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REMOVAL OF IRON FROM AQUEOUS SOLUTIONS BY ION EXCHANGE WITH NA-Y ZEOLITE

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ABSTRACT

Iron removal from aqueous solutions by batch ion exchange with a solid Na-Y zeolite has been studied. The pH of the solution was monitored continuously during the ion exchange process and the impact of pH on iron hydroxide precipitation and zeolite structural stability is discussed. In the case of the Fe(II)/Na-Y exchange system, the pH of the iron solutions was low enough to prevent the oxidation of Fe(II) and subsequent hydroxide deposition. The Al and Si contents in the solution were negligible, indicating maintenance of structural integrity, while scanning electron microscopic analysis did not reveal any structural breakdown. The ion exchange equilibrium isotherm, constructed at 291 ± 2 K and a total solution positive charge concentration of 0.1 equiv. dm^{-3}, exhibited a sigmoidal shape and a maximum exchange of 74% of the indigenous sodium content; maximum exchange was essentially independent of exchange temperature. An increase in the initial Fe(II) concentration, in the range 0.005–0.05 mol dm^{-3}, lowered the removal

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efficiency, but the external Fe(II) was preferred to the indigenous sodium over the entire concentration range. A maximum Fe(II) recovery of 84% from the maximally exchanged zeolite was achieved using 2 mol dm^{-3} solutions of NaCl as regenerant while the regenerated Na-Y delivered 68% of the original Fe(II) exchange capacity. The Fe(II) recovery was lower from samples exchanged under reflux conditions, while drying the loaded zeolite at 383 K also suppressed the degree of recovery. The treatment of Fe(III) solutions with Na-Y was not feasible due to the acidity associated with the zeolite/salt slurries, which promotes excessive hydroxide deposition and structural disintegration of the zeolite.

Key Words: Na-Y zeolite; Ion exchange; Iron removal; Water treatment.

INTRODUCTION

The removal of such hazardous heavy metals as Cu, Cd, Hg, Ni, Pb, Zn, Co, Al, and Fe from aqueous media has long been a serious environmental issue. Iron is found naturally in large concentrations in soil and rock normally in an insoluble form, but can, as a result of a series of naturally occurring complex reactions, be converted to soluble forms which often result in water contamination (1). Excess iron in ground water can also arise from the use of iron salts as coagulants during water treatment or as a by-product of pipe corrosion (1). Iron is very unlikely to cause a threat to health at the concentrations typically recorded in water supplies, but excessive amounts can certainly have detrimental effects. The EC Drinking Water Directive sets a maximum acceptable concentration (MAC) value of 0.2 mg dm^{-3} with the recommendation that concentrations should not exceed 0.05 mg dm^{-3}, while The World Organization guideline is set at the higher concentration of 0.3 mg dm^{-3} (1). The removal of iron from aqueous streams can be achieved by several processes, most commonly by precipitation, but other recovery methods have been applied such as ion exchange, electrodialysis, and biological treatment (2,3). Iron is soluble in the ferrous state, Fe(II), but is oxidized to the insoluble ferric form, Fe(III), in air (4) and the ferric iron hydrolyses readily to form highly insoluble ferric hydroxide. Conventional water treatment for the removal of iron involves the oxidation of ferrous iron and removal of ferric hydroxide by sedimentation and filtration (4,5). Although this approach is relatively simple and inexpensive, it has the decided drawback of generating a large volume of sludge for disposal, while the concentration of iron in the effluent that is produced often exceeds the target values.

Zeolites are proven ion exchange materials where the indigenous (typically sodium) charge balancing cations are not fixed rigidly to the hydrated aluminosilicate framework and are readily exchanged with metal cations in solution (6). Both synthetic (7–16) and naturally occurring (7,17–20) zeolites have been used to remove a range of toxic heavy metals from water. The application of the high surface area zeolite Y, the focus of the present study, to the removal of Cu, Ni, Cd, and Pb from water has been reported previously (15,16). The process of iron exchange with zeolites has been the subject of a number of investigations where the emphasis was placed firmly on the synthesis of efficient catalysts (21–23). The authors could not locate any fundamental studies dealing with iron removal by zeolite ion exchange as a means environmental pollution control. This may be due, in part, to the fact that the solution pH, which is necessary to circumvent iron hydroxide precipitation, is very low and zeolites can suffer structural breakdown even under weakly acid conditions (11). Hlavay et al. (24) have, however, investigated the efficiency of clinoptilolite for the removal of iron from drinking water and found that the operation of three ion exchange columns in series reduced the initial iron content (in the range 0.7–0.9 mg dm^{-3}) to below detectable levels. The purpose of this study is to assess the feasibility of applying Na-Y zeolite to the removal of iron (as ferric and ferrous ions) from aqueous media where the initial solution concentration of iron spanned the range 0.003–0.05 mol dm^{-3}. The role of pH in determining ion exchange efficiency and its impact on zeolite structure is discussed in some detail, while the possibility of a controlled release of iron from the loaded zeolite with a subsequent zeolite re-use is also considered.

EXPERIMENTAL

The starting zeolite was Linde molecular sieve LZ-52Y that has the nominal anhydrous unit cell composition $Na_{58}(AlO_2)_{58}(SiO_2)_{134}$. In order to obtain, as far as possible, the monoionic sodium form, the zeolite as received was contacted five times with 1 mol dm^{-3} aqueous solutions of $NaNO_3$. The zeolite was then washed briefly with deionized water, oven-dried at 363 K, and stored over saturated NH_4Cl solutions at room temperature; the water content was found by thermogravimetry (Perkin Elmer thermobalance) to be 24.8% w/w. Iron removal from aqueous solution by ion exchange was conducted in the batch mode. The exchange isotherms were constructed at 291 ± 2 K and at a total exchange solution concentration of 0.1 mol equiv. dm^{-3} where 1 equiv. equals 1 mol of positive charge. Ferrous iron removal was examined by contacting the zeolite with aqueous (deionized water) solutions of $FeCl_2(H_2O)_4$ in the presence or absence of known concentrations of NaCl to ensure the same initial solution phase charge concentration; a series of Fe^{2+}/Na^{+} solutions were prepared in which the iron concentration spanned the range 0.005–0.05 mol dm^{-3}. The effect of ion exchange temperature was considered by heating a Na-Y/0.05 mol dm^{-3} $FeCl_2(H_2O)_4$ suspension under reflux conditions for 24 h. Ferric iron removal was likewise examined using appropriate combinations of $FeCl_3(H_2O)_6$ (0.0033–0.0333 mol dm^{-3}) and NaCl in deionized water. The Na-Y zeolite (sieved in the mesh range 50–70 μm) was contacted with the Fe/Na solutions in sealed polyethylene bottles and the resultant slurry was agitated at 100 rpm on a Gallenkamp orbital for three days; the ratio of sorbate to sorbent was 100 cm^3 g^{-1}. The zeolite was separated from solution by repeated filtration and the metal content in the filtered liquid samples was measured after the appropriate dilution. In the case of ferrous iron determination, the treated solution was diluted in acidified (by addition of nitric acid to deliver a $pH = 4.1$) deionized water to prevent oxidation of Fe(II). The liquid phase concentrations of Fe, Na, Al, and Si were measured by atomic absorption spectrophotometry (AAS, Varian SpectrAA-10) where data reproducibility was better than ±2%. The solution phase pH changes during the ion exchange process were measured separately; 0.5 g of zeolite was added to 50 ml solutions of 0.05/0.025 mol dm^{-3} $FeCl_2(H_2O)_4$ and 0.0333 mol dm^{-3} $FeCl_3(H_2O)_6$, keeping the slurry under constant agitation. The pH was continuously monitored with a Hanna HI 9318 Programmable Printing pH Bench–Meter.

The efficiency of eluting the exchanged iron ions from the zeolite was also considered. After treatment of 0.05 mol dm^{-3} Fe(II) solution with Na-Y as described above, the resulting zeolite solid was washed and dried by vacuum filtration at room temperature. The degree of iron elution was determined by agitating (100 rpm) a 0.3 g aliquot of the sample in 15 cm^3 of NaCl solutions of varying concentration (0.1–4 mol dm^{-3}) at room temperature for 24 h; the pH of the slurry was adjusted to 4.1 by addition of NaOH. The regenerated zeolite was washed with acidified deionized water ($pH = 4.1$), equilibrated with a 0.05 mol dm^{-3} Fe(II) solution and the equilibrium iron content was determined by AAS as above. Structural changes to the zeolite were probed by Scanning Electron Microscopy (SEM), using a Hitachi S700 field emission SEM operated at an accelerating voltage of 25 kV. Samples (before and after ion exchange) for analysis were deposited on a standard aluminum SEM holder and double coated with gold. All of the chemicals employed in this study were of analytical grade and were used without further purification.

RESULTS AND DISCUSSION

Solution pH Changes During Ion Exchange

Zeolites are not only influenced by the pH of the immediate environment but are, in turn, capable of altering the pH of the media to which they are intro-

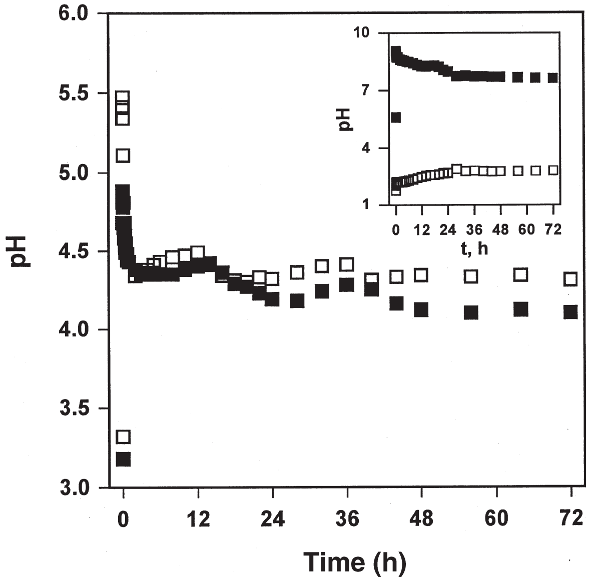

Figure 1. pH as a function of time in the Na-Y treatment of 0.05 (■) and 0.025 (❑) mol dm^{-3} Fe(II) solutions. Inset: time dependent pH profile associated with the addition of Na-Y to deionized water (■) and 0.0333 mol dm^{-3} Fe(III) solution (❑).

duced. The observed changes in solution pH with time for different initial Fe(II) concentrations are shown in Fig. 1. The initial pH of the 0.05 and 0.025 mol dm^{-3} solutions was 3.2 and 3.3, respectively. The hydrolysis of ferrous ions in solution can be represented by the following general equilibrium (25):

$$\mathrm{Fe2^+} + y\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(OH)}_y^{(2-y)+} + y\mathrm{H^+} \tag{1}$$

where the hydrolysis equilibrium constant (at 298 K) decreases in the order: $y = 1(5 \times 10^{-10}) > y = 2(3 \times 10^{-21}) > y = 3(4 \times 10^{-30})$. The predominant species in solution is then the hydrated ferrous ions. It is well established that the addition of zeolites to salt solutions results in complex pH variations where ion exchange is accompanied by a variety of hydrolytic side reactions resulting in additional hydronium ion exchange as well as precipitation of metal hydroxides (26–28). As shown in Fig. 1, the pH immediately increased upon addition of the zeolite to reach a maximum after 1–1.5 min and then fell quite dramatically to attain stable weakly acidic values (pH = 4.1–4.3). The immediate pH increase after addition of Na-Y can be attributed to a hydrolysis of the zeolite according to (26):

$$\text{Na-Y} + (\mathrm{H_2O})_x \rightleftharpoons \text{H-Y} + (\mathrm{H_2O})_{x-1} + \mathrm{Na^+} + \mathrm{OH^-} \tag{2}$$

The indigenous zeolitic sodium cations are partially exchanged by hydronium ions and the free hydroxide that is formed is responsible for the pH increase of the solution. The addition of Na-Y to deionized water was also accompanied by an immediate increase in pH to a maximum value of 9.1 that then decreased slowly to a constant value of 7.6 (see the inset to Fig. 1), due to a partial dissolution of the zeolite in the alkaline solution accompanied by a consumption of hydroxide ions (29). The decrease in solution pH in the Na-Y/Fe(II) slurry can be attributed to an uptake of the hydroxide ions originating from the hydrolysis of the zeolite, according to the following equilibrium (30–33)

$$Fe^{2+} + 2OH^- \rightleftharpoons Fe(OH)^2\ (sd) \qquad (3)$$

where (sd) denotes a solid precipitate. The degree of metal hydroxide formation is influenced by both the acidity of the salt solution and the alkalinity of the zeolite (27). The amount of ferrous hydroxide generated during the exchange process can be estimated based on the associated solubility equilibrium constant (K_{sp}) 4.87×10^{-17} (33). Where Fe(II) $= 0.05$ mol dm^{-3}, hydroxide formation is zero at pH $\leq$ 6.6 and the possibility of any Fe(II) precipitation can be discounted in this study as the pH during ion exchange remained below 5.5. Divalent ferrous ions have an association constant for the formation of $Fe(OH)^+$ that is some two orders of magnitude greater than those associated with Co^{2+}, Zn^{2+}, Ni^{2+}, and Cd^{2+} (34). Indeed, ferrous iron is known to promote hydronium exchange in zeolites and can even induce a degree of dealumination (35). However, the concentration of $Fe(OH)^+$ was estimated (from Eq. 1) to be negligible under the conditions employed in this study and the effect of $Fe(OH)^+$ formation on solution pH can also be discounted. The slow temporal pH decrease (from *ca.* 12 h onward) can be attributed to a hydronium ion re-exchange from the zeolite. The initial solution pH is dependent on the initial Fe(II) concentration, and if the initial Fe(II) concentration is sufficiently low, the pH profile is dominated by reaction (2).

The oxidation of Fe(II) to the ferric form Fe(III) and its subsequent hydrolysis in water can also serve to decrease the pH as follows (36):

$$2Fe^{2+} + 5H_2O + 1/2\ O_2 \rightleftharpoons 2Fe(OH)_3\ (sd) + 4H^+ \qquad (4)$$

The susceptibility of Fe(II) to oxidation in aqueous solution is dependent on pH and alkaline solutions that are readily oxidized to ferric hydroxide with a subsequent precipitation (37). Acidic solutions are much more stable, but a lower pH can lead to a slow hydrolysis of the framework aluminium with an accompanying gradual loss of ion exchange capacity and, ultimately, a collapse of the crystal structure. Once oxidized, the very low solubility of the ferric ions results in the precipitation of iron if the pH exceeds 3.0 even when the Fe(III) concentration is very low (38). The pH of all of the equilibrium solution phase samples was accordingly adjusted to 4.1, using acidified water to prevent oxidation of Fe(II) and any possible interference in the liquid phase iron concentration measurements caused by precipitation. The ferric iron hydrolyzes to form the highly insoluble ferric hydroxide as follows (36):

$$\mathrm{Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+} \tag{5}$$

Stumm and Lee (5) have reported that the kinetics of Fe(II) oxidation adheres to the following rate expression:

$$-[\mathrm{Fe(II)}]/dt = k[\mathrm{Fe(II)}][\mathrm{P_{O2}}][\mathrm{OH^-}]^2 \tag{6}$$

which can be rearranged to take the form

$$-\ln\{[\mathrm{Fe(II)}]/[\mathrm{Fe(II)}]_{\mathrm{i}}\} = k[\mathrm{P_{O2}}][\mathrm{OH^-}]^2 \times t \tag{7}$$

where $[\mathrm{Fe}]_{\mathrm{i}}$ and $[\mathrm{P_{O2}}]$ represents the initial concentration of ferrous iron in solution and partial pressure of oxygen, respectively, $k = 8.0 \times 10^{13}$ mol^{-2} atm^{-1} min^{-1} at 293.5 K (at 298 K, $k = 1.36 \times 10^{14}$ mol^{-2} atm^{-1} min^{-1}). The above expression is only valid where $\mathrm{pH} > 4.5$. In the pH interval 3–4.5 there is a significant departure from a second order dependence, while at $\mathrm{pH} < 3$ the rate of Fe(II) oxidation is independent of pH (31,39). The time required for the oxidation of Fe(II) to reach selected levels at 293.5 K was calculated using Eq. (7) and the results are given in Table 1. It is clear from the tabulated data that a pH below 5 is required to prevent significant Fe(II) oxidation. In this study, the solution pH was less than 4.4 for 98% of the total treatment time and the higher pH values were only attained during the initial zeolite hydrolysis stage; the degree of Fe(II) oxidation to Fe(III) is minor. It should be noted, however, that even a slight oxidation can lead to a significant pH drop and this must contribute to the pH profiles shown in Fig. 1. The changes in solution pH values at a constant initial [Fe(II)] concentration (0.05 mol dm^{-3}) at different stirring speeds in the range 60–720 rpm delivered superimposable profiles, indicating that stirring speed had no effect on the pH change.

A low pH can affect the stability of zeolites in general (7,40,41), while the structure of Na-Y is known to break down at pH less than 2.8 (11). Indeed, a solution pH below 4 should be avoided because hydrated alumina becomes ap-

Table 1. The Time Required (Calculated Using Eq. 7) for Varying Degrees of Fe(II) Oxidation at 293 K

	Time Required (Days)			
% Fe(II) Oxidation pH	1	5	20	50
4.5	4.1	21	92	285
5.0	0.4	2.1	9.2	29
5.5	0.04	0.2	0.9	2.9

preciably soluble at a pH of *ca.* 4 (40). The elution of aluminium from the zeolite lattice results in a reduction of the zeolite ion exchange capacity while competition for exchange sites by H^+ ions is more severe. The degree of aluminium extraction depends on a variety of factors, including: the nature of the acidic medium, treatment temperature, Si/Al ratio, and thermal history of the zeolites (40). As the Si/Al ratio of the Na-Y zeolite used in this study is relatively high (2.3), stability in acidic condition should be better than that exhibited by Na-X or Na-A (7,40). The Al and Si content in the Fe(II) solution (where $[\mathrm{Fe(II)}]_i =$ 0.05 mol dm^{-3}) after a treatment time of 72 h (i.e., the most "severe" conditions) were measured to ascertain the degree of structural collapse. A 0.34% removal of the zeolitic aluminium content was recorded, which compares with an even more negligible (0.07%) elution of the indigenous silicon; leaching of the aluminosilicate backbone can be regarded as negligible. Representative SEM micrographs of the parent Na-Y and a zeolite sample after ion exchange with Fe(II) are shown in Fig. 2. The geometrical crystalline features associated with Na-Y are evident and it is clear that there have been no appreciable structural changes after ion exchange. Considering the possible effects associated with solution pH in terms of zeolite structural stability, hydronium ion exchange and Fe(II) oxidation/hydroxide precipitation, an operating pH within 4.5–5.0 is accordingly proposed as optimum.

Equilibrium Ion Exchange Isotherm

The ion exchange of Fe(II) with Na-Y can be represented by the equilibrium (6):

$$\mathrm{Fe_s^{2+}} + 2\mathrm{Na_z^+} \rightleftharpoons \mathrm{Fe_z^{2+}} + 2\mathrm{Na_s^+} \tag{9}$$

where *s* and *z* represent the solution and zeolite phases, respectively. The exchange isotherm is shown in Fig. 3 where the abscissa is the equilibrium Fe(II) concentration in solution and the ordinate represents the equilibrium concentration in the zeolite phase. The isotherm exhibits a distinct sigmoidal shape which indicates an exchange site heterogeneity. The Y zeolite employed in this study is characterized (12) by an open framework consisting of two independent, though interconnecting, three-dimensional networks of cavities: (i) the accessible supercages of internal diameter 1.3 nm which are linked by sharing rings of twelve tetrahedral (free diameter = 0.7–0.8 nm); and, (ii) the less accessible sodalite units which are linked through adjoining rings of six tetrahedra which form the hexagonal prisms (free diameter = 0.20–0.25 nm). The sigmoidal profile can be attributed to an initial pronounced selectivity for Fe(II) exchange with sodium ions in the accessible supercages and the increasing involvement of exchange with parent ions located in the sodalite units at higher external ferrous ion concentration

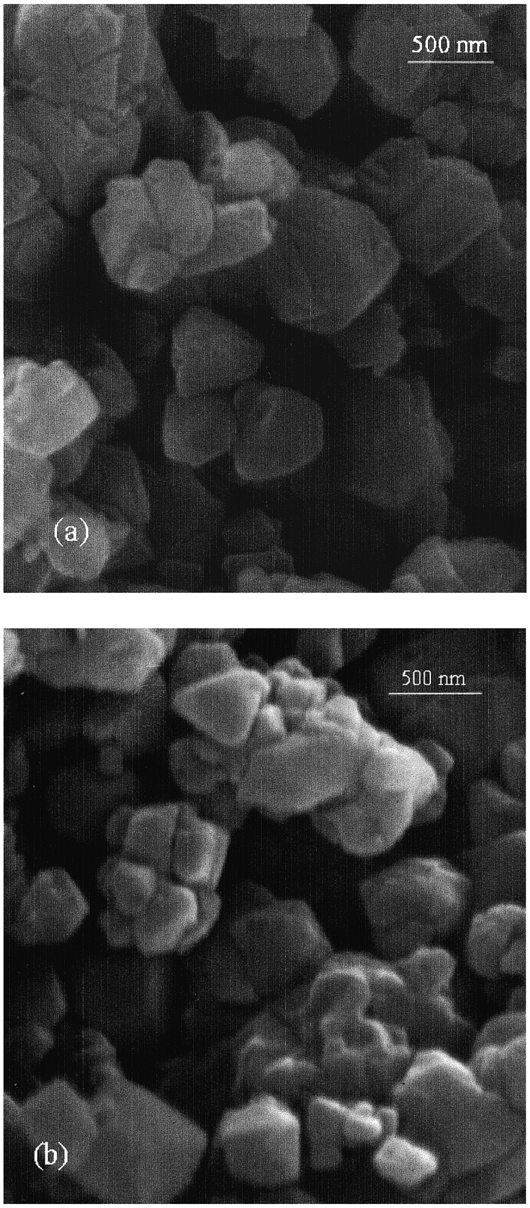

Figure 2. SEM micrographs showing the topographical features of (a) the parent Na-Y zeolite and (b) Na-Y after ion exchange with a 0.05 mol dm^{-3} Fe(II) solution.

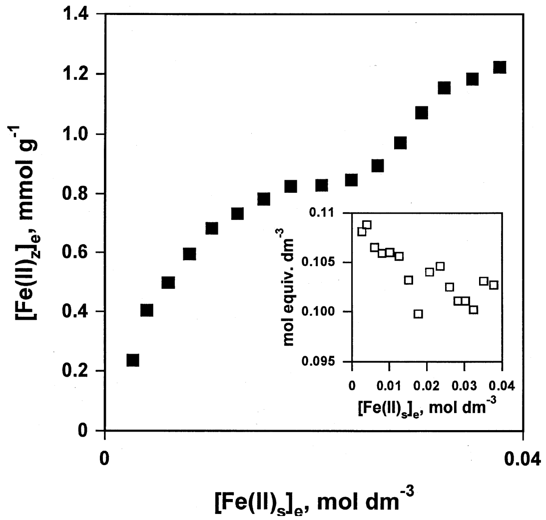

Figure 3. Fe(II) exchange isotherm obtained at a total positive charge concentration of 0.1 equivalent dm^{-3}. Inset: variation of equilibrium solution phase positive charge concentration with initial Fe(II) concentration in solution ([Fe(II)$_s$]$_i$).

(12,13). The degree of iron exchange with Na-Y increased as Fe(II) concentration increased and at the highest initial solution phase concentration (0.05 mol dm^{-3}) the equilibrium ferrous loading equaled 68 mg g^{-1} (1.2 mmol g^{-1}), which represents a 74% exchange of the indigenous sodium component. This value exceeds slightly the so-called "magic number" of 0.68 (68%) (8,10,12,13), suggesting a partial occupancy of the small cages. Firor and Seff (23) have quoted an ion radius of 0.223 nm for Fe^{2+} coordinated to three water molecules in the large cavities of a hydrated zeolite A; such a radius is of the same order as the free diameter of the hexagonal prisms in our Y zeolite. Ion exchange under reflux at 373 K delivered a maximum removal of the sodium complement in the range 66–70%, which is comparable to that achieved at room temperature. The capacity of Na-Y for exchange with Fe(II) is largely independent of temperature and therefore on the degree of Fe(II) hydration. The maximum level of Fe(II) exchange recorded in this study is similar to but higher than those reported previously, i.e. 64% (21) and 65–70% (22), where the maximally exchanged zeolites were prepared by treatment of a Linde Y zeolite (Si/Al = 2.4) with an aqueous solution of $FeSO_4$ (pH = 3.8–4.0) in a nitrogen atmosphere. The total positive charge concentrations in the equilibrium solutions are plotted as a function of the equilibrium Fe(II) concentration [Fe(II)$_S$]$_e$ in the inset to Fig. 3. The charge concentration varied within the range 0.0998–0.1088 mol equiv. dm^{-3} and there is no clear-cut dependence on

$[Fe(II)_s]_e$. The predominant exchange process involved a direct replacement of monovalent sodium by divalent iron. Moreover, there was no evidence of an "over exchange" by $(FeOH)^+$ ions as noted by Feng and Hall in the case of ZSM-5 (42) or an imbibition of the hydroxide. This is to be expected given our analysis of the equilibria in bulk aqueous phase (see Eqs. 1–5), although the intracrystalline environment in zeolites can diverge quite significantly from a purely aqueous environment (34). Nevertheless, under our stated experimental conditions the analogy does hold true and solution phase Fe^{2+} exchange with zeolitic Na^+ is essentially stoichiometric.

The removal efficiency can be conveniently quantified using the following expression:

$$\text{Removal efficiency} = \{[Fe(II)_s]_i – [Fe(II)_s]_e\}/[Fe(II)_s]_i \times 100\% \qquad (10)$$

where $[Fe(II)_s]_e$ is the equilibrium concentration of iron in solution. The removal efficiencies exhibited by Na-Y are plotted as a function of the initial solution phase iron concentration in Fig. 4, where it is evident that removal efficiency declined with increasing $[Fe(II)_s]_i$ but was essentially constant over the range 0.034–0.05 mol dm^{-3}. The residual iron concentrations in the solutions spanned the range 0.0026–0.0376 mol dm^{-3} from an initial concentration of 0.005–0.05 mol dm^{-3}. Under these conditions, a secondary "fine" treatment of the ferrous solution would be required after the "bulk" treatment by Na-Y in order to meet drinking water directives (1). Exchange selectivity can be quantified in terms of

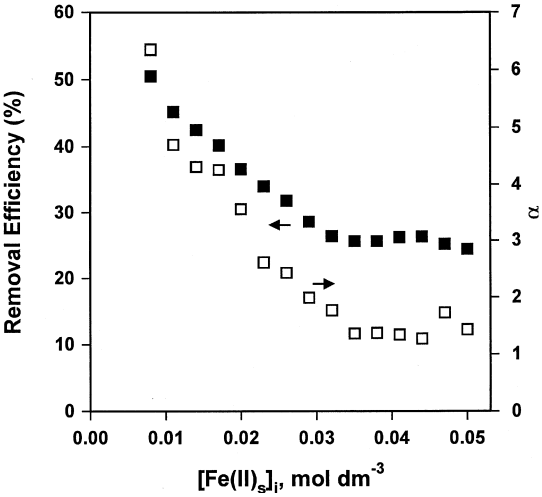

Figure 4. Fe(II) removal efficiency (■) and the associated separation factor (α,❑) as a function of the initial Fe(II) concentration in solution ($[Fe(II)_s]_i$).

the separation factor, α

$$\alpha = \frac{[\mathrm{Fe_z}]_e[\mathrm{Na_s}]_e}{[\mathrm{Fe_s}]_e[\mathrm{Na_z}]_e} \tag{11}$$

which for this system is defined as the quotient of the equilibrium concentration ratios of iron and sodium in the zeolite and in solution. If iron is preferred, the value of the separation coefficient is greater than unity, and the converse holds if sodium is favored by the zeolite. The relationship between the separation factor and $[\mathrm{Fe(II)_s}]_i$ is also illustrated in Fig. 4, where the high affinity exhibited by the zeolite phase for the entering iron ions is immediately evident with an associated separation factor in excess of 6 at low initial concentrations, and, while the value of α dropped with increasing $[\mathrm{Fe(II)_s}]_i$, the entering iron was preferred to sodium over the entire concentration range that was studied.

Zeolite Regeneration

The extent of Fe(II) elution or degree of zeolite regeneration is expressed as a function of the regenerant (NaCl) concentration in Fig. 5. The degree of Fe(II) elution was raised as the concentration of NaCl increased to reach a maximum re-

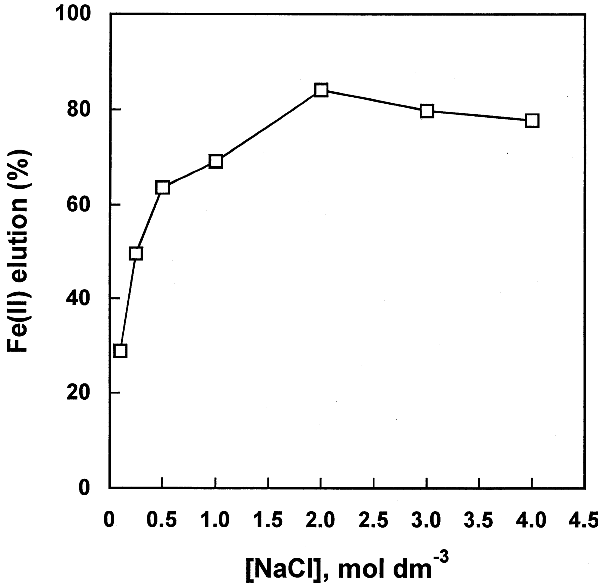

Figure 5. Percentage Fe(II) recovery into NaCl as a function of [NaCl].

covery of 84% of the zeolitic iron component at [NaCl] $= 2$ mol dm^{-3}; further increase in [NaCl] had little effect on Fe(II) recovery. Drying the samples at 383 K lowered considerably the %Fe(II) elution where less than 7% of the zeolitic iron was recovered with 0.1–2 mol dm^{-3} NaCl. This heat treatment can serve to remove some of the transition metal hydration sheath, facilitating a relocation of the divalent iron cations in less accessible sites where they are solvated by the zeolite framework oxygen atoms and are more difficult to remove (15). Higher temperatures can also facilitate the oxidation of Fe(II) (see Eq. 6), forming an iron hydroxide precipitate that remained on the zeolite. After regeneration with 2 mol dm^{-3} NaCl solution, the zeolite was filter–dried at room temperature and again equilibrated with 0.05 mol dm^{-3} Fe(II), but exhibited a decline in the degree of iron exchange (compared with the parent Na-Y) by a factor of 0.68 due to the incomplete regeneration. A regeneration of Na-Y sample exchanged with Fe(II) under reflux conditions resulted in a 70 % Fe(II) elution; the lower recovery when compared with the room temperature exchange can also be attributed to the heat treatment effect described above.

Fe(III) Treatment with Na-Y

It is well established that the hexaquo $[Fe(H_20)_6]^{3+}$ ion is too readily hydrolyzed for it to be a common reactant species (37). The solubility of ferric ions is given by the following equilibrium (25,28):

$$Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^- \tag{12}$$

Using the value of 2.79×10^{-39} for the associated Ksp that has been quoted in the literature (33), Fe(III) conversion to the hydroxide is induced at pH $= 1.7$ and is 92% complete at pH $= 2.0$ where $[Fe(III)]_i = 0.0333$ mol dm^{-3}. Furthermore, the degree of conversion has been shown to increase with increasing $[Fe(III)]_i$ (43,44). The pH required to minimize hydroxide formation is sufficiently low to induce zeolite disintegration. The solution pH observed in this study for the treatment of the most concentrated Fe(III) solution (0.0333 mol dm^{-3}) varied from 1.8 to 2.8 (see the inset to Fig. 1), and substantial precipitation of Fe(III) and decomposition of zeolite was inevitable. Based on solution phase concentrations, an erroneous maximum ion exchange of 126% was calculated as a direct result of hydroxide precipitation, while the equilibrium solution phase charge concentration spanned the range 0.088–0.094 equiv. dm^{-3}. A 7% silicon elution is markedly higher than that recorded for Fe(II) at the same initial charge concentration while a loss of 69% of the initial aluminium component suggests an appreciable structural breakdown. The latter is quite apparent from the SEM micrograph given in Fig. 6. It is clear that the Na-Y zeolite is not a feasible option for Fe(III) removal from water. Zeolites with higher Si/Al ratios are known to be more

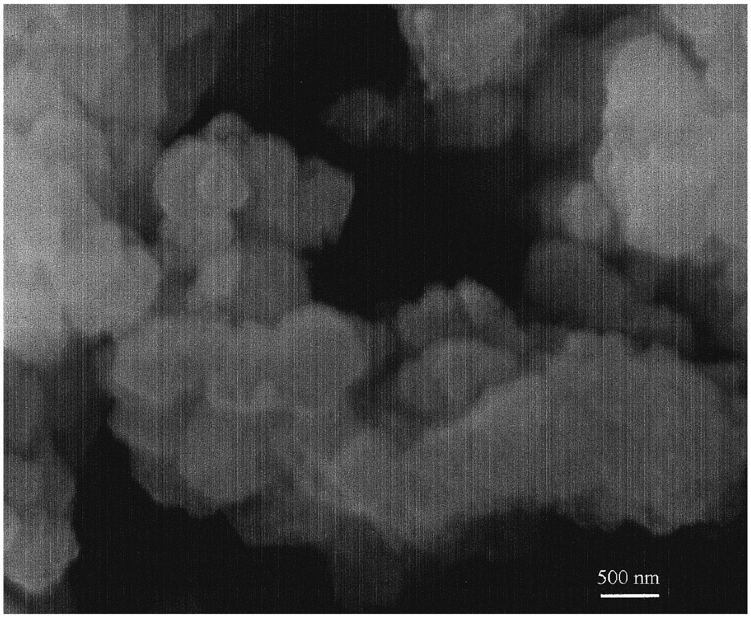

Figure 6. SEM micrograph showing the topographical features of Na-Y after ion exchange with a 0.0333 mol dm^{-3} Fe(III) solution.

stable to prolonged contact to inorganic acids at pH = 2 (7), and future studies of Fe(III) removal using zeolites will focus on such potential candidate materials as clinoptilolite and mordenite (40).

CONCLUSIONS

Sodium–based zeolite Y with a Si/Al ratio = 2.3 is effective in removing divalent iron ions from aqueous solution over the concentration range 0.005–0.05 mol dm^{-3} to yield a maximum (temperature independent) iron uptake of 68 mg Fe(II) per gram of zeolite. The zeolite exhibits a high affinity for exchange with external Fe(II), and the entering iron species is preferred over the indigenous sodium at each $[\mathrm{Fe(II)}]_i$, although the exchange efficiency does drop by a factor of 2 with increasing $[\mathrm{Fe(II)}]_i$. The solution phase pH must be maintained at 4.5–5 in order to prevent Fe(II) oxidation/$\mathrm{Fe(OH)_3}$ precipitation while the zeolite retains its structural integrity. The ion exchange isotherm is characterized by a sigmoidal shape diagnostic of an exchange site heterogeneity. The exchanged Fe(II) can be recovered by treatment with NaCl and repeated cycles of exchange/regeneration are possible although the zeolite does lose its exchange capacity with reuse; drying the loaded zeolite and/or performing the initial exchange under reflux conditions lowers the ultimate degree of Fe(II) recovery. The treatment of Fe(III) solutions with Na-Y, where $[\mathrm{Fe(III)}]_i$ is in the range 0.0033–0.0333 mol dm^{-3}, is unfeasible due to the unavoidable pH induced precipitation of $\mathrm{Fe(OH)_3}$ and disintegration of the zeolitic structure.

SYMBOLS

$[\mathrm{Fe(II)}_s]_i$	initial concentration of Fe(II) in solution (mol dm^{-3})
$[\mathrm{Fe(II)}_s]_e$	equilibrium concentration of Fe(II) in solution (mol dm^{-3})
$[\mathrm{Fe(II)}_z]_e$	equilibrium initial concentration of Fe(II) in the zeolite phase (mg g^{-1})
$[\mathrm{Fe(III)}_s]_i$	initial concentration of Fe(III) in solution (mol dm^{-3})
k	reaction rate constant in equation (7) (mole^{-2} atm^{-1} min^{-1})
K_{sp}	solubility product (mol^3 dm^{-3})
M	metal
$[\mathrm{Na}_s]_e$	equilibrium concentration of sodium in solution (mol dm^{-3})
$[\mathrm{Na}_z]_e$	equilibrium initial concentration of sodium in the zeolite phase (mg g^{-1})
$[\mathrm{OH}^-]$	concentration of OH^-(mol dm^{-1})
$[\mathrm{P_{O2}}]$	oxygen partial pressure (atm)
sd	solid
t	time

Greek Letters

α	separation factor

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