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A. I. Zouboulis[a]; D. Zamboulis[a]; K. A. Matis[a]
[a] LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY CHEMISTRY DEPARTMENT, ARISTOTLE UNIVERSITY, THESSALONIKI, GREECE

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Foam Flotation of Zeolites: Application for Zinc Ion Removal

A. I. ZOUBOULIS, D. ZAMBOULIS, and K. A. MATIS
LABORATORY OF GENERAL AND INORGANIC CHEMICAL TECHNOLOGY
CHEMISTRY DEPARTMENT
ARISTOTLE UNIVERSITY
540 06 THESSALONIKI, GREECE

Abstract

In this paper the solid/liquid separation of a NaY zeolite, a known cation exchanger, was investigated in the laboratory by foam flotation from aqueous suspensions. The main parameters affecting the process in batch experiments, such as the pH of the suspension, the type of collector, the cationic collector concentration, the zeolite concentration, and the ionic strength were examined. The optimum conditions for removal (flotation) of more than 95% of the zeolite were determined. Following flotation of the zeolite in the Na form, zinc ions were chosen to serve as an application for ion exchange by the zeolite (for metal recovery), followed by foam floatation of the exchanged form of the zeolite from solution.

INTRODUCTION

Many researchers in water or wastewater treatment have worked with particulate–solution systems, such as bacteria, ferric oxide, clays, active carbon, etc.; see, for instance, Grieves (*1*). Certainly another example—due to their particle size—may be the zeolites (molecular sieves).

Zeolites are highly crystalline, hydrated aluminosilicates with a very high internal surface area in the form of micropores of fixed geometry (*2*). They are used for their sorptive, catalytic, and ion-exchange properties (*3*). The ion-exchange properties of the zeolites have been well studied (*4*). The use of zeolites in beds has several limitations due to their solubility at low pH's and principally the increase in pressure drop across the bed during operation (*5*). In contrast, research on the flotation of the zeolites is limited, appearing in the literature as a Mobil patent (*6*) and as a few Japanese publications (*7*, *8*). In a quite similar field, zeolites have been applied in mineral processing for increased flotation selectivity and recovery (*9*).

The objectives of the present work are metal ion concentration and recovery. Application is envisaged in hydrometallurgy and also in industrial wastewater treatment when ion exchange is operated in a continuous stirred tank reactor type, or even, in cases of possible particle losses, from bed operations. The latter are more conventional with granular media.

Preliminary results on zeolite floatation following metal-ion exchange have been recently presented (*10*) by the authors, where zeolites were considered as a model of fine particles; the technique as applied to effluent treatment was also reviewed.

Zinc ion exchange by resins was previously practiced in hydrometallurgy (*11*). Flotation was proposed as an alternative separation method for zinc ions and other heavy metals ions from dilute aqueous solutions; for instance, precipitate flotation of zinc sulfide (*12*) or hydroxide (*13*) and zinc ion flotation by dithiocarbonates (*14*).

Recently, fine particles (and ultrafines) have received considerable attention in various industries because of increasing need for processing and controlling them. As far as technology is concerned, today there are many processes available to treat fine particles. The more conventional are various forms of sedimentation and filtration which present such different problems as high retention times and filter blockages. Flotation, a unit operation established in mineral processing, constitutes a rather unique case of a solid–liquid–gas separation method. It was tried in the present work due to the advantages it offers (low retention time, etc.) as a second stage following ion exchange.

EXPERIMENTAL

The laboratory flotation microcell and its arrangement was a typical dispersed-air system at the bench scale, as described elsewhere (*13*, *15*). Special care was taken for foam collection. A 100-cm^3 dispersion was tested in all the experiments. In most of them (unless otherwise stated), deionized water of 70–85 μmho conductivity was used and, in certain cases, tap water of 550–650 μmho.

In preliminary flotation experiments (*10*) a retention time of 600 s was observed as the optimum for a gas (nitrogen) flow rate of 1.66 cm^3/s. These values were used in the present work unless otherwise stated. Conditioning time did not affect flotation percent recoveries. Also, ethanol alone was not able to float the zeolite particles.

Three cationic and one anionic flotation collectors (surfactants) were tried: laurylamine (in 0.5% ethanol solution), cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, and sodium oleate. The ionic strength of the solution was varied by adding sodium salts—chloride, sulfate, and citrate—and also calcium chloride.

Zinc was introduced as a solution of zinc sulfate heptahydrate, usually as 50 ppm Zn^{2+}. The colorimetric zincon method at 620 nm was the analytical tool for zinc ion solutions, while turbidimetry at 510 nm was used for zeolite dispersions.

The zeolite used was a synthetic zeolite (NaY); its density was 1.92 g/cm^3. NaY zeolites have a faujasite-type structure (*2*), the Si/Al ratio was 2.4, and the crystallographic unit cell content is given by the formula $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]\cdot 250H_2O$. The zeolite size distribution analysis, obtained by laser diffraction, is given as Fig. 1, and it confirms the postulate of fine particles.

Sixteen Na^+ ions located in the hexagonal prisms, out of the 56 in the crystallographic unit cell, are not exchangeable. The ion-exchange capacity of the NaY zeolite is therefore 72% of the theoretical or 2.3 meq/g. So for 100 cm^3 of 50 ppm zinc solution, it was calculated that 0.664 g of the NaY zeolite were required to obtain complete removal.

The ion-exchange reaction was rapid. In preliminary ion-exchange experiments (*10*) the stoichiometrically required quantity of zeolite (0.664 g) gave removals of Zn^{2+} ions of over 80%. In subsequent experiments a 50% excess of the stoichiometrically required quantity of zeolite gave re-

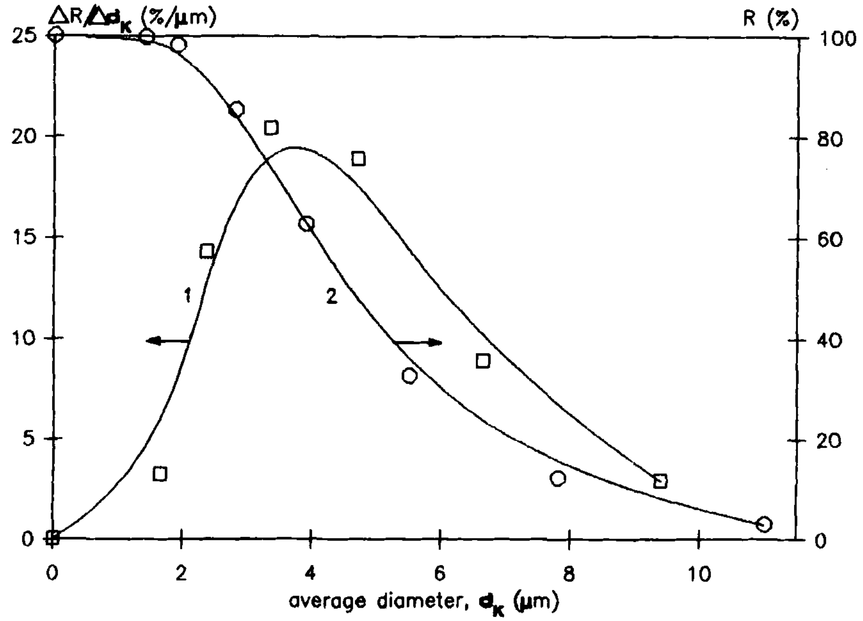

FIG. 1. Particle size distribution curves: (1) frequency basis and (2) cumulative basis for the remaining (R).

movals of over 90% after 300 s of ion exchange. In similar experiments where the solid/liquid separation of zeolites was accomplished either by centrifugation or by filtration, the results were similar.

RESULTS AND DISCUSSION

The foam flotation (or separation) of zeolite from water suspensions applied initially in this paper comprised one of the various flotation techniques available (*16*). Four different flotation collectors were tried: three cationic and one anionic. These experiments were carried out at a pH of approximately 7.6 and with an initial zeolite concentration of 0.664 g/L, used also in the following work. The results for the effect of concentration of surfactant on zeolite removal are presented in Fig. 2. The behavior of the three cationic surfactants was found to be quite similar. A concentration of 1 × 10^{-5} *M* of surfactant was necessary for satisfactory flotation of the zeolite. In small concentrations a problem with foam stability was noticed. When sodium oleate, an anionic collector, was used, the recoveries were nil, as expected from preliminary electrophoretic experiments. This indicated that the collector was not at all absorbed on the negatively charged

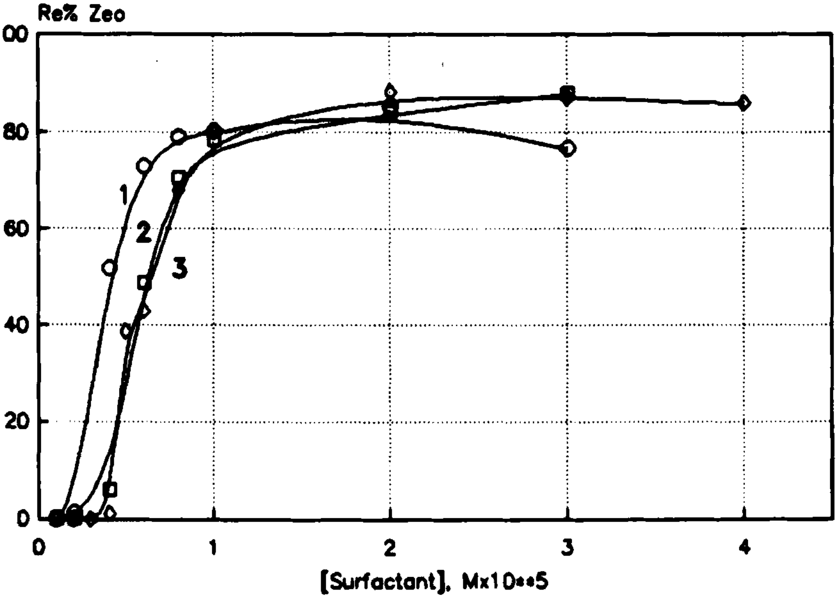

FIG. 2. Effect of collector (surfactant) concentration on zeolite flotation recovery for pH 7.6: (1) laurylamine, (2) cetyl pyridinium chloride, and (3) cetyl trimethylammonium bromide (water solutions).

surface of the zeolite particles, assuming an electrostatic attraction. Furthermore, the size of the sodium oleate molecule was too big to be adsorbed inside the zeolite pores.

In parallel experiments with 4 × 10^{-6} *M* laurylamine in 0.5% ethanol solution, it was observed that the mixing time influenced only the pH of the suspension and not at all the recovery, indicating that adsorption of the collector on the zeolite surface was rapid. With increasing mixing time, the pH decreased from 8.4 to 7.2 after 900 s without influencing the zeolite recovery.

It was also noticed that laurylamine gave better results for a broader pH range when introduced as ethanolic rather than as an aqueous solution, as shown in Fig. 3. It is generally known that ethanol acting as a foaming agent decreases the bubble size (*16*) and forms a more stable foam layer. On the other hand, an increase in collector concentration resulted in increased zeolite recovery and also increased the foaming (decrease of surface tension).

The pH of the suspension has usually been realized to be a crucial parameter in flotation techniques (*15*, *16*). A pH value around 7.6, as

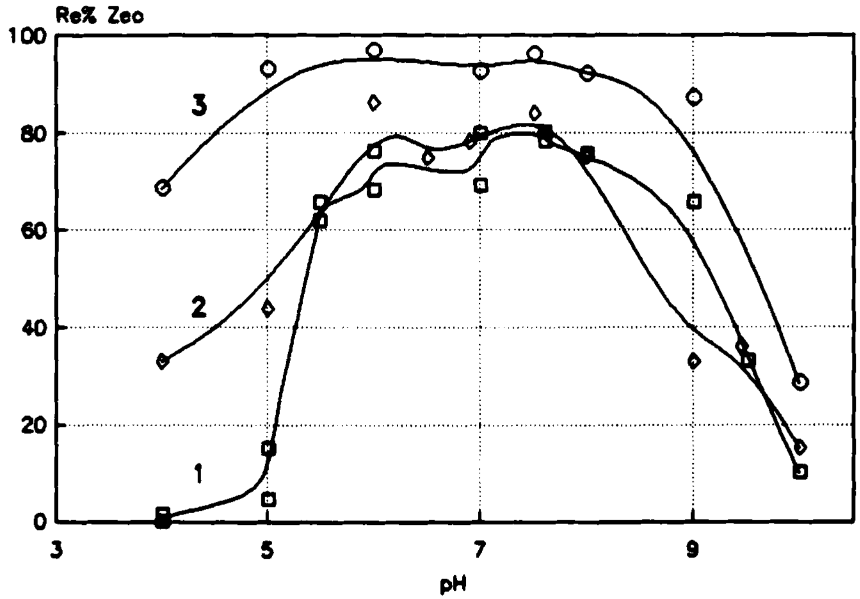

FIG. 3. Effect of pH on zeolite recovery using as collector laurylamine in various concentrations: (1) 1 × 10^{-5} *M* in water, (2) 0.25 × 10^{-5} *M* in 0.5% ethanol solution, and (3) 0.4 × 10^{-5} *M* in 0.5% ethanol solution.

shown, was found to be the optimum, but with the collector concentrations used in this work the zeolite recoveries were not affected substantially within the pH range 5.5 to 9.5, which is an advantage of this technique. This was verified in further experiments with other collectors; see Fig. 4. The zeolite instability at a pH below about 5 prohibited flotation, probably due to the collapse of its framework. Also, at a pH approximately above 10, the concentration of the active species of the collector (RNH_3^+) was reduced, resulting in the precipitation of the amine and subsequently in reduced zeolite recoveries.

The zeolite initial concentration in the dispersion was then examined with two different collector concentrations, shown in Fig. 5. Cetyl trimethylammonium bromide (in water solutions) and laurylamine (in 0.5% ethanol solution) were used as collectors. The method was found applicable over a wide initial zeolite concentration range (up to 10 g/L).

The ionic strength of the suspension was also investigated because it was found to be a critical parameter in ion flotation (*16*). The relative results are presented in Fig. 6 for higher values of ionic strength than in previous experiments; laurylamine was the collector (0.4×10^{-5} *M*). More or less similar results were reported for cetyl trimethylammonium bomide (*10*).

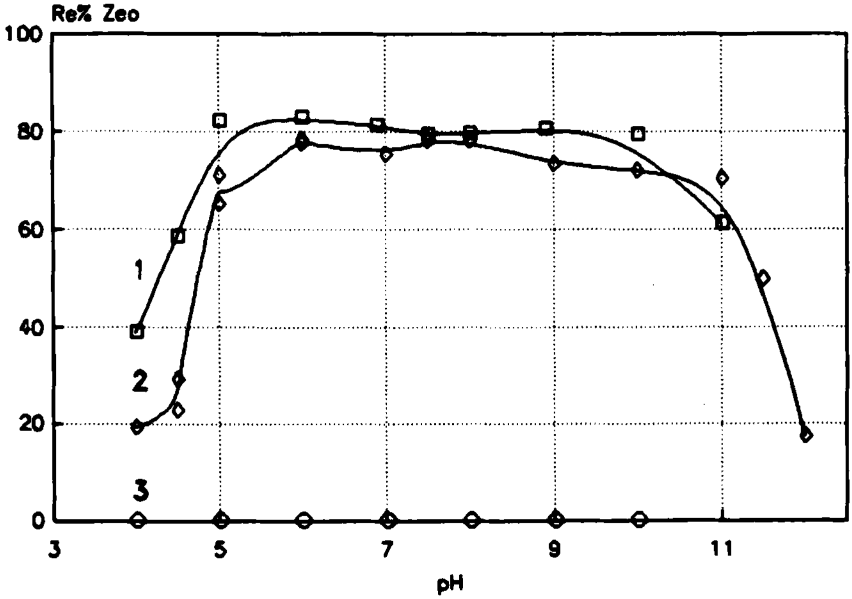

FIG. 4. Effect of pH on zeolite recovery, using as collectors: (1) cetyl trimethylammonium bromide, (2) cetyl pyridinium chloride, and (3) sodium oleate.

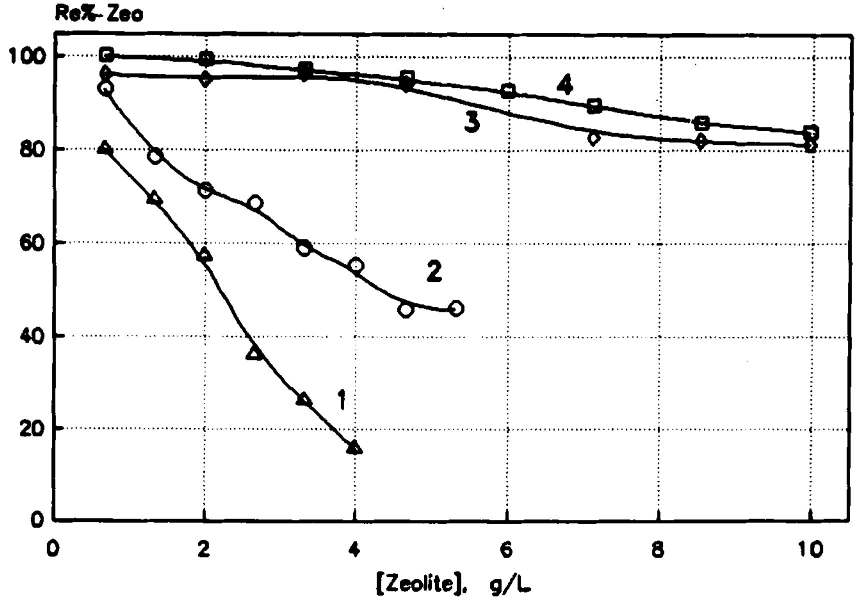

FIG. 5. Effect of zeolite initial concentration on recovery by different collectors (pH 7.6 to 9.4): (1) 1 × 10^{-5} *M* cetyl trimethylammonium bromide, (2) 0.4 × 10^{-5} *M* laurylamine (in 0.5% ethanol solution), (3) 5 × 10^{-5} *M* cetyl trimethylammonium bromide, and (4) 2 × 10^{-5} *M* laurylamine (in 0.5% ethanol solution).

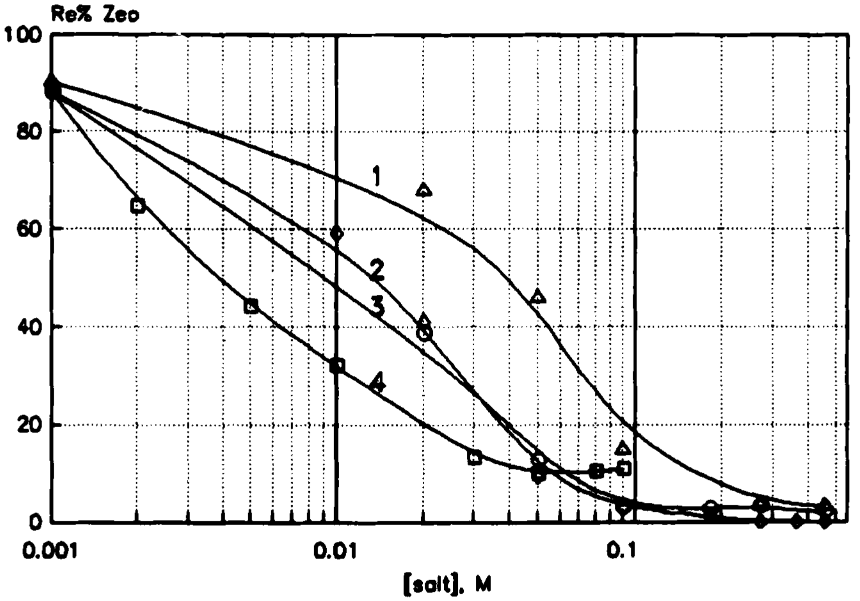

FIG. 6. Effect of ionic strength on zeolite recovery by laurylamine (in 0.5% ethanol solution) adding various salts (semilogarithmic graph): (1) sodium chloride, (2) sodium sulfate, (3) calcium chloride, and (4) sodium citrate (varying pH).

Inhibition of recovery was in the order: citrate > sulfate > chloride. Calcium chloride was more inhibiting than sodium chloride (common anion).

It is noted that the pH value in these experiments varied from 6.3 to 9.7. A pH correction is expected to improve flotation recoveries (see also Figs. 3 and 4) or, alternatively, an excess of collector, as also noticed in germanium ion flotation (*15*). The reason for the recovery decrease might be competition for the collector between the zeolite and the ions from the added salts.

Experiments on the ion exchange of zinc ions followed by flotation of the exchanged form of the zeolite were undertaken. The results for cetyl trimethylammonium bromide (water solutions) and laurylamine (in 0.5% ethanol solution) are given in Figs. 7 and 8, respectively; the quantity of zeolite used was a 50% excess above the theoretical quantity required for 100% removal of the zinc ions. The pH of the solution varied from 6.3 to 6.9. Foaming by large bubbles was observed in one case due to a nonsufficient quantity of the collector used and to the absence of any frother (see Fig. 7); this gave low zeolite flotation recoveries. Nearly complete recoveries of the zeolite were obtained in all other cases.

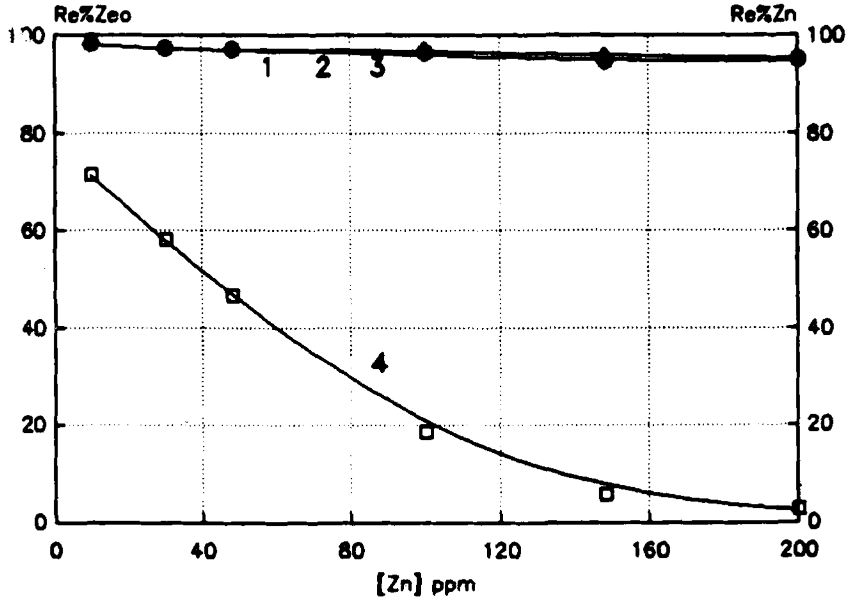

FIG. 7. Ion-exchange removal of zinc ions by zeolite (Curves 1 and 3) followed by flotation recovery of the exchanged form of the zeolite (Curves 2 and 4) by cetyl trimethylammonium bromide at two different collector concentrations. 5 × 10^{-5} *M*: (1) zinc removal, (2) zeolite recovery. 1 × 10^{-5} *M*: (3) zinc removal, (4) zeolite recovery.

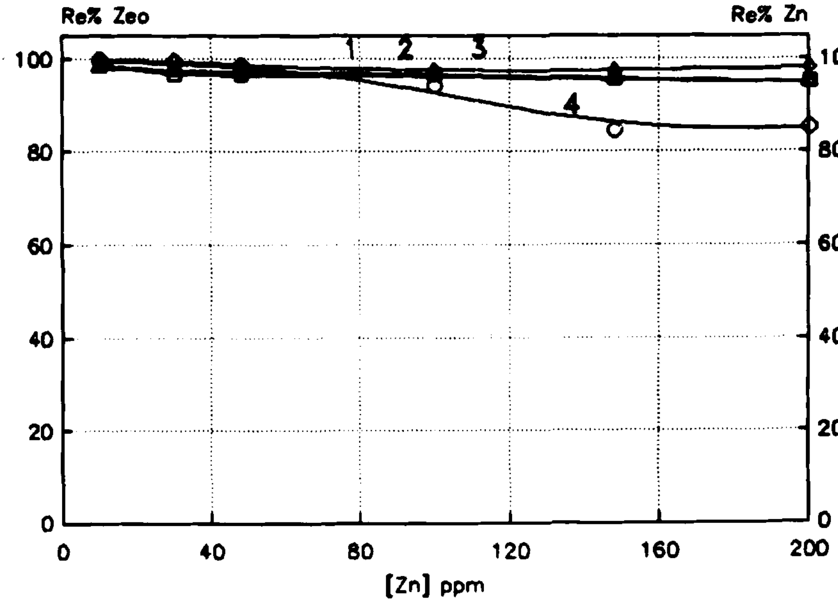

FIG. 8. Ion-exchange removal of zinc ions by zeolite (Curves 1 and 3) followed by flotation recovery of the exchanged form of the zeolite (Curves 2 and 4) by laurylamine (in 0.5% ethanol solution) at two different collector concentrations. 5×10^{-5} *M*: (1) zinc removal, (2) zeolite recovery. 1×10^{-5} *M*: (3) zinc removal, (4) zeolite recovery.

Finally, the work was repeated in tap water (Fig. 9). The results for laurylamine (also with cetyl trimethylammonium bromide) gave slightly decreased removals due to some collector consumption by the tap water salts. Hence, an excess of collector was necessary.

The ion exchange of zinc ions by zeolite is known to be a completely reversible reaction (*4*). Zinc ions would be easily recovered from the floated zeolite in a sodium chloride solution, which is important from the hydrometallurgical point of view. The zeolite, possibly with a further addition of collector, would be recycled in the envisaged process. There is no point, therefore, to further separate the collector from the floated zeolite.

It was noticed in experiments of the flotation of zeolite from aqueous suspensions in the absence of zinc ions, that zeolite removal by cationic collectors was possible. In earlier work on zinc precipitate flotation by laurylamine (*13*), it was found that for a pH around 7.6—which in this work was the optimum for zinc ion removal—zinc removals were very low because zinc hydroxide precipitated only around pH 9. Hence, an electrostatic interaction model was expected between the collector and the exchanged form of the zeolite; this behavior led to the observed flotation.

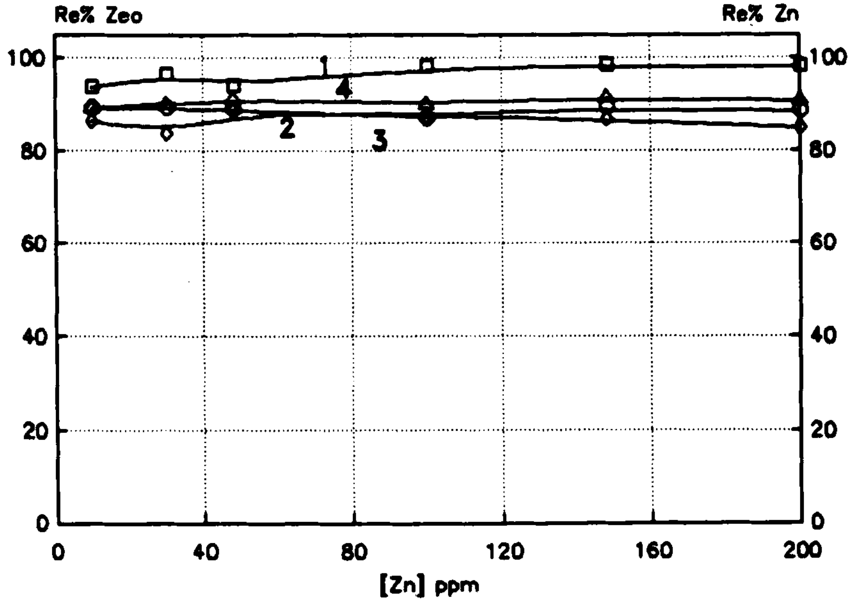

FIG. 9. Ion-exchange removal of zinc ions by zeolite in tap water (Curves 1 and 3) followed by flotation recovery of the exchanged form of the zeolite (Curves 2 and 4) by laurylamine (in 0.5% ethanol solution) at two different collector concentrations (pH 7 to 7.5). 5 × 10^{-5} *M*: (1) zinc removal, (2) zeolite recovery. 1 × 10^{-5} *M*: (3) zinc removal, (4) zeolite recovery.

To complete the discussion, we note the particle size range of the zeolite (see Fig. 1); 85% of the particles were in the 5.5 ± 1.9 μm size range. The significance of particle size and its consequences in flotation have been examined by many reviewers, including Fuerstenau (*17*). For obvious economic reasons, in flotation the upper grain size limit of floatability was the one to which the most attention was paid; fines are often a troublesome problem. There are numerous processing systems in which the ores must be deslimed; for more details see Somasundaran, Matis, and Gallios (*18*). Certainly the role of particle/bubble size needs further attention.

It was generally concluded that the results obtained were promising and that zeolite foam flotation from dilute aqueous dispersions can be regarded as a possible solid/liquid separation method in the range investigated. Similar results were found for the two main cationic flotation collectors used, due to the negative charge of the zeolite framework.

CONCLUSIONS

Zeolites are often used for the ion exchange of metal ions (such as zinc ions). Due to their small particle size, the solid/liquid separation of zeolites from dispersions presents several problems. It was proved experimentally in this work that the foam flotation of zeolites by laurylamine in ethanol solution or cetyl trimethylammonium bromide collectors (at pH values around 7.6) gives a satisfactory separation. These findings may open the way for foam flotation in the important field of fine particles processing.

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