with increasing concentration of the two cations. It can be seen from Figure 3 that at low concentration (< 50 mg/L), there is little competitive adsorption between the two ions but for higher concentrations, copper is preferentially removed.

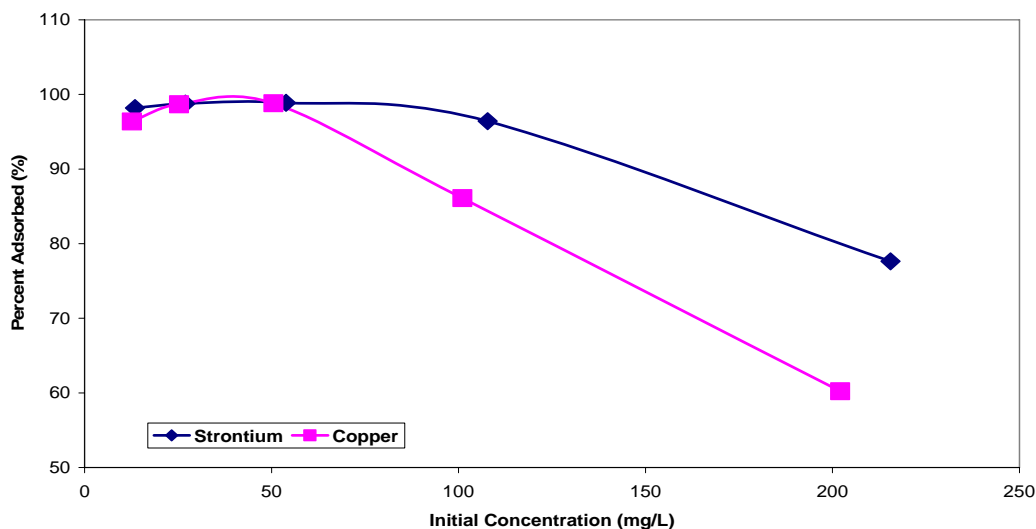


Figure 3. Effect of initial concentration of cation on percent removal obtained with chabazite

3.2 Column experiments

The column hydrodynamics including pressure drop analysis, fluidization and bed segregation behavior of the zeolite particles were investigated and reported in other studies (Gallant et al., 2009). The bed was operated above the minimum fluidization velocity in the expanded mode of operation. The column adsorption runs were performed in two stages: the first set of experiments were once through where the metal solution was not circulated back to the column, and for the second set of experiments the metal solution was recycled back to the column.

This gave some insight into bypassing in the bed and mode of operation for adsorbent particles utilization. These experiments were conducted with solution containing about 25 mg/L of copper and zinc ions. It can be seen in Figure 4 that the adsorption of copper is more efficient than zinc which agree with the batch adsorption data in the previous section. It can be observed that fractional removal for zinc decreased steadily or concentration of zinc ions in the outlet increased steadily with increasing volume of solution processed. However, for copper ion the fractional removal remains steady before dropping quickly. This could be attributed to different adsorption rates for the two ions indicating differences in their kinetics of adsorption. The fractional removal dropped to about 98 % towards the end for once through runs. These once through column experiments were used to establish the weight of adsorbent required to achieve the drinking water standards for copper and zinc in the treated water. It was observed that higher removal could be obtained by recirculating the column outlet to inlet tank. Figure 5 shows that relative outlet concentration (ratio of outlet to inlet concentration) could

reach below 0.01. This mode of operation leads to completely back mixed operation in the column thus avoiding bypass effects. A clear indication of bypassing during the startup phase was observed with the bed of clinoptilolite particles when high initial concentrations were observed (Figure 5). However, high removal could be obtained eventually with the recirculating flow mode of operation. Further work being conducted to study kinetics of adsorption, competitive adsorption in single and mixed bed systems and modeling of column operation will be subject of future publication.

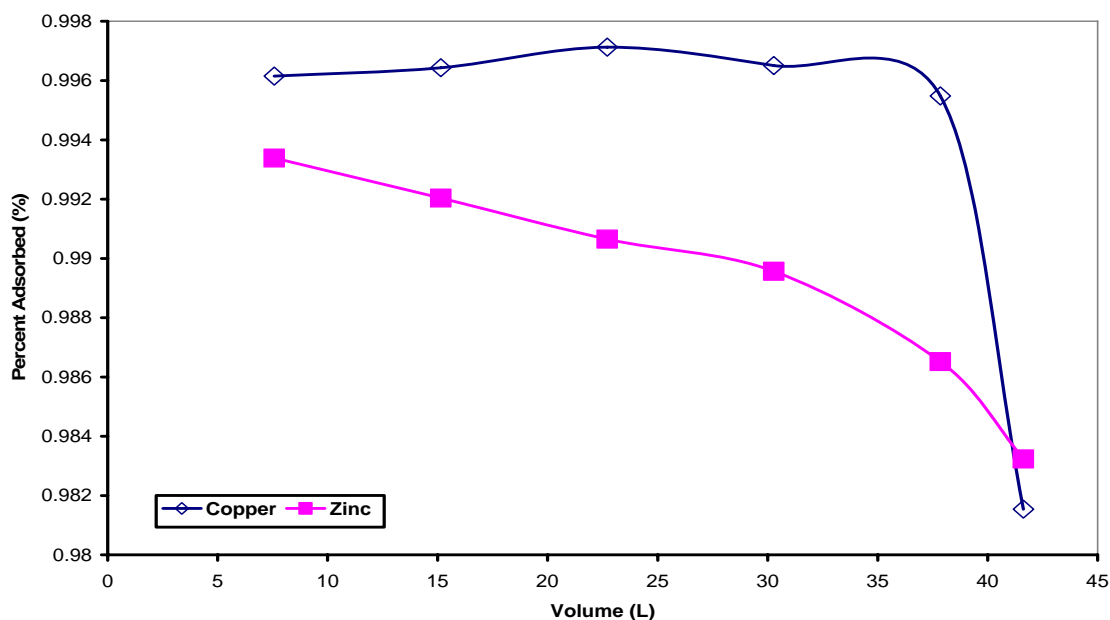


Figure 4. Metal adsorption from solution of copper and zinc obtained with chabazite in once through column operation.

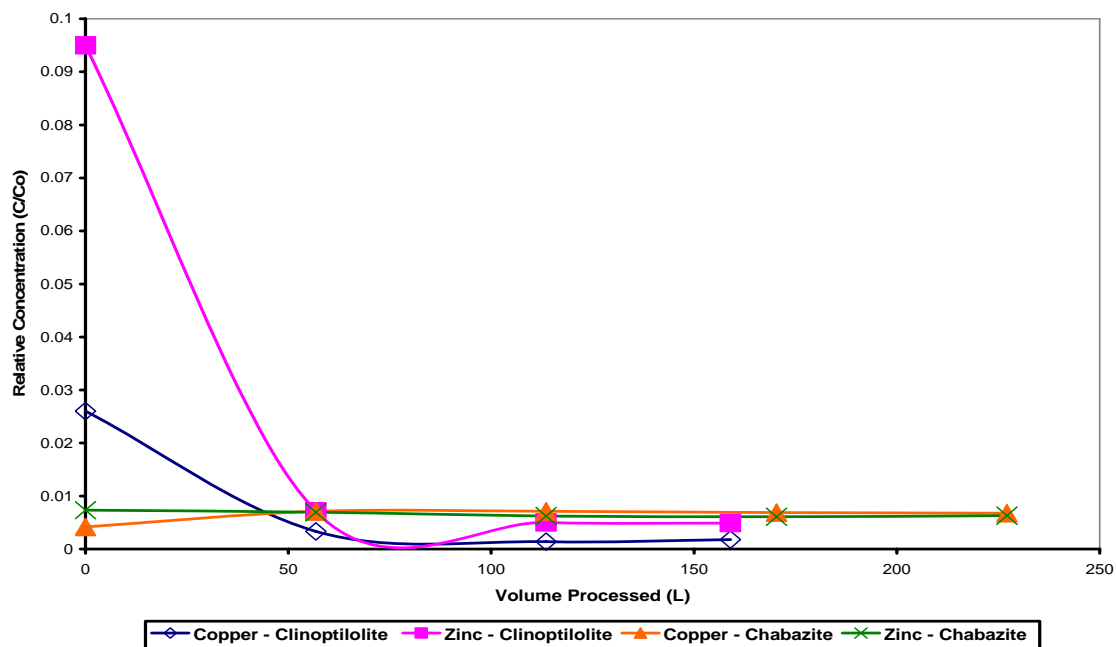


Figure 5. Adsorption results obtained when column was operated in recirculating mode.

4. Conclusions

Experiments conducted with natural zeolites clinoptilolite and chabazite established sequence of removal of selected metal ions and provided basis for experiments in column operation. Since cesium is easily removed by both zeolites, it would be economical to remove cesium first from the multication solution using lower cost zeolite. Experiments in the columns showed good removal efficiencies in fluidized bed mode. However improved utilization of bed can be achieved by operating in recirculating mode. This mode of operation can be useful for final polishing step or to treat off-spec product to achieve high removal efficiencies and optimum utilization of the particles in the bed.

5. References

- E. Alvarez-Ayuso, A. Garcia-Sanchez, and X. Querol. "Purification of Metal Electroplating Waste Waters using Zeolites." *Water Research*, Vol. 37, 2003, pp.4855-4862.
- S. Babel and T. A. Kurniawan. "Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review." *Journal of Hazardous Materials* , Vol. B97, 2003, pp. 219-243.
- S.E. Bailey, T.J. Olin J, R.M. Bricka and D.A. Adrian "Review of Potentially Low-Cost Sorbents for Heavy Metals." *Water Research*, Vol. 33, No. 11, 1999, pp. 2469-2479.
- E. Erdem, N. Karapinar, and R. Donat. "The Removal of Heavy Metal Cations by Natural Zeolites." *Journal of Colloid and Interface Science*, Vol. 280, 2004, pp. 309-314.
- J. Gallant, A. Prakash and L.E.W. Hogg, "Fluidization and Hydraulic Behavior of Natural Zeolite Particles used for Removal of Contaminants from Wastewater", Submitted to *Canadian J. of Chemical Engineering*, 2009.
- K.S. Hui, C.Y.H. Chao, and S.C. Kot, "Removal of Mixed Heavy Metal Ions in Wastewater by Zeolite 4A and Residual Products from Recycled Coal Fly Ash", *Journal of Hazardous Materials*, Vol. B127, 2005, pp. 89-101.
- H. Mimura and T. Kanno, "Distribution and Fixation of Cesium and Strontium in Zeolite A and Chabazite", *Journal of Nuclear Science and Technology*, Vol. 22[4], 1985, pp. 284-291.
- S.K. Ouki and M. Kavannagh. "Performance of Natural Zeolites for the Treatment of Mixed Metal-Contaminated Effluents." *Waste Management & Research*, Vol. 15, 1997 pp. 383-394.
- S.K. Ouki, C. R. Cheeseman and R. Perry, "Natural Zeolite Utilisation in Pollution Control: A Review of Applications to Metals Effluents." *J. Chem. Tech. Biotechnol.*, Vol. 59, 1994, pp. 121-126.
- M.J. Semmens and W. P. Martin. "The Influence of Pretreatment on the Capacity and Selectivity of Clinoptilolite for Metal-Ions." *Water Research*, Vol. 22, 1998, pp. 537-542.
- B. Teppen and D.M. Miller, "Hydration Energy Determines Isovalent Cation Exchange Selectivity y Clay Minerals", *Soil Sci. Soc. Am. J.*, Vol. 70, 2006, pp. 31-40.
- H. van Bekkum, E. M. Flanigen, and J. C. Jansen. *Introduction to Zeolite Science and Practice*, Amsterdam ; New York: Elsevier, 1991.