



Exchange diffusion of Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} into analcime synthesized from perlite

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Abstract

The zeolite analcime was synthesized, in its sodium form, from a perlite (volcanic glass) deposit at Lopburi, Thailand. Particle size analysis was used to approximate the radius of the analcime particles as 3.87×10^{-6} m. XRD, XRF, ^{29}Si MAS NMR and thermal analysis confirmed the product as analcime of good purity. Diffusion exchange of Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} for $^{22}\text{Na}^{+}$ from the synthetic analcime was investigated in the temperature range 298–333 K. Diffusion coefficients (D) were calculated using the Barrer, Barri and Klinowski equation. E_a , ΔS^* and ΔG^* values showed that all the channel sites were involved in the observed diffusion processes.

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1. Introduction

Understanding the diffusion of cations, water molecules or cation–water complexes through zeolite frameworks has importance because most industrial uses of ion exchange depend critically on kinetics [1]. The use of clinoptilolite for waste water treatment [2] has encouraged some measurement of the rates of exchange between cations [3,4] but little attention has been paid to cation exchange rates in other zeolites, apart from those for self-exchange [5].

Analcime has a relatively compact structure compared with other zeolites and has an idealized unit cell of $\text{Na}_{16}[\text{Al}_{16}\text{Si}_{32}\text{O}_{96}]16\text{H}_2\text{O}$ [6]. The cubic unit cell is composed of four-, six-, and eight-membered oxygen rings that form three non-intersecting channels. These channels encompass 24 small cavities, of which 16 are occupied by sodium cations [7]. Analcime can be readily synthesized by hydrothermal processes, and the Si/Al ratios of synthetic analcimes are in the range of 1.5–3 [8].

Barrer reported that analcime can act as an ion sieve [9], and Dyer and Yusof carried out extensive studies on cation and water self-diffusion, concluding that analcime has the potential for use in the storage and disposal of titrated water [5,10].

This work describes studies on cation exchange diffusion processes for the uptake of heavy metals cations (Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) into a synthetic sodium analcime prepared from an economically available perlite (volcanic glass) deposit.

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Province in central Thailand. The preparative methods have been described previously [9].

2.2. Characterization

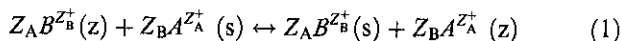
The chemical compositions of perlite and analcime were determined by the wavelength dispersive X-ray fluorescence spectrophotometer (XRF), (Model Negative Magix Pro, Phillips). The silicon–aluminum ordering of analcime was characterized by ^{29}Si MAS NMR, using a Varian Unity Inova spectrometer. Determination of the cation exchange capacity (CEC) of analcime was done by isotope dilution. XRD (Bruker, Model D5005), SEM (Model JSM6400, JEOL) and thermal analyzer (TGA-DTA), SDT 2960 were also used to characterize the analcime. A laser particle size analyzer, Malvern Instrument, Mastersizer S was used to determine the analcime particle size. Results of these characterizations have been reported in a previous work [9].

2.3. Construction of exchange isotherm

The equilibrium times of cation exchange isotherm were checked by prior kinetic experiments [9]. Isotherms were constructed using isotope dilution analysis. Tared 0.1 g aliquots of analcime, previously labeled with ^{22}Na nitrate solutions (Amersham International, UK) of known activity, were equilibrated with 20 mL solutions of Cu, Ni, Pb and Zn [Total normality (T_N) = 0.01 N] as appropriate, in plastic containers sealed with parafilm. The containers were then rotated about their horizontal axes in a thermostatically controlled air oven until equilibrium was reached (2 days). They were then centrifuged and samples taken for determination of solution radioactivity. The activities in the liquid phase were measured by liquid scintillation counting. Isotherms were constructed at 298, 313 and 333 K. Reverse exchanges were monitored for all the cations studied.

2.4. Ion exchange [10]

The ion exchange process can be represented by



where Z_A , Z_B , respectively, are the charges of the cations A and B and the symbols 'z' and 's' refer to the zeolite and solution phases, respectively. The thermodynamic equilibrium constant (K_a) is evaluated from

$$\ln K_a = (Z_B - Z_A) + \int_0^1 \ln K_c dA_Z \quad (2)$$

K_a can be obtained from the graphical integration of the plot of $\ln K_c$ against A_Z , where K_c is the Kielland coefficient.

The free energy of exchange, ΔG^0 , then is determined by

$$\Delta G^0 = \frac{-RT}{Z_A Z_B} \ln K_a \quad (3)$$

3. Results

The ion exchange isotherms, for the four heavy metal ions (M) uptake into analcime, are plotted as (M_s), the equivalent ionic fractions in solution, versus (M_z), the concentrations of M in the zeolite as determined by isotope dilution analysis, and are shown in Figs. 1–4, with the Kielland plots of $\ln K_c$ against M_z . The Kielland plots were constructed using a program available on the University of Salford network. This program made all the required adjustments for ionic activity coefficients and is based on the methodology described by Fletcher and Townsend [11]. Standard free energies (ΔG^0),

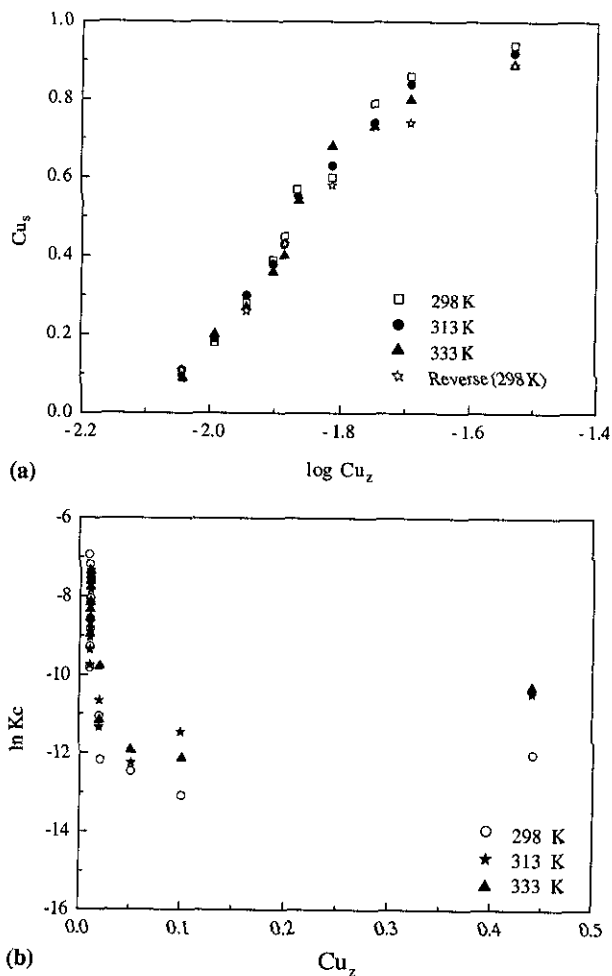
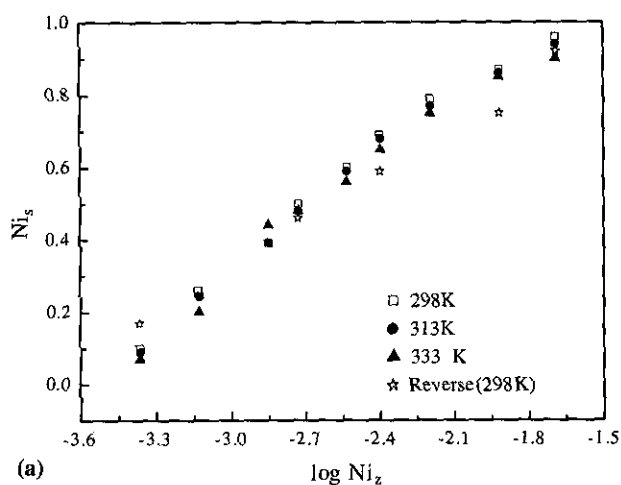
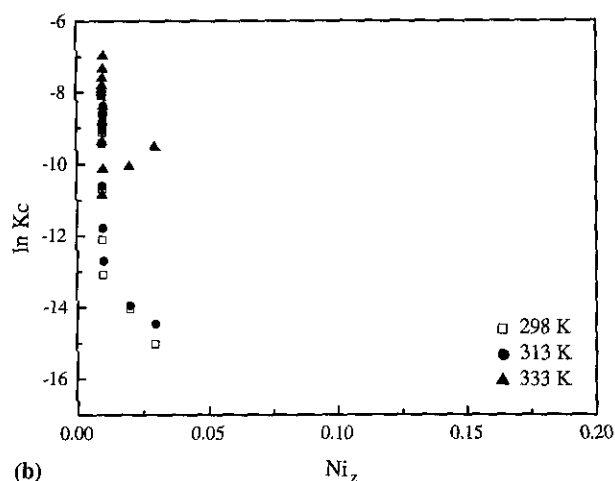


Fig. 1. Ion exchange isotherms for $\text{Na}^+ \leftrightarrow 1/2 \text{Cu}^{2+}$ exchange in analcime at $T_N = 0.01 \text{ N}$ (a) and their Kielland plots (b).



(a)



(b)

Fig. 2. Ion exchange isotherms for $\text{Na}^+ \leftrightarrow 1/2 \text{Ni}^{2+}$ exchange in analcime at $T_N = 0.01 \text{ N}$ (a) and their Keilland plots (b).

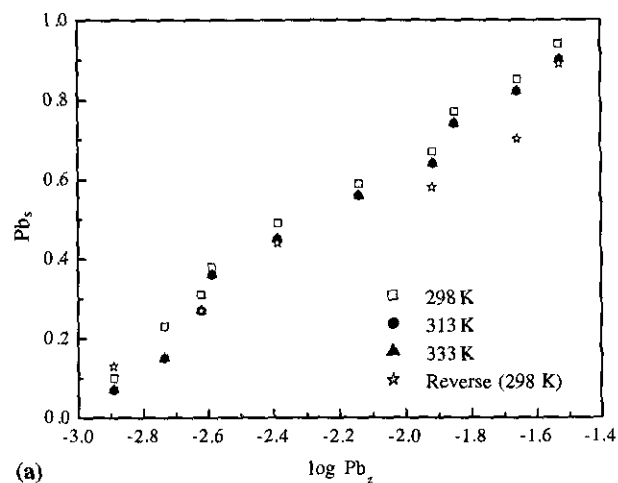
enthalpies (ΔH^0) and entropies (ΔS^0), for each cation pair studied, were generated by the same program. Values obtained are summarized in Table 1.

4. Discussion

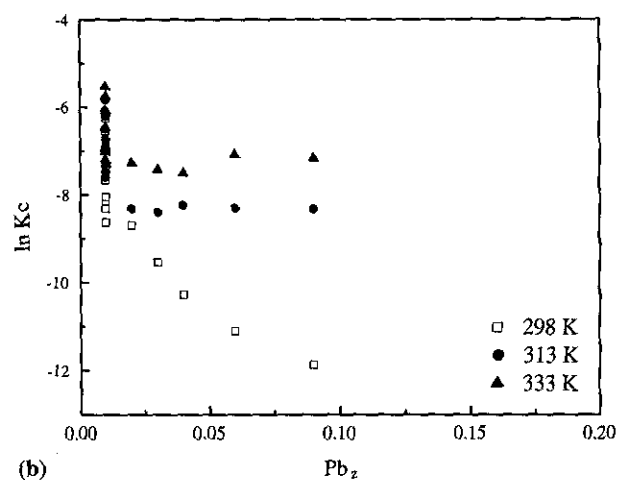
4.1. Isotherms

The isotherms (Figs. 1–4) were of good reversibility and the isotherms for Na/Pb, Cu, Zn had indications of sigmoidal shape. This suggests the presence of ion exchange sites of differing energy [12], viz: in the three non-intersecting channels of the analcime framework. Previous kinetic experiments showed that the sodium cations initially present in these channels were all replaceable by the cations studied herein [9].

Inspection of the isotherm shapes suggests that copper and zinc have slightly differing selectivities in approximately 50% of the exchange sites, with an in-



(a)



(b)

Fig. 3. Ion exchange isotherms for $\text{Na}^+ \leftrightarrow 1/2 \text{Pb}^{2+}$ exchange in analcime at $T_N = 0.01 \text{ N}$ (a) and their Keilland plots (b).

creased preference for sites at higher loadings of the in-going cation. Lead shows a slight change of selectivity above c.66% exchange. This may reflect the small differences in channel dimensions enhanced by the relatively larger Pb^{2+} ion.

4.2. Thermodynamic parameters

The ΔG^0 values (Table 1) enable the construction of a cation selectivity series, showing that the order of selectivity of the analcime synthesized from natural Thai perlite for the cations studied was; $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$, at 298 K. Table 1 also shows that these values are influenced by entropy changes, apart from the case of Na/1/2Cu exchange.

Pb^{2+} had the lowest ΔG^0 value, despite its large cation radii, which reflected its ease of polarisability coupled with its lowest enthalpy of cation hydration, $\Delta H_{\text{hd},y}$, ($-1480 \text{ kJ mol}^{-1}$) [13], amongst the cations studied. This result corresponded to that of Ahmed et al. [14]

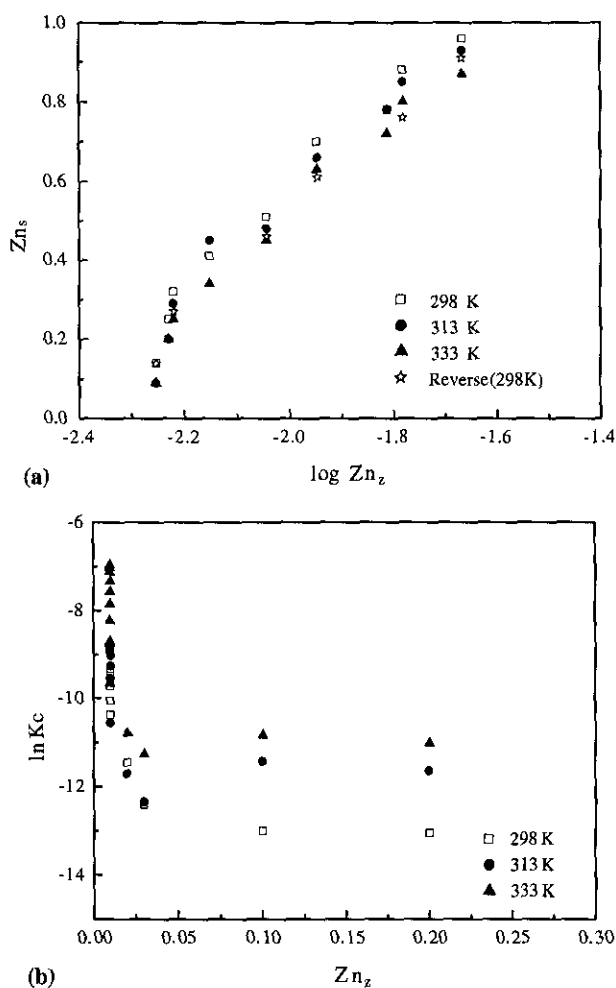


Fig. 4. Ion exchange isotherm for $\text{Na}^+ \leftrightarrow 1/2 \text{Zn}^{2+}$ exchange in analcime at $T_N = 0.01 \text{ N}$ (a) and their Kielland plots (b).

Table 1
Thermodynamic parameters for Na^+ /heavy metal ion exchange in analcime at various temperatures

In-going cation	T (K)	K_a	ΔG^0 (kJ mol ⁻¹)	H^0 (kJ mol ⁻¹)	ΔS^0 (J K ⁻¹ mol ⁻¹)
Cu^{2+}	298	2.0×10^{-6}	16.3	13.7	-8.8
	313	6.2×10^{-6}	15.6		-6.2
	333	6.6×10^{-6}	16.5		-8.5
Ni^{2+}	298	1.1×10^{-7}	19.9	62.0	141
	313	1.7×10^{-7}	20.8		132
	333	1.9×10^{-5}	15.2		141
Pb^{2+}	298	3.3×10^{-6}	15.7	43.0	156
	313	9.5×10^{-5}	12.0		160
	333	1.4×10^{-4}	12.3		149
Zn^{2+}	298	2.5×10^{-7}	18.9	38.9	145
	313	3.4×10^{-6}	16.4		146
	333	7.2×10^{-6}	16.4		137

who reported that ions with low charge densities were present in a less hydrated environment and so interacted more strongly with the zeolite framework. Barrer et al.

[15] also found that larger, less strongly hydrated, cations tended to concentrate in the zeolite in contrast to smaller, more hydrated ions, which tended to remain in solution.

Analcime has less preference for the smaller divalent cations because of their stronger ability to hold water molecules around them. The least preferred cation was Ni^{2+} , which had the highest enthalpy of hydration ($-2106 \text{ kJ mol}^{-1}$ [13]) of the in-going cations.

Major contributions to the observed positive entropy changes arise from the fixing of one divalent cation, and a water molecule, in the zeolite framework to replace two monovalent cations [15]. These changes can be expected to be approximately the same for the cation pairs studied and the results in Table 1 confirm this, with the $\text{Na} \leftrightarrow 1/2\text{Cu}$ exchange being a major exception. Contributions to ΔS^0 can also arise from changes in cation solvation [16], so entropy changes result from changes in water-cation environments created during exchange when cations with differing hydration spheres move between the solution and solid phases [17]. Negative entropy changes tend to reflect a net release of water molecules to the aqueous phase when cations are fixed to exchange sites in the zeolite phase. Here the relatively lightly hydrated sodium cation is being replaced by cations of a more hydrated nature, as shown by their higher heats of hydration. Only in the case of copper cations does this seem to create an overall negative change in entropy and this is linked to a much smaller enthalpy of exchange.

Fig. 5 plots ΔG^0 values against ΔH_{hyd} for Na^+ exchanging with Pb^{2+} , Cu^{2+} , Zn^{2+} and Ni^{2+} and confirms the link between free energy change and cation

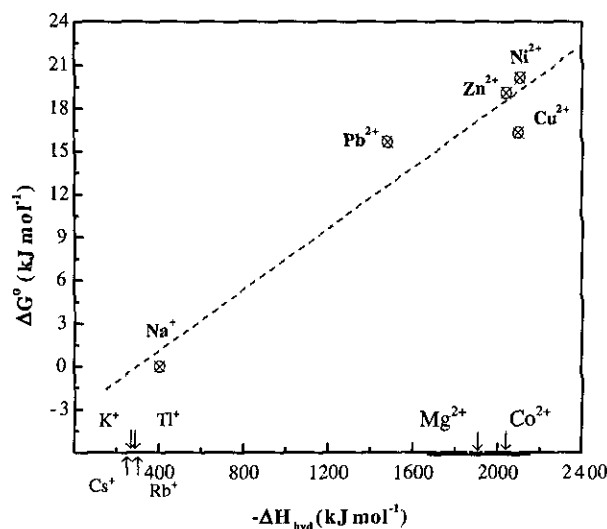


Fig. 5. Plot of ΔG^0 (kJ mol⁻¹) against ΔH_{hyd} (kJ mol⁻¹) for Na^+ exchange with Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} in analcime at 298 K.

Table 2
Comparison of selectivity series for zeolite ion exchange of heavy metals

Zeolite	Selectivity series	References
Analcime (ANA)	Pb > Cu > Zn > Ni	This work
Mordenite (MOR)	Cu > Zn > Ni	[4]
Clinoptilolite (HEU)	Pb > ZnCu	[17]
	Pb > Cu > Zn > Ni	[18]
	Pb > ZnCu > Ni	[19]
Chabazite (CHA)	Pb > Zn > Cu > Ni	[18]
Linde X (FAU)	Cu > Zn > Ni	[20]
Linde Y (FAU)	Cu > Zn > Ni	[20]
	Pb > Cu > Ni	[21]
Zeolite NaPc (GIS)	Pb > Zn > Ni	[22]

hydration energies. The low enthalpy and entropy values for the $\text{Na}^+ \leftrightarrow 1/2\text{Cu}^{2+}$ process might be explained by the copper cations retaining water molecules as they assume sites in the zeolite. Kinetic studies carried out earlier have given rise to a similar suggestion for zinc, but the plot in Fig. 5 does not confirm this.

Few ΔG^0 values for ion exchange in Na-analcime have been reported. Fig. 5 suggests Mg^{2+} and Co^{2+} exchange in Na-analcime should be low as experienced by Balgord and Roy [8]. On the other hand, when the hydration energies [12] of K^+ (-321 kJ mol^{-1}), Rb^+ (-296 kJ mol^{-1}), Cs^+ (-263 kJ mol^{-1}), and Tl^+ (-326 kJ mol^{-1}) are compared to that of Na^+ (-405 kJ mol^{-1}), full exchange into analcime is observed [7,8] as expected from Fig. 5.

4.3. Other zeolite selectivity for heavy metals

Table 2 lists selectivity series for other zeolites with respect to the cations under study. They are seen to be broadly similar despite variations in zeolite structure and Si/Al ratio. The relatively poor removal of Ni^{2+} by zeolites has been ascribed by Sherry [23] to the high stability of its aqueous complex in line with earlier comments.

Cu^{2+} and Zn^{2+} cations slightly differ in the order of their replacement [17–19] in chabazite and clinoptilolite. This may be because both the zeolite samples examined in the references cited are natural zeolites of sedimentary origin, with high Si/Al frameworks.

5. Conclusions

The cation selectivity series for the toxic metals studied in analcime, synthesized of Thai natural perlite has been found to be: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. This trend was like those quoted in the literature for several other zeolites (natural and synthetic). The zeolite selec-

tivity for these metals depends on the cation size and the cation hydration energy.

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References

- [1] R. Szostak, *Handbook of Molecular Sieves*, Van Nostrand Reinhold, New York, 1992, p.70.
- [2] X. Cheng, P. Zhao, J.F. Stebbins, *Am. Mineral.* 85 (2000) 1030.
- [3] J.D. Sherman, *AIChE Symp. Ser.* 179 (1978) 100.
- [4] R.M. Barrer, R.P. Townsend, *J. Chem. Soc. Faraday Trans. 1* (72) (1975) 661.
- [5] R.M. Barrer, in: L.B. Sand, F.A. Mumpton (Eds.), *Natural Zeolites Occurrence Properties Use*, Pergamon Press, Oxford, UK, 1978, p. 392.
- [6] R.M. Barrer, L. Hinds, *J. Chem. Soc.* (1953) 1879.
- [7] R.M. Barrer, *J. Chem. Soc.* (1950) 2342.
- [8] W. Balgord, R. Roy, *Adv. Chem. Ser. Am. Chem. Soc.* 101 (1971) 140.
- [9] A. Dyer, *Modern theories of ion exchange and ion exchange selectivity with particular reference to zeolites*, in: *Inorganic Ion Exchangers in Chemical Analysis*, CRC Press, Boca Raton, FL, USA, 1992, p. 33.
- [10] A. Dyer, *An Introduction to Zeolite Molecular Sieves*, John Wiley & Sons, Chichester, UK, 1988, p. 67.
- [11] P. Fletcher, R.P. Townsend, *J. Chem.Soc., Faraday Trans. 1* (78) (1982) 1741.
- [12] R.M. Barrer, J. Klinowski, *Philos. Trans. R. Soc., London* 285 (1977) 637.
- [13] G. Wulfsberg, *Inorganic Chemistry*, University Science Book, USA, 2000, p.57.
- [14] S. Ahmed, S. Chughtai, M.A. Keane, *Separat. Purificat. Technol.* 13 (1998) 57.
- [15] R.M. Barrer, J.A. Davies, L.V.C. Rees, *Inorg. Nucl. Chem.* 30 (1968) 3333.
- [16] H.S. Yoder, C.E. Weir, *Am. J. Sci.* 258 (1960) 420.
- [17] M.J. Semmens, M. Seyforth, in: L.B. Sand, F.A. Mumpton (Eds.), *Natural Zeolites Occurrence Properties Use*, Pergamon Press, Oxford, UK, 1978, p. 517.
- [18] S.K. Ouki, M. Kavanagh, *Waste Manage. Res.* 15 (1997) 384.
- [19] K.D. Mondele, R.M. Carland, F.F. Aplan, *Miner. Eng.* 8 (1995) 535.
- [20] A. Maes, A. Cremers, *J. Chem. Soc., Faraday Trans. 1* (71) (1975) 265.
- [21] U.D. Joshi, O.N. Joshi, S. Stamhamkar, V.P. Joshi, B.B. Idage, V.V. Joshi, V.P. Shiralkar, *Thermochim. Acta* 378 (2000) 121.
- [22] A. Moirou, E. Vaxevanidou, G.E. Christidis, I. Paspaliaris, *Clay Clay Miner.* 48 (2000) 563.
- [23] H.S. Sherry, *Ion Exchange* 2 (1969) 89.