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Use of zeolitized pumice waste as a water softening agent

I. Arrigo *, P. Catalfamo, L. Cavallari, S. Di Pasquale

Department of Industrial Chemistry and Material Engineering, University of Messina, Salita Sperone 31, I-98166 Messina, Italy

Abstract

Important pumice quarries are located on the island of Lipari (Italy) where an intense activity of extraction, transformation and trade of pumice takes place. Nevertheless, the finest fraction amounting to about 60% of mined pumice is discarded and disposed off in open-sky pits. This implies economic losses for mining industries and environmental problems for neighbouring villages. In order to find a sustainable use of this waste, we resumed and improved an old extractive process with aqueous sodium alkali, where a sodium silicate concentrated solution was produced together with an unextracted residue partially converted into zeolite P in Na$^+$ form and now we are searching for suitable applications of this residue.

In this paper, we relate about its use as a low cost water softening agent on the basis of results obtained from several tests both in batch systems and column. They show that, at room temperature, the residue works well with calcium and badly with magnesium, whereas, at 60 °C, also the affinity toward Mg ions increases to acceptable levels.

Repeated regenerations of the residue with concentrated NaCl solutions do not appreciably compromise the performance. The limits for the possible use as water softening agent are defined.
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Keywords: Ion exchange; Zeolite; Water softening; Pumice mine wastes

1. Introduction

A well-known method of extracting silica from pumice lapillus (a mining waste) with caustic soda, designed to produce alkaline silicates [1], allows an 80% energy saving when compared to today's most commonly used method (melting at 800–1000 °C of silica sand with soda) [2]. We recently re-examined the method in our laboratories in order to maximize extraction yields using as little reagent and time as possible. The optimized process, besides yielding a highly concentrated sodium silicate aqueous solution, also led to the simultaneous conversion of a high proportion (≥50%) of the unextracted residue into zeolite P (Fig. 1) [3,4]. Pure synthetic zeolite P, particularly in the "Maximum Aluminium P (MAP)" composition, has been suggested as a water softener [5] despite its being much less effective in the removal of Mg^{2+} (compared to Ca^{2+}) hardness at room temperature. In the present case, we are faced with an approximately half zeolitized lapillo (ZL) material, obtained as a low-cost co-product (ZL) of sodium silicate, which deserves better to become a useful product than to be

disposed off as waste. Consequently, it might be sold at a price (200 €/t) similar to that of natural zeolites which is an order of magnitude lower compared to that of the corresponding pure synthetic forms.

In order to verify this conjunction, it was highly interesting to test the real performance of the partially zeolitized product as a water softening agent, gaining additional but not, in our opinion, overlapping information with respect to what is already known on the pure zeolite.

For these reasons, tests were performed of the sodium form of ZL with calcium and magnesium ions in aqueous solution to verify the feasibility of its use as a water softener [6–9].

2. Experimental part

2.1. Characterization of the zeolitised product

The solid product derived from the extraction process was washed up to neutral reaction, dehydrated overnight at $T = 110$ °C and submitted to various characterization techniques.

- The crystal structure was determined by X-ray powder diffraction by *Philips X-Pert* diffractometer operating with the

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* Corresponding author. Tel.: +39 090 6765603; fax: +39 090 391518.
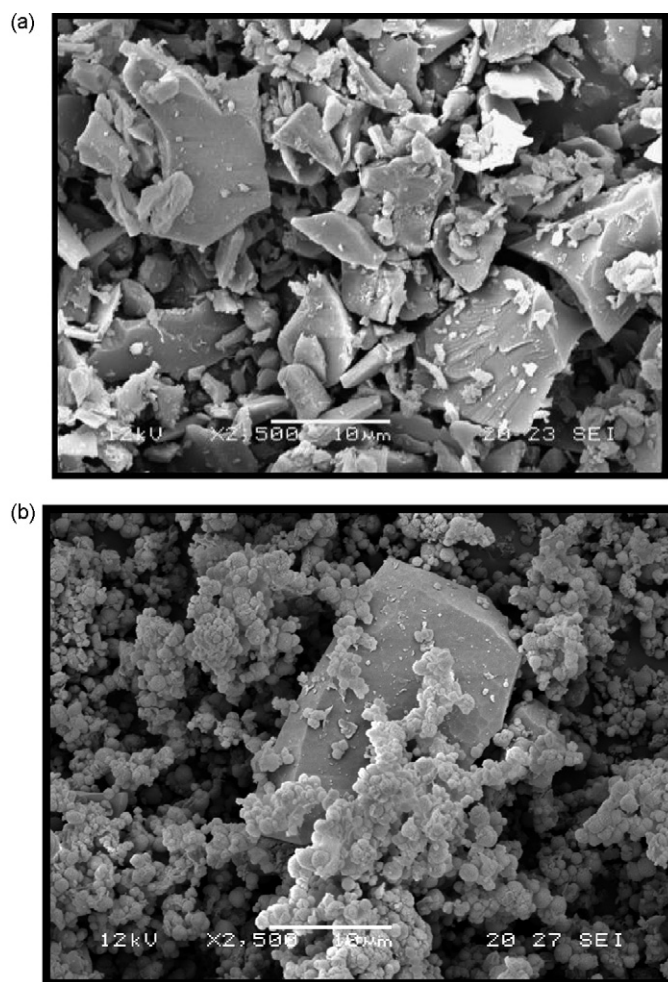 *E-mail address:* ileana.arrigo@unime.it (I. Arrigo).

(a)

(b)

Fig. 1. (a) SEM image of unzeolitized "Lapillo" pumice and (b) zeolitized pumice.

Ni β-filtered Cu Kα radiation ($\lambda = 1.54050$) at 40 kV and 30 mA. Continuous scans were collected with scan rates of $0.05°\,min^{-1}$ in the 2θ range 5–50°.

- The degree of crystallinity was determined by cation exchange (CE) measurements after an equilibration test of a weighed amount with an excess of a standard calcium chloride aqueous solution.
- The surface area was determined by N_2 physisorption at 77 K using an *ASAP 2010 MICROMERITICS*.
- The morphology by scanning electron microscopy (SEM) using a *Jeol 5600 LV* instrument, operating with an accelerating voltage of 12 kV with SEM micrographs taken after coating by gold sputtering.
- The chemical composition by an energy dispersive spectroscopy (EDS) microprobe (Oxford INCA ENERGY-400 with PENTAFET Si(Li) detector).

2.2. Ion-exchange tests

The same 1.0 g aliquot of dried ZL was submitted to CE equilibrium steps with a 200 mL aliquot of $CaCl_2$ (or $MgCl_2$) aqueous solutions [containing about 4 meq/L of Ca^{2+} or Mg^{2+}], and then filtered and contacted undried with further $(Ca, Mg)Cl_2$ aqueous aliquots both at room temperature and at 60 °C. The same experiment was carried out by contacting 1.0 g aliquots of dried ZL with a number of 200 mL aliquots of tap water, containing both Ca^{2+} and Mg^{2+}[approximately 4 meq/L] at a predetermined hardness of 20 °F.

Each step was kept under stirring for 15 min and then the filtered solutions were analysed for pH, by a Mettler pH-meter, for not adsorbed Ca^{2+} and Mg^{2+} by means of a volumetric EDTA titration at pH 10 (total hardness) and for the selective determination of calcium at a pH 12, where magnesium ions are precipitated as hydroxide and do not interfere with the determination of calcium. Magnesium can be calculated by subtracting calcium from total hardness [10].

ZL regeneration was carried out by contacting the Ca + Mg saturated ZL with 150 ml of a 3 M NaCl solution for 15 min.

The described tests were repeated in order to check if the exchanger performance changes after the regeneration steps.

At last, a test was performed under continuous tap water flowing in a column ($l = 10$ cm, $\phi = 1.5$ cm), packed to 3.5 cm with 1.0 g of ZL; the latter was first pelletized with a sodium silicate binder up to particle sizes of 2 ± 0.5 mm[1]; 1.6 L of tap water of 18 °F (containing about 3.60 meq/L of $Ca^{2+} + Mg^{2+}$) flowed across the column at a rate of 14 mL/min until EDTA titrations of successive aliquots of water exiting from the column showed no more Ca and Mg ions absorption. This test, as well as the previous one, was repeated with the regenerated ZL.

3. Results

3.1. Characterization of zeolitized product

As shown by the SEM image the lapillo surface before the treatment appears irregular and characterized by large smoothed grains having sharp edges typical of an amorphous phase (Fig. 1a). After caustic treatment (Fig. 1b), we can see that the structure of the unextracted solid product is mostly re-organized in small aggregates that prefigure a diffuse presence of small crystallites an order of magnitude smaller (1–4 μm) than original lapillo particles (10–40 μm, see Fig. 1a).

The crystallization is confirmed by the XRD pattern, which also indicates formation of zeolite P (Fig. 2) [12].

As to the chemical composition, the EDS microprobe showed that the SiO_2 (75%) and Al_2O_3 (12%) contents of the lapillo pumice change into about 54% SiO_2 and 24% Al_2O_3 in the unextracted residue obtained after the second step of SiO_2 extraction by sodium alkali, giving a solid product weighing 40% as before and having a Si/Al ratio of about 2.2 (Table 1).

CE capacity measurements gave 2.8–3.3 meq of sodium exchanged with calcium in 1 g of sodium exchanger. On the basis of: (a) the estimated CE capacity of about 4.9 meq/g for zeolites having a Si/Al ratio of 2.2 [11]; and (b) exchanges for only few tenths of CE capacity by the amorphous precursor

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[1] The pelletised ZL showed, in a blank test, a CE capacity ≈20% lower than the same amount of ZL powder. The decrease in CE was due to ligand dilution and to a decrease in surface area. It was also in agreement with previous results [11].
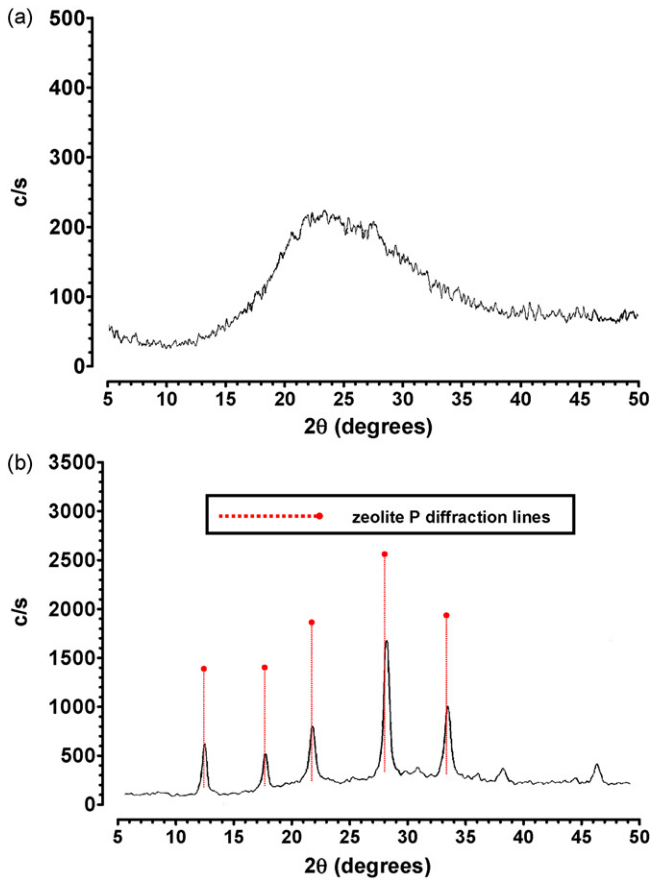
Fig. 2. (a) XRD pattern of unzeolitized "Lapillo" pumice and (b) zeolitized "Lapillo" pumice; (●) zeolite P diffraction pattern.

Table 1

Chemical composition of lapillo pumice and zeolitized pumice by energy dispersive spectroscopy (EDS) microprobe

	Lapillo pumice (%)	Zeolitized product (%)
Na_2O	3.01	14.23
Al_2O_3	11.98	24.39
SiO_2	74.98	54.60
K_2O	5.48	3.37
CaO	1.12	1.75
$FeO + Fe_2O_3$	2.69	2.83

of zeolite P (i.e., the unextracted phase coming from the first extraction step of lapillo pumice), we estimated a degree of zeolitization at least 60%.

Moreover, BET data (Table 2) show an interesting formation of meso and micro-porosity, not visible in the SEM images and totally absent in lapillo pumice.

Table 2
BET surface area

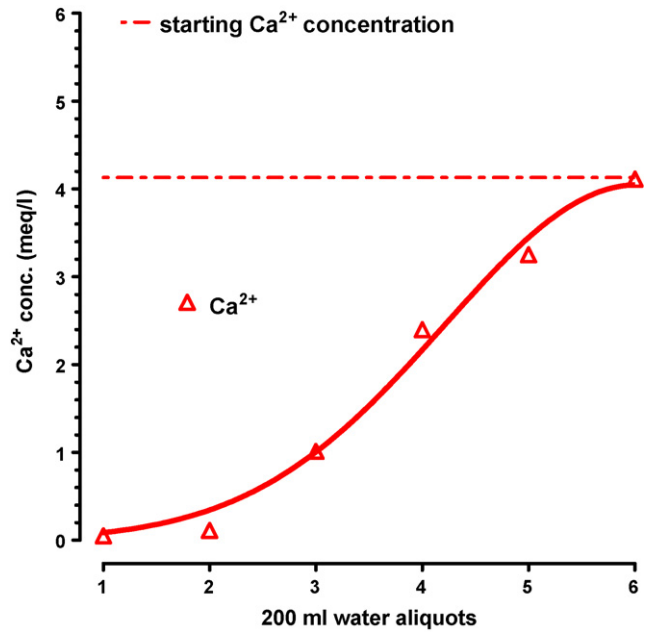| Samples	Lapillo pumice (m^2/g)	Zeolitized product (m^2/g)
BET surface area	1.19 ± 0.016	34.40 ± 0.12
Micropore area	0.04	3.57
External surface area	0.78	30.55

Fig. 3. Ca^{2+} residual concentrations (meq) in $CaCl_2$ after softening equilibrium steps of batch system at room temperature.

3.2. Ion-exchange tests

In all tests pH maintained approximately neutral before, during and after the exchange.

The data shown in Figs. 3–7 refer to pre-equilibrium exchange tests at room temperature or at $60\,^\circ$C of the same 1 g aliquot of ZL in Na^+ form contacted with three up to eight successive 200 mL aliquots of diluted calcium and/or magnesium chloride aqueous solutions. In particular, Figs. 3 and 4 refer to ca. 4 meq/L solutions of calcium chloride and magnesium
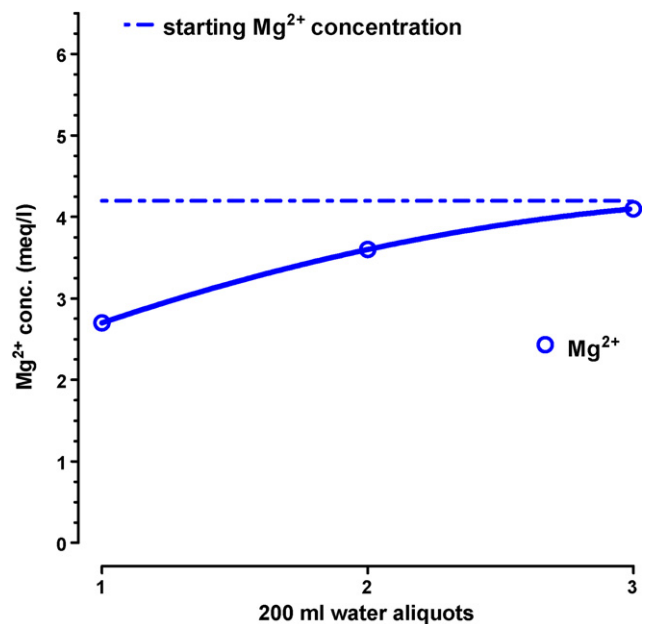

Fig. 4. Mg^{2+} residual concentrations (meq) in $MgCl_2$ after softening equilibrium steps of batch system at room temperature.
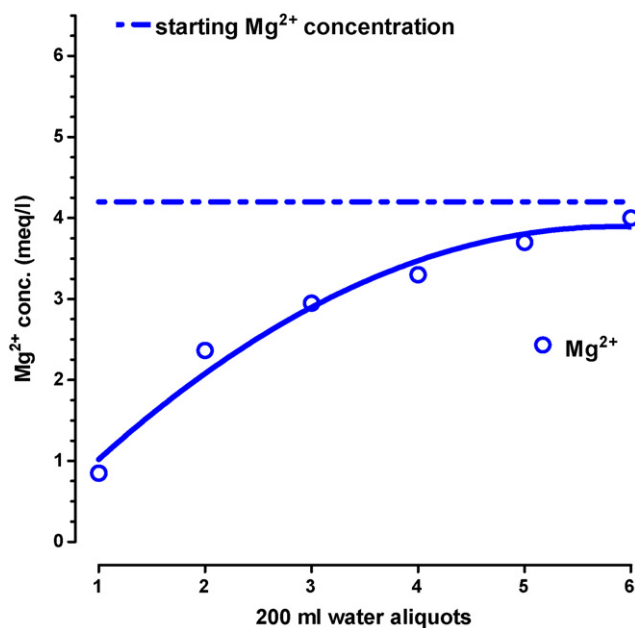
Fig. 5. Mg^{2+} residual concentrations (meq) in $MgCl_2$ after softening equilibrium steps of batch system at 60 °C.

Fig. 7. Ca^{2+} and Mg^{2+} residual concentrations (meq) in tap water after softening equilibrium steps of batch system at 60 °C.

chloride respectively, at room temperature. These show a much higher affinity towards ZL for calcium than sodium (≈92% of ions exchanged at first contact) and a lower one for magnesium (≈35% of ions exchanged at first contact). This different affinity has been observed for other zeolites (e.g. zeolite A) [13,14] and could be due to the higher hydration energy of magnesium and the greater volumetric dimensions of its hydrated ion in diluted aqueous solutions in comparison to calcium and even sodium ions, that would impede penetration of the channels. This is confirmed by the test of Fig. 4, carried out at 60 °C,
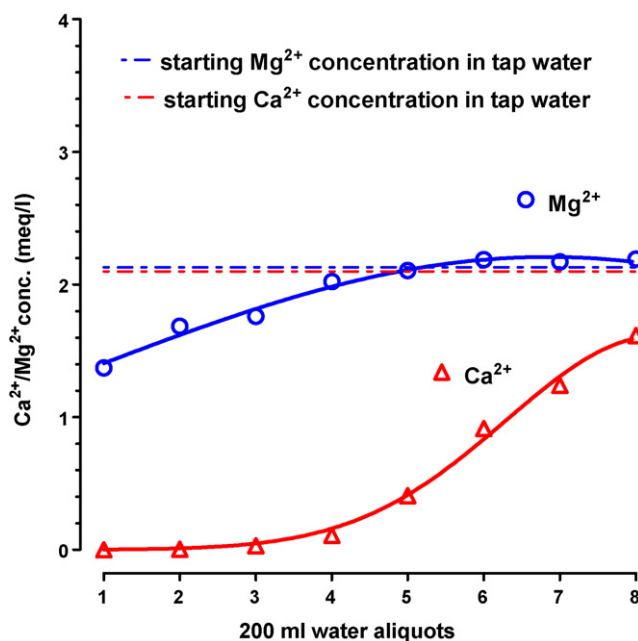
where an increase from 35 to 80% in the percentage of magnesium exchanged with sodium ions is observed at first contact, as a result of the weakening of the hydration bonds.

Figs. 6 and 7 refer to diluted solutions of calcium and magnesium ions (tap water) at room temperature (Fig. 6) and at 60 °C (Fig. 7). They confirm a far higher affinity (relative to sodium) of calcium (≈100% exchange) than of magnesium (≈35% exchange) ions towards ZL, while at $T = 60$ °C an increase in the affinity of magnesium (from 35 to 87% exchange) in relation to sodium ions is observed.

Even in subsequent contacting steps of the same 1 g aliquot of ZL with successive fresh aliquots of tap water (200 ml) the high affinity of calcium ions towards sodic ZL is confirmed: in fact, after the fifth step ZL is still able to attract 80% of the calcium present in that aliquot of water at room temperature (Fig. 6). If we add the meqs of Ca and Mg that are retained by the same 1 g aliquot of ZL after eight contacts, these are equal to ≈2.80 meq/g at room temperature and ≈3.28 meq/g at 60 °C.

In regenerating the 1 g aliquot of ZL saturated, as described above, i.e., with an excess of 3 M aqueous solution of NaCl, a quantity of Ca^{2+} and Mg^{2+} similar to that absorbed was released, indicating complete regeneration even for calcium.

Figs. 6 and 7 also show that as soon as the zeolitised residue is saturated, further contacts with fresh aliquots of tap water determine substitution of part of the previously fixed magnesium with calcium ions. This trend increases at 60 °C (Fig. 7). Further investigations could be interesting for future applications of this property [15].

The column tests showed that at room temperature one gram of sodium ZL is capable of retaining an overall quantity of Ca and Mg ions of around 3.0 meq; nevertheless, the hardness of the water passing the column was only greatly lowered but never zeroed (Fig. 8).

Fig. 6. Ca^{2+} and Mg^{2+} residual concentrations (meq) in tap water after softening equilibrium steps of batch system at room temperature.
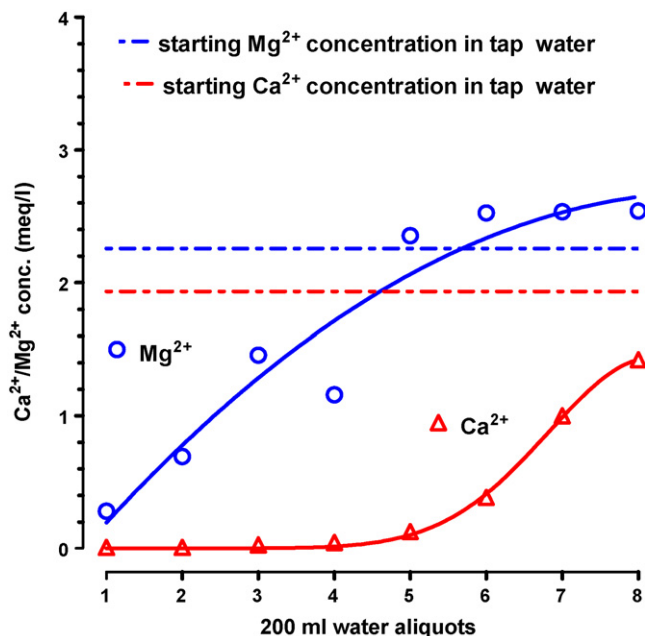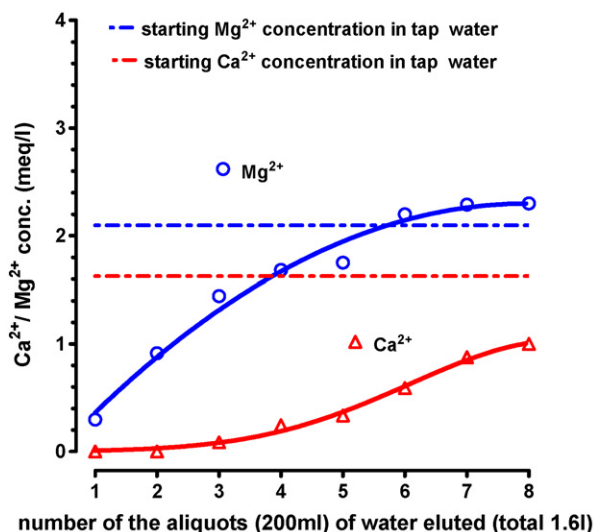
Fig. 8. Ca^{2+} and Mg^{2+} ions concentration in tap water aliquots passed through a column packed with 1 g ZL in sodium form at room temperature.

4. Conclusions

From the above, ZL in sodium form, derived as a zeolitized unextracted residue from extraction with caustic soda of amorphous silica from pumice lapillus, shows high affinity towards calcium ions and low affinity towards magnesium ions, at least at room temperature. In water softening, where hardness (both calcic and magnesic) must be totally eliminated, ZL alone would not make a suitable alternative to commonly used polymer-based cationic exchangers but it should be considered that these products could be marketed at up to a tenth of the cost of polymer-based exchangers. Moreover, they are far less sensitive than the latter to temperature increases and to the presence of oxidants. Consequently, we are of the opinion that they might be proposed in conjunction with traditional resins in a process involving initial contact of the water to be softened with a sodic ZL bed (that would account for up to 2/3 of the softening), followed by further contact with a smaller bed of traditional cationic resins in sodium form (to complete the softening process by retaining the excess magnesic hardness not retained by the previous bed). To this end, high exchange capacity (3 meq/g), at least towards calcium, good resistance to repeated regeneration and the other desirable qualities, in particular lower costs, would improve the water softening process and make it more economic.

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