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Viability of the Use of Polymer-Assisted Ultrafiltration for Continuous Water Softening

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ABSTRACT

We examined the viability of a continuous metal-removing process using polymer-assisted ultrafiltration. The proposed system has two connected sections at different pH. Each section has an ultrafiltration membrane that filters the aqueous solution and retains the polymer. In the first section, the metal is attached to the polymer. In the second section, the metal is detached. The polymer is recycled, and then recovered, by pumping from the second section into the first section. Preliminary experiments provided sufficient information for simulations of the continuous removal of Ca^{2+} from water. A poly(acrylic acid–maleic anhydride) sodium salt was selected as the polymer. Ceramic membranes of 5 kDa cut-off were used to filtrate the aqueous solutions. We show that the proposed system continuously removes Ca^{2+} from water in a satisfactory way.

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INTRODUCTION

High-quality water resources are scarce in many areas. A potential solution to this water shortage is the development of processes that improve the quality of brined groundwater. For many years, ion exchange processes have been used for this purpose.[1] More recently, reverse osmosis and nanofiltration have also been used for this function. At the same time, other possible processes have been analysed. For example, a polymer assisted ultrafiltration (UF) process was shown to be promising for removal of metallic species from aqueous streams. The basis is that the metallic species are retained after binding with water-soluble polymers and the unbound species pass through the membranes. Most research deal with the separation of heavy metals.[2–9] Polymers with ligand groups are usually tested, such as amines,[2–4,7,8,10] anionic polyelectrolytes with phosphonic,[11] sulfonic,[12–16] and carboxylic[17,18] groups. The use of natural polymers[4,10,19] and polyelectrolytes anchored to the membrane[20] are growing alternatives. In water-softening applications, it has been reported that with the help of an anionic polymer UF might be useful.[12,13] Recently, UF with the help of a cationic polymer has also been shown to be valuable.[10]

On the whole, water softening using a polymer assisted UF process is analogous to the established ion exchanger process. In the conventional ion exchange process, the ion exchanging groups can be attached either to a polymeric network (solid resin) or to an organic radical hydrophobic enough to make the compound practically insoluble in the aqueous phase, but soluble in an organic solvent. The first situation corresponds to classical ion exchangers and the second to liquid extractants with ion exchange properties.[21] In both cases, it is simple to separate the ion exchanger phase from the aqueous phase. In contrast, in the polymer-assisted UF process an ion exchanger microphase or soluble polyelectrolyte has to be separate from the aqueous phase by ultrafiltration. There are certain advantages to this technique: the great variety of available polyelectrolytes, the kinetic noncontrolling ion diffusion in the ion exchange process, the possibility to pump and handle the ion exchanger material. A drawback is that we cannot use a fixed packed bed of solid ion exchanger material, which makes it difficult to work with plug-flow mode for the metal concentration in the aqueous phase. This limitation also makes it difficult to maintain very low concentrations of the exchanged metal ion in the out-stream. Only mixed flow mode is possible for the metal concentration, and no significant differences in metal concentration can be observed in the whole aqueous phase and the out-stream. In the polymer assisted UF process, the polymer needs to be continuously maintained in a basically unsaturated state to have low metal concentration throughout the aqueous phase and the out-stream. Therefore, continuous regeneration of the polymer may be a good solution. We propose a continuous water softening process by continuously regenerated polymer assisted UF.

THEORY TO PREDICT METAL REJECTIONS

A theoretical model was developed to predict metal rejection, R_i, in an ultrafiltration membrane in the presence of weakly ionised polyelectrolyte. The model was tested in a system where the metal cations were Ca^{2+} and Na^{+}.

The model considers that the aqueous solution has two phases: the macroions and their bound counterions, with volume V_p, and the remaining solution, with volume V. The phase that contains the macroions, or polyelectrolyte phase, is similar to the ion exchanger phase in commercial ion exchange resins. These two phases are separable by ultrafiltration membranes.

We define conventional chemical equilibrium constants according to the law of mass action. In this case, the exchange of counterions (Ca^{2+}, Na^{+}, and H^{+}) is expressed by two independent reactions

$$Ca^{2+} + 2{\cdot}PH \leftrightarrow P_2Ca + 2{\cdot}H^{+} \tag{1}$$

$$Na^{+} + PH \leftrightarrow PNa + H^{+} \tag{2}$$

The term P is used to represent one equivalent of polyelectrolyte cation–exchange. Then, the chemical equilibrium constants are:

$$K_{Ca,H} = \frac{q_{P_2Ca}{\cdot}C'^{2}_{H^+}}{C'_{Ca^{2+}}{\cdot}q^{2}_{PH}} \tag{3}$$

$$K_{Na,H} = \frac{q_{PNa}{\cdot}C'_{H^+}}{C'_{Na^+}{\cdot}q_{PH}} \tag{4}$$

where molar concentrations C'_i and q_i refer to the solution and polyelectrolyte phases, respectively.

We can substitute one of the two independent reactions by other combinations of both:

$$Ca^{2+} + 2{\cdot}PNa \leftrightarrow P_2Ca + 2{\cdot}Na^{+} \tag{5}$$

for which the chemical equilibrium constant is:

$$K_{Ca,Na} = \frac{q_{P_2Ca} \cdot C'^{2}_{Na^+}}{C'_{Ca^{2+}} \cdot q^2_{PNa}} = \frac{K_{Ca,H}}{K^2_{Na,H}} \tag{6}$$

Reaction (5) is not hydrogen-ion dependent and its equilibrium constant can be taken as a polyelectrolyte selectivity coefficient in the exchange between calcium and sodium ions.

We have an additional component: the carboxylic acid groups, which reduce the ionic exchange capacity of the polyelectrolyte by lowering the pH. The dependence of the ionic capacity of the polyelectrolyte phase, Q, on pH is given by the following equation

$$Q = \frac{1}{1 + 10^{pKa-pH}} \cdot Q_m \tag{7}$$

where Q_m is the maximum ionic capacity of the polyelectrolyte phase, corresponding to wholly ionized acid groups, and $\mathrm{p}Ka = -\log Ka$, where Ka is the ionization constant. For acrylic polymers pKa is about 4.75.[22] The value 4.75 for the pKa is approximate since it depends on the chemical composition of the polymer and the ionic strength of neutral salt added.[17,23]

In this work, we assumed that the equilibrium constants in Eqs. (3) and (4) depend on polyelectrolyte ionic form and, therefore, on pH. Other than this, we assumed that the selectivity coefficient in the exchange among calcium and sodium ions, defined in Eq. (6), is not pH dependent.

The ratio V/V_P depends on equivalent polyelectrolyte concentration on the whole solution, C_P (eq L^{-1}), and polyelectrolyte mass concentration on the polyelectrolyte phase, ρ_p (g L^{-1}):

$$\frac{V}{V_P} = \frac{\rho_P}{C_P \cdot M_P} - 1 = \frac{Q_m}{C_P} - 1 \tag{8}$$

where M_P is the molecular weight of the equivalent polyelectrolyte cation–exchange (g eq^{-1}).

If the polyelectrolyte phase is totally retained by the ultrafiltration membrane and unbound ions are not rejected at all, the analytical concentration of calcium and sodium ions in the permeate will be the same as the concentration of calcium and sodium ions in the solution phase in the retentate.

The equilibrium molar concentrations of calcium and sodium ions in the solution and polyelectrolyte phases are obtained by a mass balance of the different species in the solution and polyelectrolyte phases as well as forcing the fulfillment of the two independent chemical equilibrium constants (Appendix I).

CONTINUOUS WATER SOFTENING PROCESS

In this study, we tested, by means of experiments and simulations, a continuous water softening process that uses ultrafiltration units in the presence of a weakly ionized polyelectrolyte. The polyelectrolyte was poly(acrylic acid–maleic anhydride) sodium salt. The process flow sheet is shown in Fig. 1. The system has two similar sections, and each section is composed of a tank and an ultrafiltration unite. Section 1 is fed with raw water, F_0, a base stream (NaOH), B, and a polyelectrolyte stream that comes from Section 2. At the same time, Section 1 produces a treated water stream, $P1$, where the calcium content is very low and a retentate stream that feeds Section 2. The pH in Section 1 is approximately 7. The acid–base adjustment to obtain accurate neutral treated water may be finalized later in an additional process. In tandem, Section 2 is fed with an acidic stream (HCl), A, and the stream that comes from the retentate of the ultrafiltration unit of Section 1. At the same time, Section 2 produces a calcium concentrated water stream, $P2$, and a retentate stream that recycles the polyelectrolyte toward Section 1. Section 2 pH is acidic.

In Section 1, the polyelectrolyte is nearly ionized and binds the main calcium ions. Therefore, the treated water stream that comes from this section's permeate of the membrane, contains hardly any calcium ions. In Section 2, the polyelectrolyte is unionized, because the pH is kept lower than

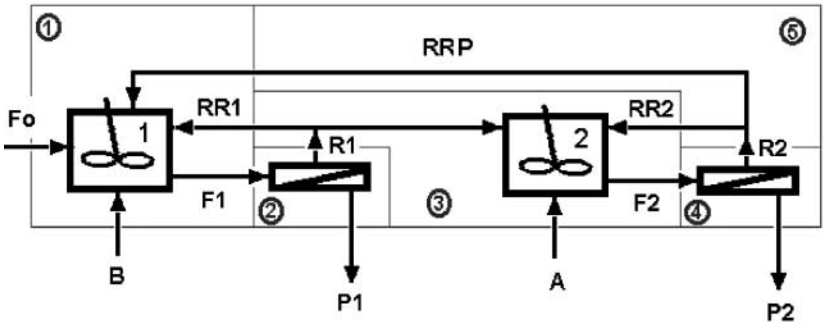

Figure 1. Flow sheet for a continuous water softening process using polymer-assisted ultrafiltration unites.

$pK_A - 2$. So, in this section, the polyelectrolyte releases all calcium ions, and the $P2$ stream is a concentrated calcium water stream. It is assumed that chemical equilibrium is reached in both sections. The potentiometric measurements confirm that the chemical rates are fast. On the other hand, if problems of nonequilibrium are detected in one section, they can be solved by going up the mean residence time of this section by increasing the volume of this section.

Conversely, if the polyelectrolyte phase is totally retained by the membranes, no reduction of polyelectrolyte can take place while the process is running. Certainly, after a running time, only the constant retainable part of the polyelectrolyte remains in the system, and only a small quantity of polyelectrolyte, perhaps produced by polymer degradation due to friction, could leak. In this case, periodic polyelectrolyte additions must be done to maintain a constant polymer level in the system. On the other hand, as we explain as follows, at $pH = 7$, the membrane polymer retention is always much higher than at low pH. Therefore, this slight possible polymer leakage is directed to the concentrated calcium water stream and not to the soft water. Moreover, another way to ensure the absence of the polymer in the soft water is to use a membrane of lower MWCO in Section 1 than in Section 2.

Given a raw water feed flow, $F_0 = 100$ ($\mathrm{L\,time^{-1}}$), and its calcium concentration, C_{CaFo} ($\mathrm{mol\,L^{-1}}$), there is a series of dimensionless variables that determine the running of the process. These variables and their meaning are summarized in Table 1.

To verify the validity of the process, we have developed and verified a mathematical model. The mathematical model has two components: 1) the mass balances to determine the analytical molar concentrations and mass flow

Table 1. Dimensionless variables that determine the running of the continuous water softening process.

Variables	Equivalence	Meaning
a	A/Fo	Acid feed flow
ab	$(A \cdot C_A)/(B \cdot C_B)$	Acid–base feed ratio
af	$(A \cdot C_A)/(Fo \cdot C_{CaFo})$	Acid–calcium feed ratio
b	B/Fo	Base feed flow
P	P1/Fo	Production of treated water
PP	$(N_P/V_T)C_{CaFo}$	Polymer–calcium ratio
$r1$	RR1/R1	Recycled retentate flow in Section 1
$r2$	RR2/R2	Recycled retentate flow in Section 2
r_0	RRP/Fo	Recycled polyelectrolyte

rates, and 2) the prediction for metal rejections. In principle, the mass balances do not need to be verified. However, predictions for metal rejections must be confirmed with experiments. We then confirmed these predictions with experiments. The following sections show the experiments used to support the model for the prediction of metal rejections.

Simulations were done with a number of imposed restrictions. (1) In section 1, the equivalent calcium concentration, C_{Ca}, must be lower than the equivalent polyelectrolyte concentration, C_P. We observed that polyelectrolyte is not soluble when the polyelectrolyte counterions are only calcium. In fact, polyelectrolyte is only soluble if $2{\cdot}C_{Ca} \leq C_P/1.25$. Because the process performance increases when $2{\cdot}C_{Ca}$ comes near C_P, we have accepted the condition:

$$\frac{C_{PR1}}{2{\cdot}C_{CaR1}} = 1.25 \tag{9}$$

In these circumstances, the polyelectrolyte is always soluble and the efficiency is higher. (2) The pH of the treated water, $P1$, was fixed at 7.00. (3) The pH in Section 2 must be low enough to keep the polyelectrolyte unionized ($\mathrm{pH}_2 < pK_A - 2$). Therefore, in Section 2, we impose

$$\frac{C_{HR2}}{C_{PR2}} > 1 \tag{10}$$

The analytical concentration of protons must be higher than the analytical concentration of equivalents polyelectrolyte cation–exchange. (4) The equivalent acid concentration in the acid feed flow, C_A, was fixed at 12 (mol/L). The equivalent base concentration in the base feed flow, C_B, was fixed at 19 (mol/L).

After these restrictions, the collection of dimensionless variables that determine the running of the process are: *af*, *P*, *r1*, *r*2, and *ro*. The rest of the variables are determined by these restrictions: Restriction 1 determines the variable *PP*, Restriction 2 determines the variable *ab*, Restriction 3 reduces the number of possible solutions, and Restriction 4 determines the variables *a* and *b*.

Inasmuch as the variables that determine the running mode are fixed, the simulations were made as follows: (1) We assume the calcium and sodium rejections in the membrane of Section 1. At the same time, the calcium and sodium rejections in the membrane of Section 2 was fixed to zero. This conjecture was justified for Restriction 3. Moreover, this assumption was verified in the experiment. (2) We solve all the mass balances to calculate the analytical molar concentrations and mass flow rates of the different species in the different streams (Appendix II). (3) We calculate the calcium and sodium rejections of Section 1 from the analytical concentrations of the different species in the retentate *R*1 (see "Theory" to predict membrane rejections and Appendix I), (4) We compare the assumed calcium and sodium rejections with the calculation. If the calculated calcium and sodium rejections do not coincide with our supposition, we change initial rejections until they match.

EXPERIMENTAL

Chemicals

Poly(acrylic acid–maleic anhydride) sodium salt, Trade Name Acusol 497 was obtained from Norsohaas. All the rest of the reagents were pure grade and used as received. $CaCl_2$, NaCl, HCl were supplied by Carlo Erba. The pure water used in this study was prepared using a Milli-Q water purification system and passed through a 45-μm pore diameter filter. For the polymer analysis, Reagent 1 was prepared dissolving 25 g of Hyamine 1622 (Merck) in 1 liter of water. Reagent 2 was a 30 % (w/V) aqueous solution of trisodium citrate (Merck).

The polyelectrolyte was determined by spectrometry at 420 nm, measuring the absorbance 15 minutes after the addition 0.2 mL of Reagents 1 and 2 to a 5-mL problem or standard solution. Calcium was analyzed by atomic absorption, sodium by flame photometry, and chloride by capillary electrophoresis. pH was measured on a Crison pH meter.

To separate the polyelectrolyte short chains, a 4% aqueous solution of the commercial polymer was dialysed through a 12–14 kDa membrane (Visking Medicell International, size 12). The remaining polymer in the retentate cell was used for the following ultrafiltration experiments. It has a proportion of polymer/Na of 5.17 (w/w) and when filtered through 5-kDa membrane, negligible concentrations of both polyelectrolyte and sodium were found. This indicates that there is no sodium excess and that it has a M_p value of 119 ($g\,eq^{-1}$).

Ultrafiltration Device

Ceramic membranes of 5 kDa molecular weight cut-off (MWCO) supplied by Tami were used in all the experiments. The ceramic membranes are tubular with three channels. The cross section area of each channel was $0.129\,cm^2$ and the length 25 cm. The total filtration area was $95.5\,cm^2$.

The UF device is standard equipment and consists of a reservoir tank, pump, closed-pipe pressure dampener to prevent pressure oscillation, pressure gauges, an ultrafiltration cell and flow meters for retentate and permeate. The retentate stream circulated tangential to the membrane. The applied transmembrane pressure was 100 kPa and the retentate velocity was 11.2 $\mathrm{cm\,s^{-1}}$. The temperature was kept at 25°C.

Between runs, membranes were successively soaked in pure water, 1% HNO_3 solution, pure water, 1% NaOH – 150 ppm NaClO solution, and, finally, in pure water.

Steady Ultrafiltration Runs

The system was filled with definite quantities of polyelectrolyte, $CaCl_2$, and water in order to obtain prescribed concentrations of polyelectrolyte and calcium. Both permeate and retentate were returned to the stirred feed tank to achieve a steady-state operation. The feed-retentate zone can be considered well mixed and homogeneous and with a volume of 473 mL. The permeate zone had a volume of 27 mL. After 1 hour of running, 20 mL of permeate and 1 mL of retentate were collected. pH was also measured.

A collection of different experiments were performed by repeatedly adding 20 mL into the system of a new concentrated solution of NaCl or HCl. The 20 mL corresponds to the volume collected in permeate in the previous experiment. Two kinds of experiments were performed: (1) experiments where polyelectrolyte and calcium concentrations in the feed were almost constant and sodium concentration was continuously increased, and (2) experiments where polyelectrolyte and calcium concentrations in the feed were almost constant and the concentration of protons was continuously increased.

The purpose of these experiments was to find the two independent equilibrium constants, $K_{\mathrm{Na,H}}$ and $K_{\mathrm{Ca,Na}}$, that would give good estimates for calcium and sodium rejections.

Batch Ultrafiltration Runs

Experiments were initiated in the same way as the steady-state ones, but ultrafiltrations were performed until 80% of the initial feed volume had been filtered. Permeate samples were collected in fractions of 20 mL. Samples of retentate were about 1 mL.

Two batch ultrafiltration experiments were done: one at $\mathrm{pH} = 7.2$ and the other at $\mathrm{pH} = 2.9$. The purpose of these experiments was to confirm that the estimates for calcium and sodium rejection happened as expected at the pHs values specified in Sections 1 and 2 in the continuous water softening process. In addition, the model was verified by predicting the retentate and permeate concentrations throughout the concentration process.

RESULTS

A set of blank experiments were performed to determine whether calcium and sodium ions are retained by the membrane when polyelectrolyte is not present in the feed. Null or very low rejections for sodium and calcium were obtained when the polyelectrolyte was not present and the ion concentrations were high or moderate. However, at very low concentrations of sodium, the sodium rejection was appreciable.

On the other hand, the membrane rejection for the polyelectrolyte was very high. Appreciable permeability for the polymer was only found at pH below 5. At the same time, an increase in the polymer concentration leads to a lower rejection. However, in all cases, the polymer rejection was always higher than 95%.

A potentiometric titration of a 0.015 M polyelectrolyte solution with 5 M HCl was performed to determine the equilibrium constant, $K_{\mathrm{Na,H}}$, and its dependence on pH. A value of ρ_{p} should be assumed to do the computations. In this work, we assumed that $\rho_{\mathrm{P}} = 500(\mathrm{g\,L^{-1}})$, which means that there is about 50% water in the polyelectrolyte phase. The consequences of taking a different value for this parameter will be discussed later. The calculated values for $K_{\mathrm{Na,H}}$, that fit the experimental pH throughout the titration, were calculated with Eq. I-5 (see Appendix I). The initial molar concentrations of the different species, C_i^{o} and q_i^{o}, are known, $Q_m = \rho_P/M_P$ and the other required values for the calculation, Q, V/V_P and $C_{\mathrm{Na+}}$, were obtained with Eqs. (7), (8), and (I-7). A good fit for the calculated values of $K_{\mathrm{Na,H}}$ vs. pH, in the range: $2.75 < \mathrm{pH} < 8$, is: $K_{\mathrm{Na,H}} = 69000\,\mathrm{pH}^{-10.5}$. The value of the equilibrium constant is not relevant when the pH is lower than 2.75. At these pHs, the polyelectrolyte does not becomes ionic.

The observed calcium and sodium rejections of experiments in series 1 and 2 have been used to fit the selectivity coefficient, $K_{\mathrm{Ca,Na}}$. Calculations were performed by simultaneous resolution of Eqs. I-5, I-6 and I-7 (see Appendix I), where $K_{\mathrm{Ca,Na}}$ was previously assumed and calcium and sodium rejections calculated. These calculated values were matched to the experimental values by adjusting the previously assumed $K_{Ca,Na}$. A value of 25, independent of pH, gives good predictions for calcium and sodium rejection for all these experiments. Figures 2 and 3 show experimental and predicted calcium and sodium rejection in series 1, where polyelectrolyte and calcium concentrations in the feed were almost constant and sodium concentration was continuously increased.

Figures 4 and 5 show experimental and predicted calcium and sodium rejection in series 2 experiments, where polyelectrolyte and calcium concentrations in the feed were almost constant and the concentration of protons was continuously increased.

From the experimental data, we deduce that the affinity of the polyelectrolyte for calcium ions is stronger than the affinity for sodium ions. At basic or neutral pH, if there is sufficient polyelectrolyte, almost all calcium ions are bound to the polyelectrolyte and so the calcium rejection is almost 100%. In this situation, the carboxylic groups in the polyelectrolyte that are not bound to calcium are bound to sodium. The initial protons added in the solution mainly replace sodium but not calcium. Only when all the sodium in the polyelectrolyte is replaced by protons can the calcium in the polyelectrolyte be replaced by subsequent protons.

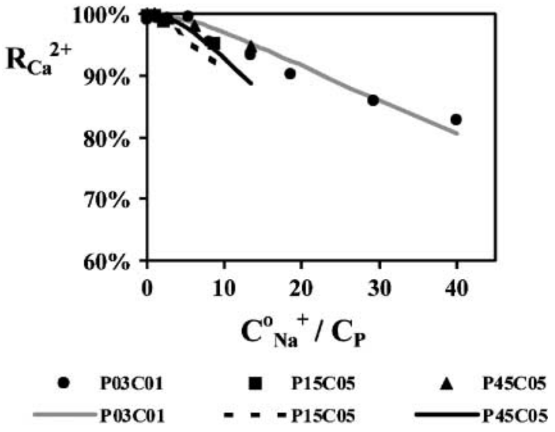

Figure 2. Experimental (*points*) and predicted (*lines*) calcium rejection for steady UF runs. Effect of sodium additions on calcium rejection. ●: $C_P = 0.003\,M$ and $C^o_{CaCl2} = 0.001\,M$ (P03C01). ■: $C_P = 0.015\,M$ and $C^o_{CaCl2} = 0.005\,M$ (P15C05). ▲: $C_P = 0.045\,M$ and $C^o_{CaCl2} = 0.005\,M$ (P45C05).

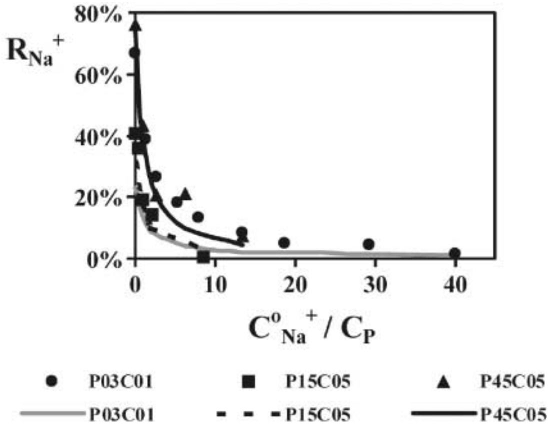

Figure 3. Experimental (*points*) and predicted (*lines*) sodium rejection for steady UF runs. Effect of sodium additions on sodium rejection. ●: $C_P = 0.003$ M and $C^o_{CaCl2} = 0.001$ M (P03C01). ■: $C_P = 0.015$ M and $C^o_{CaCl2} = 0.005$ M (P15C05). ▲: $C_P = 0.045$ M and $C^o_{CaCl2} = 0.005$ M (P45C05).

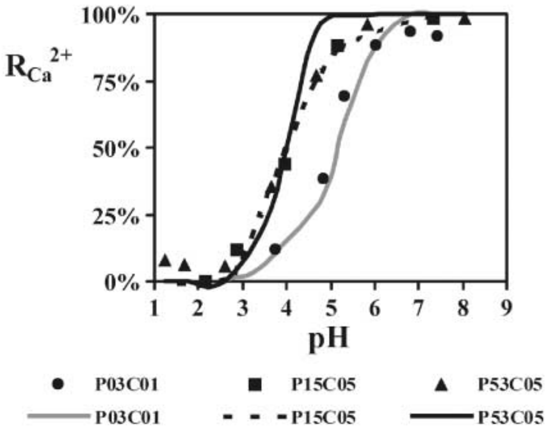

Figure 4. Experimental (*points*) and predicted (*lines*) calcium rejections for steady UF runs. Effect of pH on calcium rejection. ●: $C_P = 0.003$ M and $C^o_{CaCl2} = 0.001$ M (P03C01). ■: $C_P = 0.015$ M and $C^o_{CaCl2} = 0.005$ M (P15C05). ▲: $C_P = 0.053$ M and $C^o_{CaCl2} = 0.005$ M (P53C05).

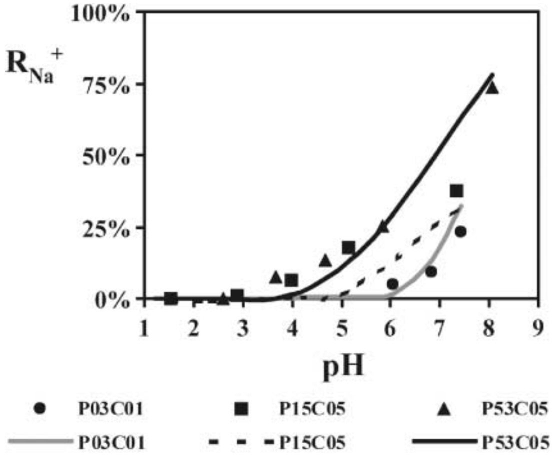

Figure 5. Experimental (*points*) and predicted (*lines*) sodium rejections for steady UF runs. Effect of pH on sodium rejection. ●: $C_P = 0.003$ M and $C^o_{CaCl2} = 0.001$ M (P03C01). ■: $C_P = 0.015$ M and $C^o_{CaCl2} = 0.005$ M (P15C05). ▲: $C_P = 0.053$ M and $C^o_{CaCl2} = 0.005$ M (P53C05).

For this work, we have assumed that $\rho_P = 500\,(\mathrm{g\,L^{-1}})$. This assumption may seem arbitrary, however, other values of ρ_P were tested to find the effect of ρ_P value on the predicted calcium and sodium rejections. Simulations using a ρ_P value from 200 to 1000 $(\mathrm{g\,L^{-1}})$ showed that the calculated calcium and sodium rejections were similar to those calculated with $\rho_P = 500\,(\mathrm{g\,L^{-1}})$. We can prove that the equilibrium constant $K_{Na,H}$ is independent of the assumed value of ρ_P. In contrast, the equilibrium constant $K_{Ca,Na}$ is inversely proportional to the ρ_p/C_P. So, the information of a determined value of $K_{Ca,Na}$ for a given polymer should include the assumed value of ρ_p to make precise predictions for calcium and sodium rejections. However, if the affinity of the polyelectrolyte for calcium is much higher than the affinity for sodium, it is sufficient to determine the magnitude or range of $K_{Ca,Na}$ since the simulations will be only slightly sensitive to the ρ_p value considered.

To verify the model, two batch ultrafiltration runs were done, one at pH = 7.2 and the other at pH = 2.9. The initial concentrations were: $C_P = 0.015$ M and $C^o_{CaCl2} = 0.005$ M, in the experiment at pH = 7.2, and $C_P = 0.0143$ M and $C^o_{CaCl2} = 0.047$ M, in the experiment at pH = 2.9. No significant quantities of polyelectrolyte were found in the permeates of either experiment. Therefore, the filtrated percentage of the initial feed volume, V_{per}/V_o, and the experimental polyelectrolyte concentration in the retentate,

C_P, throughout the experiments fulfils the following equation:

$$C_P = \frac{C_{P,initial}}{1 - (V_{per}/V_o)} \tag{11}$$

where $C_{P,initial}$ is the initial polyelectrolyte concentration in the retentate, V_{per} is the filtrated volume, and V_0 is the initial feed volume.

The retentate and permeate concentrations were calculated by solving the mathematical model by intervals. The polyelectrolyte concentration was assumed constant in each interval and was changed from one interval to other according to Eq. (11). The molar concentrations calculated by the model in each interval were the initial concentrations used to calculate the molar concentrations for the next interval. The total sodium and calcium concentrations in the retentate, C_i^R, were obtained with the following equation.

$$C_i^R = \frac{V \cdot C_i' + V_P \cdot q_i}{V + V_P} = \frac{(V/V_P) \cdot C_i' + q_i}{V/V_P + 1} \tag{12}$$

where $\mathrm{V/V_P}$ depends on $\mathrm{C_P}$ through Eq. (8). The sodium and calcium concentrations in the permeate are the equilibrium concentrations in the solution phase, $\mathrm{C_i'}$.

Figure 6 shows the predicted and experimental values for polyelectrolyte, calcium, and the sodium concentrations in the retentate and sodium concentration in the permeate for the batch ultrafiltration experiment carried out at pH = 7.2. No calcium or polyelectrolyte were detected in the permeate. The fact that calcium was not detected indicates that the maximum calcium content could be the detection limit of the atomic absorption technique used (about 0.01 ppm). The affinity of the polyelectrolyte for the calcium ions is so strong at this pH that no free calcium can be detected in the solution phase. The experimental sodium concentration in the permeate slowly increases with the polyelectrolyte concentration in the retentate. This point is not well predicted by the model. A possible explanation for this may be that the sodium rejection at low polyelectrolyte concentration is not well predicted by the equation that calculates sodium rejection because the sodium concentration in the solution phase is higher than the sodium concentration in the permeate. We can see a similar feature in the steady ultrafiltration experiments where sodium concentration was continuously increased (see Fig. 2) and the predicted sodium rejection was accurate for $C_P = 0.045\,\mathrm{M}$ and lower than the experimental expectations for $C_P = 0.003$. Aside from this point, the model predicted the remaining concentrations very well.

Figure 7 shows the predicted and experimental values for polyelectrolyte, calcium, and sodium concentrations in the retentate and calcium and sodium

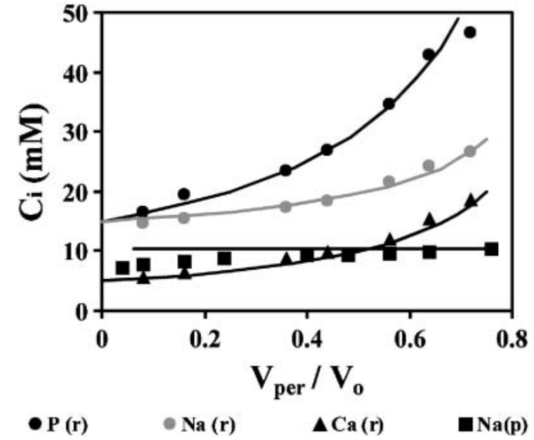

Figure 6. Experimental (*points*) and predicted (*lines*) concentrations in the batch ultrafiltration experiment at pH = 7.2. P(r): polyelectrolyte in the retentate. Ca(r): calcium in the retentate. Na(r): sodium in the retentate. Na(p): sodium in the permeate. The initial concentrations were: $C_P = 0.015\,M$ and $C^o_{CaCl2} = 0.005\,M$.

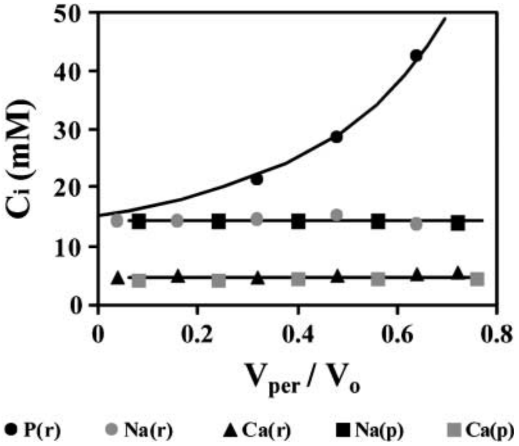

Figure 7. Experimental (*points*) and predicted (*lines*) concentrations in the batch ultrafiltration experiment at pH = 2.9. P(r): polyelectrolyte in the retentate. Ca(r): calcium in the retentate. Na(r): sodium in the retentate. Na(p): sodium in the permeate. Ca(p): calcium in the permeate. The initial concentrations were: $C_P = 0.0143\,M$ and $C^o_{CaCl2} = 0.047\,M$.

concentration in the permeate for the batch ultrafiltration experiment carried out at $\mathrm{pH} = 2.9$. This situation seems simple as at this low pH the polyelectrolyte is not ionized. So, the sodium and calcium of the system is not linked to the polyelectrolyte and, therefore, no membrane effect on its concentrations are detected.

SIMULATIONS

Since the equilibrium constants were known, we simulated the proposed continuous water softening process using the described mathematical model. The water hardness for the raw feed water was 500 ppm of $CaCO_3$ (Ca 5 mM). The treated water productions were fixed at 90 and 95%. The recycled retentate flows in both sections, $r1$ and $r2$, were fitted at 99.5% for all cases, except for one where 85.0% was also tested. Then, with the indicated restrictions (see section "Continuous Water Softening Process") only two variables remain undetermined: the acid–calcium feed ratio, *af*, and the recycled polyelectrolyte, r_o.

The acid–calcium feed ratio, *af*, denotes the process cost due to the added acid and base. The global acid–base feed ratio, *ab*, must be 1 for the overall process with neutral out-streams. The acid–base feed ratio in the definite process must be higher than 1 to give an acidic permeate stream in Section 2. Therefore, we neutralize that stream and this additional base makes the global acid–base feed ratio equal to 1. Since each calcium ion needs two protons to be removed from the polyelectrolyte and the polyelectrolyte two hydroxide ions to be ionized again, an ideal process needs to use a minimum acid–calcium feed ratio of 2. So, values of acid–calcium feed ratio less than 2 are not able to remove all calcium ions. Obviously, in a real process, the acid–calcium feed ratio must be rather higher than 2 to remove the main calcium ions.

Simulations with a Treated Water Production of 90%

When the water treated production is 90% ($P = 90$) and the acid–calcium feed ratio is set lower than 2.60, no acceptable solutions can be found for any value of r_o. In these cases, there are not enough protons in Section 2 to keep the polyelectrolyte unionized and $C_{\mathrm{HR2}}/C_{\mathrm{PR2}} < 1$. On the contrary, when we set the acid–calcium feed ratio higher than 2.60, we have a range of r_o values that give valid solutions. At the same time, the number of r_o values that give valid solutions increase as the acid–calcium feed ratio also increases. Figure 8 shows the ratio $C_{\mathrm{HR2}}/C_{\mathrm{PR2}}$ for different acid–calcium feed ratios and its

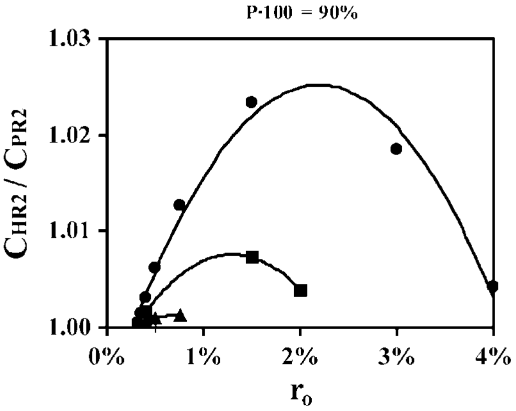

Figure 8. C_{HR2}/C_{PR2} for different acid–calcium feed ratios, *af*, and its dependence on r_o. ◆: *af* = 2.60; ▲: *af* = 2.70; ■: *af* = 3.0; ●: *af* = 3.45.

dependence on r_o. In all cases, the minimum valid r_o value was 0.32%. In contrast, the maximum valid r_o values depend on *af*. When *af* was 2.60, the minimum and the maximum valid r_o values were nearly identical. However, when *af* was 3.45, the range of valid r_o values was at its maximum. For a given *af* value, each range of valid r_o values has a concrete value that gives the maximum value for C_{HR2}/C_{PR2}. This particular value is the mean in the interval of valid r_o values. Moreover, as the *af* value increases its maximum value for C_{HR2}/C_{PR2} also increases.

To establish the efficiency of the process, we have defined the calcium reduction, *CR*, as follows.

$$CR = 1 - \frac{C_{CaP1}}{C_{CaFo}} \cdot 100 \tag{13}$$

When $CR = 100$ the treated water has zero calcium, and when $CR = 0$ the treated water has the same amount of calcium as the raw feed water.

The calcium reduction was only dependent on r_o and slightly increases as r_o decreases. The apparent single effect of the acid–calcium feed ratio was to diminish the range of valid r_o values. Furthermore, in all cases, the obtained calcium reductions were higher than 99.4%. Figure 9 shows the calcium reduction for different acid–calcium feed ratios and its dependence on r_o when $P = 90\%$.

Simultaneously, the polymer–calcium ratio, *PP*, defined in Table 1 and quantified for the total number of equivalent polyelectrolyte units introduced in the device, was only dependent on r_o. Figure 10 shows the dependence of polymer–calcium ratios versus r_o. When r_o is low, the relative polymer

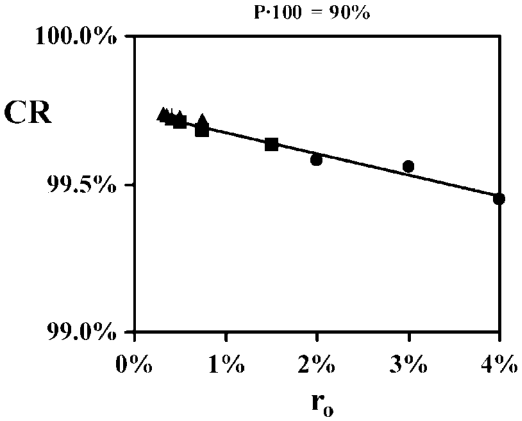

Figure 9. Calcium reductions for different acid–calcium feed ratios, *af*, and its dependence on r_o. ◆: $af = 2.60$; ▲: $af = 2.70$; ■: $af = 3.0$; ●: $af = 3.45$.

amount coming from Section 2 to Section 1 is also low. In order to fulfill the restriction $C_{\mathrm{PR1}} = 1.25 \cdot 2 \cdot C_{\mathrm{CaR1}}$, we need to introduce a large quantity of polyelectrolyte so that *PP* increases quickly. At the same time, C_{PR2} also increases quickly and eventually there is not sufficient acid in Section 2 to keep the polyelectrolyte unionized. So, there is a limit for low r_o. If we reduce the recycled retentate flow in each section, the polymer–calcium ratio also becomes smaller; however, the profile of r_o dependence is the same.

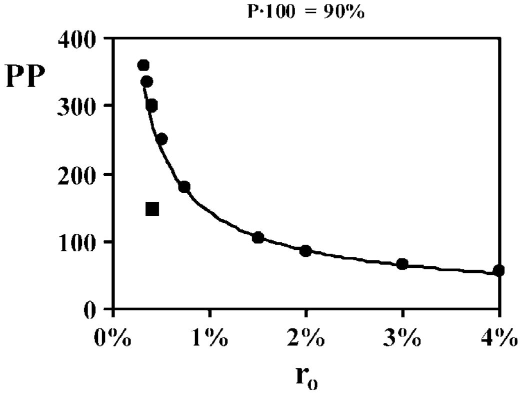

Figure 10. Dependence of polymer–calcium ratio, *PP*, on r_o. ●: for r1 = r2 = 99.5%; ■: for r1 = r2 = 85.0%.

Another noticeable point is the pH in the permeate of Section 2, pH_{P2}. As stated above, *af* determines the process cost and we can work at different r_o for each value of *af*. A good selection for r_o is the one that gives higher values for C_{HR2}/C_{PR2}, assuring the complete unbinding of calcium ions on the polymer. Despite the fact that at the minimum workable value for *af* there is only one possible value for r_o and C_{HR2}/C_{PR2} is hardly 1. Figure 11 shows the pH_{P2} for different *af* when we use a r_o that gives higher values for C_{HR2}/C_{PR2}.

Simulations with a Treated Water Production of 95%

When we set the treated water production to 95%, we saw a similar behavior for the different variables that we noticed before for treated water production of 90%. At this point, the minimum acceptable acid–calcium feed ratio was 2.70. The range of valid values for r_o for each *af* value was reduced by half. The polymer calcium ratios, *PP*, were slightly increased. The pH_{P2} operating at a r_o that gives higher values for C_{HR2}/C_{PR2} were also similar. And finally, the calcium reduction was only slightly diminished. Figure 12 shows the calcium reduction for different acid–calcium feed ratios and its dependence on r_o and *P*. Therefore, we can conclude that an increase of treated water production does not necessarily involves a great reduction of water softening performance.

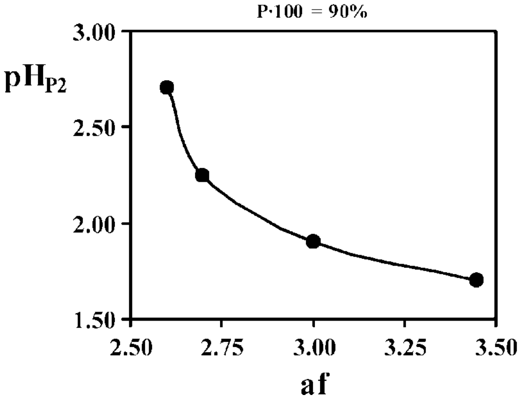

Figure 11. pH_{P2} vs. *af* when we use a r_o that gives the highest values for C_{HR2}/C_{PR2}.

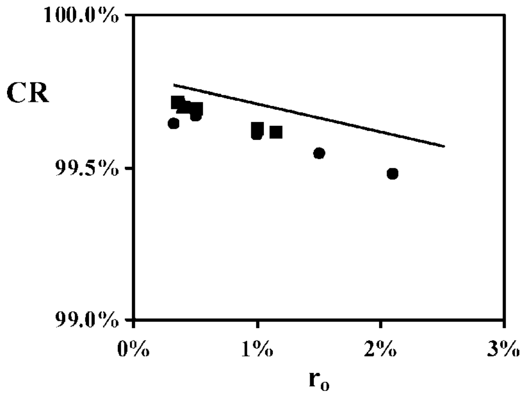

Figure 12. Calcium reduction for different acid–calcium feed ratios and its dependence on r_o and P. The line corresponds to $P = 90\%$ and the points to $P = 95\%$ (▲: *af* = 2.70; ■: *af* = 3.00; ●: *af* = 3.45).

CONCLUSION

A continuous metal-removing process using polymer-assisted ultrafiltration has been proposed. At the same time, a mathematical model for metal ion retention in ultrafiltration experiments of solutions of high molecular weight polymers and metal ions has been developed. Preliminary experiments provided sufficient information for simulations of the continuous removal of Ca^{2+} from water. The acid–calcium feed ratio and the recycled polyelectrolyte are the most important parameters that determine the process viability. The simulations show that the proposed system can continuously removes Ca^{2+} from water in a satisfactory way. The water softening performance was rather high, even with greatly treated water productions.

APPENDIX I

Mathematical Model to Calculate the Equilibrium Molar Concentrations of Calcium, Sodium, and Hydrogen Ions in the Solution and Polyelectrolyte Phases

Firstly, we assign arbitrary initial molar concentrations to the different species in the solution and polyelectrolyte phases in accordance with the analytical concentrations of the different species in the whole solution. Then, we use the mass balances for the species:

$$q_{P_2Ca} = q^o_{P_2Ca} + \frac{V}{V_P} \cdot (C'^o_{Ca^{2+}} - C'_{Ca^{2+}}) \tag{I-1}$$

$$q_{PNa} = q^o_{PNa} + \frac{V}{V_P} \cdot (C'^o_{Na^+} - C'_{Na^+}) \tag{I-2}$$

$$q_{PH} = q^o_{PH} + \frac{V}{V_P} \cdot [(C'^o_{H^+} - C'_{H^+}) + (C'_{OH^-} - C'^o_{OH^-})] - (Q_m - Q) \tag{I-3}$$

where C^o_i and q^o_i are the initial molar concentrations of the species in the solution and polyelectrolyte phases, respectively. At the same time, we have:

$$Q = 2 \cdot q_{P_2Ca} + q_{PNa} + q_{PH} \tag{I-4}$$

Then, we assume an arbitrary initial value for the pH to calculate $K_{Na,H}$ and Q. Then, we take the water-dissociation equilibrium constant and substitute Eqs. (I-1), (I-2), and (I-3) into Eqs. (4), (6), and (I-4) and solve these equations to obtain the molar concentrations of calcium, sodium, and hydrogen ions in the solution phase. Then, the calculated pH must coincide with the previously assumed values. Otherwise, we have to vary the assumed pH until it matches. Finally, the molar concentrations of calcium, sodium, and hydrogen ions in the polyelectrolyte phase can be obtained by equations (I-1), (I-2), and (I-3).

APPENDIX II

Mathematical Model to Calculate the Analytical Molar Concentrations and Flow Rates of the Different Species and Streams in the Continuous Water Softening Process

The projected water softening unit has been divided in five regions in order to facilitate the mass balances (see Fig. 1).

The global mass balances are:

$$Fo + B + RRP + RR1 = F1 \tag{II-1}$$

$$F1 = R1 + P1 \tag{II-2}$$

$$R1 + A + RR2 = RR1 + F2 \tag{II-3}$$

$$F2 = R2 + P2 \tag{II-4}$$

$$R2 = RR2 + RRP \tag{II-5}$$

On the other hand, from the definitions of the dimensionless variables:

$$A = a{\cdot}F0$$

$$B = b{\cdot}F0$$

$$P1 = P{\cdot}F0$$

$$RR1 = r1{\cdot}R1$$

$$RR2 = r2{\cdot}R2$$

$$RRP = r_o{\cdot}F0$$

The calcium mass balances are:

$$F0{\cdot}C_{CaFo} + RRP{\cdot}C_{CaR2} + RR1{\cdot}C_{CaR1} = F1{\cdot}C_{CaF1} \tag{II-6}$$

$$F1{\cdot}C_{CaF1} = R1{\cdot}C_{CaR1} + P1{\cdot}C_{CaR1}(1 - R_{Ca1}) \tag{II-7}$$

$$R1{\cdot}C_{CaR1} + RR2{\cdot}C_{CaR2} = RR1{\cdot}C_{CaR1} + F2{\cdot}C_{CaF2} \tag{II-8}$$

$$F2{\cdot}C_{CaF2} = R2{\cdot}C_{CaR2} + P2{\cdot}C_{CaR2}(1 - R_{Ca2}) \tag{II-9}$$

The sodium mass balances are:

$$B{\cdot}C_B + RRP{\cdot}C_{NaR2} + RR1{\cdot}C_{NaR1} = F1{\cdot}C_{NaF1} \tag{II-10}$$

$$F1{\cdot}C_{CNaF1} = R1{\cdot}C_{NaR1} + P1{\cdot}C_{NaR1}(1 - R_{Na1}) \tag{II-11}$$

$$R1{\cdot}C_{NaR1} + RR2{\cdot}C_{NaR2} = RR1{\cdot}C_{NaR1} + F2{\cdot}C_{NaF2} \tag{II-12}$$

$$F2 \cdot C_{NaF2} = R2 \cdot C_{NaR2} + P2 \cdot C_{NaR2}(1 - R_{Na2}) \tag{II-13}$$

The polymer mass balances are:

$$RRP \cdot C_{PR2} + RR1 \cdot C_{PR1} = F1 \cdot C_{PF1} \tag{II-14}$$

$$F1 \cdot C_{PF1} = R1 \cdot C_{PR1} \tag{II-15}$$

$$F2 \cdot C_{PF2} = R2 \cdot C_{PR2} \tag{II-16}$$

If the volume of both Sections are identical, then

$$PP = \frac{(1/2) \cdot (C_{PF1} + C_{PF2})}{C_{CaF0}} \tag{II-17}$$

The chlorine mass balances are:

$$F0 \cdot 2 \cdot C_{CaF0} + RRP \cdot C_{ClR2} + RR1 \cdot C_{ClR1} = F1 \cdot C_{ClF1} \tag{II-18}$$

$$F1 \cdot C_{ClF1} = R1 \cdot C_{ClR1} + P1 \cdot C_{ClP1} \tag{II-19}$$

$$R1 \cdot C_{ClR1} + RR2 \cdot C_{ClR2} + A \cdot C_{A} = RR1 \cdot C_{ClR1} + F2 \cdot C_{ClF2} \tag{II-20}$$

$$F2 \cdot C_{ClF2} = R2 \cdot C_{ClR2} + P2 \cdot C_{ClP2} \tag{II-21}$$

To accomplish the electroneutrality in the streams, the following equations must be fulfilled

$$C_{HR1} + C_{NaR1} + 2 \cdot C_{CaR1} = C_{ClR1} + C_{PR1} \tag{II-22}$$

$$C_{HR2} + C_{NaR2} + 2 \cdot C_{CaR2} = C_{ClR2} + C_{PR2} \tag{II-23}$$

$$C_{HP1} + C_{NaP1} + 2 \cdot C_{CaP1} = C_{ClP1} \tag{II-24}$$

$$C_{HP2} + C_{NaP2} + 2 \cdot C_{CaP2} = C_{ClP2} \tag{II-25}$$

$$C_{HF1} + C_{NaF1} + 2 \cdot C_{CaF1} = C_{ClF1} + C_{PF1} \tag{II-26}$$

$$C_{HF2} + C_{NaF2} + 2 \cdot C_{CaF2} = C_{ClF2} + C_{PF2} \tag{II-27}$$

The pH in the treated water, pH_{P1}, is a fixed value.

$$pH_{P1} = -\log(C_{HP1}) \tag{II-28}$$

The pH in the product $P2$ is calculated assuming that the carboxylic acid groups of the polymer are unionized, since $pH_{P2} < pK_A - 2$.

$$pH_{P2} = -\log(C_{HP2}) = -\log\left(\frac{C_{HR2}\cdot(1+(V/V_P)_{R2}) - Q_m}{(V/V_P)_{R2}}\right) \qquad \text{(II-29)}$$

This system of 29 equations has 29 unknown variables: C_{CaF1}, C_{CaF2}, C_{CaR1}, C_{CaR2}, C_{NaF1}, C_{NaF2}, C_{NaR1}, C_{NaR2}, C_{PF1}, C_{PF2}, C_{PR1}, C_{PR2}, C_{ClF1}, C_{ClF2}, C_{ClR1}, C_{ClR2}, C_{ClP1}, C_{ClP2}, C_{HF1}, C_{HF2}, C_{HR1}, C_{HR2}, C_{HP1}, C_{HP2}, F1, F2, R1, R2, and P2. On the other hand, we can calculate: $C_{CaP1} = C_{CaR1}(1 - R_{Ca1})$, $C_{CaP2} = C_{CaR2}(1 - R_{Ca2})$, $C_{NaP1} = C_{NaR1}(1 - R_{Na1})$, and $C_{NaP2} = C_{NaR2}(1 - R_{Na2})$.

NOTATION

Symbols

A	Acid feed flow, $af\cdot F_o\cdot C_{CaFo}/C_A$ ($L\,time^{-1}$)
a	dimensionless acid feed flow, A/Fo
ab	acid–base feed ratio, $(A\cdot C_A)/(B\cdot C_B)$
af	acid–calcium feed ratio, $(A\cdot C_A)/(Fo\cdot C_{CaFo})$
B	base feed flow, $af\cdot Fo\cdot C_{CaFo}/(ab\cdot C_B)$ ($L\,time^{-1}$)
b	dimensionless base feed flow, B/Fo
C'_i	equilibrium molar concentrations of specie i in the solution phase of volume V ($mol\,L^{-1}$)
C'_{ij}	equilibrium molar concentrations of specie i in the solution phase of volume V in the stream j ($mol\,L^{-1}$)
C_A	equivalent acid concentration in the acid feed flow ($eq\,L^{-1}$)
C_B	equivalent base concentration in the base feed flow ($eq\,L^{-1}$)
C_i	analytical molar concentrations of specie i on the whole solutions, $= (q_i + C'_i\cdot(V/V_P)/[1 + (V/V_P)])$ ($mol\,L^{-1}$)
C_{ij}	analytical molar concentrations of specie i in the stream j ($mol\,L^{-1}$)
C^o_i	initial molar concentrations of specie i in the solution phase of volume V ($mol\,L^{-1}$)
C_P	equivalent polyelectrolyte concentration on the whole solution ($eq\,L^{-1}$)
CR	calcium reduction
C^R_i	molar concentrations of specie i in the retentate of the batch ultrafiltration experiments ($mol\,L^{-1}$)

F_1	feed flow in the membrane of Section 1 ($\mathrm{L\,time^{-1}}$)
F_2	feed flow in the membrane of Section 2 ($\mathrm{L\,time^{-1}}$)
F_0	raw water feed flow ($\mathrm{L\,time^{-1}}$)
K_a	polyelectrolyte ionization constant
M_P	molecular weight of the polyelectrolyte equivalent cation-exchange unit ($\mathrm{g\,eq^{-1}}$)
N_P	total number of polyelectrolyte equivalent units introduced in the device (eq)
P	dimensionless production of treated water, P_1/F_0
P_1	product flow of treated water ($\mathrm{L\,time^{-1}}$)
P_2	product flow of calcium concentrated water ($\mathrm{L\,time^{-1}}$)
pKa	$= -\log \mathrm{Ka}$
PP	polymer–calcium ratio, $(\mathrm{N_P/V_T})/\mathrm{C_{CaFo}}$
Q	ionic capacity of the polyelectrolyte phase ($\mathrm{eq\,L^{-1}}$)
q_i	equilibrium molar concentration of specie i in the polyelectrolyte phase of volume V_P ($\mathrm{mol\,L^{-1}}$)
Q_m	maximum ionic capacity of the polyelectrolyte phase ($\mathrm{eq\,L^{-1}}$)
q_i^o	initial molar concentration of specie i in the polyelectrolyte phase of volume V_P ($\mathrm{mol\,L^{-1}}$)
$r1$	dimensionless recycled retentate flow in Section 1, $\mathrm{RR_1/R_1}$
R_1	retentate flow in Section 1 ($\mathrm{L\,time^{-1}}$)
R_2	retentate flow in Section 2 ($\mathrm{L\,time^{-1}}$)
$r2$	dimensionless recycled retentate flow in Section 2, RR2/R2
R_i	membrane rejection of specie i, $= 1 - ((\mathrm{V/V_P} + 1)\cdot \mathrm{C}'_\mathrm{i})/((\mathrm{V/V_P})\cdot \mathrm{C}'_\mathrm{i} + \mathrm{q_i})$
Rij	membrane rejection of specie i in Section j
r_o	dimensionless recycled polyelectrolyte, RRP/Fo
$\mathrm{RR_1}$	recycled retentate flow in Section 1 ($\mathrm{L\,time^{-1}}$)
$\mathrm{RR_2}$	recycled retentate flow in Section 2 ($\mathrm{L\,time^{-1}}$)
RRP	polymer recycled flow ($\mathrm{L\,time^{-1}}$)
V	volume of the solution phase (L)
V_P	volume of the polyelectrolyte phase (L)
V_T	total volume of Sections 1 and 2 (L)

Greek Symbols

ρ_p	polyelectrolyte mass concentration in the polyelectrolyte phase ($\mathrm{g\,L^{-1}}$)

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