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Seawater as Auxiliary Reagent in Dual-Temperature Ion-Exchange Processing of Acidic Mine Waters

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This paper reports the results of studying dual-temperature ion-exchange concentrations of Cu^{2+} from acidic mine waters on acrylic resin Lewatit R 250-K in applying seawater as a regenerant. Application of seawater as an auxiliary reagent has been shown to enhance selective concentration of copper. Loading of the resin in the initial seawater form with mine water at 20 °C followed by thermostripping with hot mine water at 80 °C has been shown to result in an 3-fold increase of copper concentration in the first portions of the eluate. The repetitive thermosorption−thermostripping concentration cycles appear to be less efficient and give around 25% increase of Cu^{2+} concentration. The applicability of seawater for regeneration of the resin in the course of ion-exchange treatment of mine water has been successfully demonstrated, and the flow sheet of a proposed process is presented.

Introduction

The processes, which are commonly exploited for the treatment of metal-bearing industrial wastewaters and effluents to remove and/or to recover most valuable and/or toxic constituents (*1*−*7*), can be classified into two groups:

1. *Nonspecific technologies* such as precipitation and evaporation.

2. *Recovery technologies* involving ion exchange, extraction, membrane separation, electrowinning, and some others.

Current economic and ecological analyses of the various processes available for the recovery of metals from wastewaters favor in many instances ion exchange (*3, 6*). Even though ion exchange is favored, one must take into account the primary disadvantage of this treatment technique, which relates to the resin regeneration step. This step requires application of aggressive chemicals (e.g., acid and/or alkali) and is known to be the main source of wastes in ion-exchange technology. Hence, ion-exchange methods providing the ability to exclude (at least partially) the regeneration step are of particular interest. The group of methods of this type include dual-temperature ion-exchange processes (*8*−*15*) and allied techniques (*16*−*18*). Although the advantages of the above techniques are quite obvious, the practical application of these methods is still very limited. The following factors can stimulate the development of the above techniques: (1) the possibility of their combination with conventional ion-exchange methods; (2) the application of non-aggressive and easily available auxiliary reagents, such as seawater for regeneration of the ion exchanger, and (3) the reduction in energy expenditure for heating solution under treatment and the regenerant (e.g., seawater) applied. The last problem can be successfully solved by using conventional or concentrated sunlight (in the areas with high level of solar radiation) as the principal and ecologically clean energy source (sun-boiler systems). An alternative solution can be the use of seawater in the cooling cycles of the steam power stations. An estimation shows that in this case almost 50% of the overall power costs could be written off (*6*).

In a recent (*11*), we reported the data on ion-exchange equilibrium of seawater metal ions on carboxylic resins at different temperatures. A significant increase of the equilibrium separation factor, α, at elevated temperatures was observed for Ca^{2+}−Na^{+} and Mg^{2+}−Na^{+} exchanges. These results provide a selective thermostripping of Ca^{2+} and Mg^{2+} from the resins equilibrated with seawater at 80 °C by applying cold seawater at 10 °C.

Although during the last two decades there has been a growing interest in the recovery of different valuable minerals from seawater (see, ref (*6*) and references cited therein), practically no reports on applying seawater as an auxiliary agent in ion-exchange separation processes can be found in the literature.

In our recent paper (*15*), we have demonstrated the applicability of the reagentless dual-temperature ion-exchange process for selective concentrations of copper from the native acidic mine waters on a carboxylic cation exchanger Lewatit R 250-K. The present study was undertaken (1) to study the regeneration of a carboxylic ion exchanger in a form of mine water metal ions with natural seawater and (2) to study the conditions for concentrating copper from acidic mine water by reagentless dual-temperature ion-exchange technique.

Experimental Section

Materials, Apparatus, and Analytical Methods. The work was performed with samples of the native acidic mine waters of the Rio Tinto area, known to be the natural generic metal-bearing effluents originated from the pyritic ore deposits typical for the southern provinces of Spain and Portugal.

Samples of the natural Mediterranean seawater used in the present study were obtained from the area near Tarragona (Spain). Natural seawater was boiled and then filtered for the removal of organic matter before its use in the experiments. The composition (macrocomponents) of seawater was as follows: ionic species/C (ppm): Ca^{2+}/450; Mg^{2+}/1370; Na^{+}/11 135, and pH = 8.1. The ion exchanger, a macroporous polyacrylic resin bearing carboxylic groups, Lewatit R 250-K, was kindly supplied by Bayer Hispania Industrial, S.A., NaOH and H_2SO_4 of analytical grade were purchased from Probus (Spain) and used as received. The concentrations of metal ions were determined by atomic emission spectroscopy (ICP-AES technique) using an ARL Model 3410 spectrometer (Fisons, USA) provided with a minitorch. The uncertainty of metal ions determination was less than 1.5%. Determination of H^{+} and OH^{-} ions was carried out by potentiometric titration using a Crison pH-meter 507 (Spain) provided with a combined glass electrode. Thermostatic glass columns (of 1.4 cm i.d.) connected with a thermostat (Haake D1, Germany) were used to study the ion-exchange equilibrium at different temperatures. The construction of these columns provides simultaneously the heating (or cooling) of both resin and entering solution phases.

The conditioning of Rio Tinto water samples (RTW) was carried out by adjusting the pH to 3.4−3.5 with concentrated NaOH solution and bubbling of air through the solution during

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TABLE 1. Composition of Natural (Before and After Treatment) and Artificial (Used in Different Thermostripping−Sorption Cycles) Rio Tinto Water Samples

C (ppm)	pH	SO_4^{2-}	Fe^{3+}	Cu^{2+}	Zn^{2+}	Al^{3+}	Mn^{2+}	Mg^{2+}	Ca^{2+}	Na^{+}
initial	1.8	17 430	4 527	117	1 217	560	87	940	480	22
treated	3.5	17 350	3	115	1 275	530	90	950	475	3 550
artificial	3.5	17 884	0	120	4 700	530	0	0	0	3 500
1st concn	3.5	17 365	0	171	4 731	318	0	0	0	3 565
2nd concn	3.5	17 557	0	200	4 706	186	0	0	0	3 565
3rd concn	3.5	17 212	0	255	4 668	106	0	0	0	3 588
4th concn	3.5	17 106	0	326	4 519	49	0	0	0	3 687

several days to oxidize Fe(II) to Fe(III). The final removal of the $Fe(OH)_3$ precipitate was carried out by filtration using a sintered glass filter and a water pump. The composition of RTW samples, before and after this treatment, are shown in Table 1, where the compositions of artificially prepared RTW concentrates are also given.

Thermosorption and Thermostripping. All the experiments were carried out under dynamic conditions in the thermostatic columns previously described (*11*). The columns were loaded with a certain portion of the ion exchanger, which remained constant during all the series of experiments. The total capacity of the resin bed was determined prior to the equilibrium studies by applying a standard technique (*11*). Then, the resin was converted into either RTW or seawater ions and equilibrated at a selected temperature.

Thermostripping and thermosorption experiments were carried out as follows: after equilibration of the resin with the RTW sample at 80 and 20 °C, respectively, the excess of the solution over the resin bed was removed so that its level coincided with that of the resin bed. Then, the temperature was decreased or increased (for thermosorption or thermostripping). After equilibration of the system at a given temperature, the RTW of the same composition was passed through the column at a constant flow rate and collected in portions where concentrations of metal ions were determined. RTW solution was passed until the ion-exchange equilibrium at each temperature was achieved. In the series of consecutive thermostripping−thermosorption experiments with RTW concentrates, the composition of the initial solutions used corresponded to that of the sample of thermostripping solution obtained during the previous thermostripping-thermosorption cycle that contained the highest concentration of Cu^{2+} (see Table 1). Thermosorption from RTW samples on the resin in the seawater ions was carried out by passing the solution through the column in a fluidized mode (from bottom to top) at constant flow rate of 40 cm^3/min to prevent clogging of the resin bed with $Al(OH)_3$ precipitate, which appeared in the first portions of solution passing through the column. The regeneration of the resin with seawater was carried out at 80 °C after equilibration of the resin bed with RTW at the same temperature.

Results and Discussion

The typical concentration-volume histories obtained in two sequential thermostripping-thermosorption cycles are shown in Figure 1. The first cycle was carried out after the loading of Lewatit R 250-K resin in the initial seawater ions with natural RTW at 20 °C by thermostripping with the same RTW sample at 80 °C (see curve 1 in Figure 1). Then the resin was cooled and equilibrated with cold RTW at 20 °C (thermosorption), followed by the second thermostripping at 80 °C. The specific capacity of the resin bed used in this series of experiments was 8.4 mequiv/g. RTW was passed at a flow rate of 1.6 cm^3/min. As seen in Figure 1, the first thermostripping leads to intensive desorption of copper from the resin while Al^{3+} is sorbed. This results in a decrease of Al^{3+} concentration in the first portions of the eluate and in an increase of Cu^{2+} ion concentrations. The concentration degrees of the rest of RTW metal ions have been shown to be much less than those of Cu^{2+} and Al^{3+} (depletion degree in this case) and are not shown in Figure 1 (*15*).

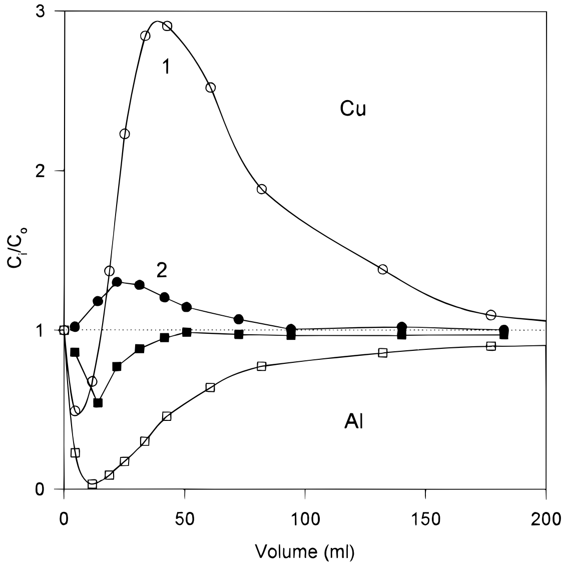

FIGURE 1. Thermostripping breakthrough curves for Cu^{2+} and Al^{3+} from Lewatit R 250-K resin: first thermostripping (1) and second thermostripping (2). $T = 80$ °C, solution flow rate = 1.6 cm^3/min.

The thermostripping process leads to a partial desorption of RTW metal ions such as Cu^{2+} and some others (except Al^{3+}) from the resin. The unloaded resin phase is able to take them up again without any additional treatment after decreasing the temperature (in our case 20 °C) in the system and carrying out the repetitive thermosorption (*11*). However this latter process has been observed to be of far less efficient than the first loading of the resin in the seawater ions form. This can be attributed to unfavorable conditions of the second thermosorption process, which in fact proceeds “against” the selectivity of the resin that follows from the respective values of equilibrium separation factors for RTW ion couples reported elsewhere (*15*). Nevertheless, the repetition of the thermosorption−thermostripping cycles with RTW concentrates (see Table 1) on the resin in the RTW ions allows us to carry out reagentless dual-temperature concentration of copper as has been reported elsewhere (*13*). As follows from the results shown in Figure 2, the degrees of copper concentration and aluminium depletion in each sequential cycle are of the same order of magnitude as in the second one shown in Figure 1 (see curve 2). On the other hand, the situation can be significantly improved after treating (regeneration) the resin with seawater (see curve 1 in Figure 1). Since the regeneration of the resin bed must be fulfilled right after thermostripping, it seems reasonable to carry out this stage of the process without alteration of the temperature, i.e., at 80 °C.

The concentration−volume histories of the regeneration of the resin with hot seawater at 80 °C are shown in Figure 3. Desorption of Zn^{2+} and Mn^{2+} from the resin proceeds

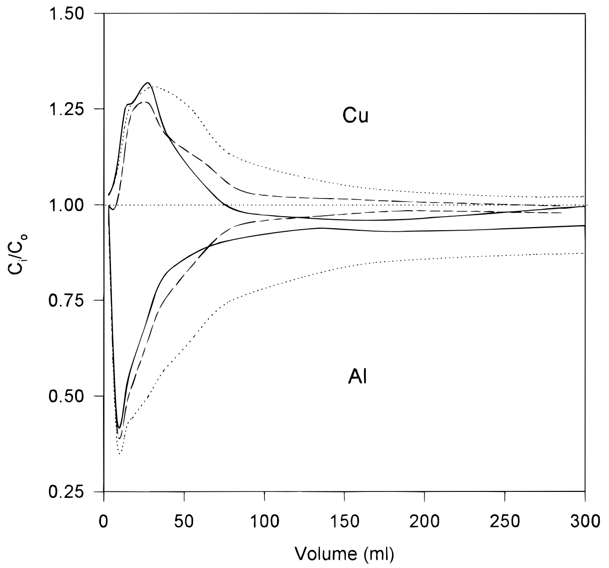

FIGURE 2. Concentration−volume histories for second thermostripping in different sequential cycles: first cycle (solid line), second cycle (dashed line), and third cycle (dotted line).

much faster than Cu^{2+} and Al^{3+} (see Figure 3a). The former are completely removed from the resin phase with 5 bed volumes of seawater while for the elution of Cu^{2+} 15 bed volumes of the regenerant is needed. Al^{3+} appears the most difficult to remove admixture, and the complete regeneration of the resin bed can be achieved after passing approximately 30 bed volumes of hot seawater. As seen in Figure 3b, Mg^{2+} and Na^{+} fulfill in fact the functions of displacers and are sorbed during the regeneration. After treatment with seawater and a proper cooling, the resin is prepared for the next thermosorption−thermostripping cycle.

Results of the repetitive experiments on sequential thermostripping−thermosorption cycles with RTW concentrates (see Figure 2) on the resin in the seawater ions (in regeneration of the resin with seawater after each thermostripping) testifies to the significant enhancement of the copper concentration process, which is seen in Figure 4. Indeed, as follows from the comparison of the results shown in Figure 2 with those presented in Figure 4, concentration degrees of copper in each cycle are much higher when using the resin in the seawater ions form at the loading stage.

The effect observed can be attributed to the partial hydrolysis of the resin in the seawater ions form. The capacity of Lewatit R 250-K resin toward macrocomponents of seawater has been determined to equal (in equivalent fractions): 0.31 (Ca^{2+}), 0.50 (Mg^{2+}), and 0.19 (Na^{+}) (*11*). A carboxylic resin in the Na form readily undergoes the hydrolysis (as a salt formed by a weak polyacid and a strong base) according to the following reaction:

$$\text{R-COONa} + H_2O \rightleftarrows \text{R-COOH} + \text{NaOH} \qquad (1)$$

Loading of the partially hydrolyzed resin with RTW is accompanied by precipitation of RTW metal ion hydroxides (due to the presence of alkali in the resin phase) in accordance with their solubility. The solubility sequence for cations of conditioned (iron-free) RTW can be written in terms of the respective solubility products (*19*), K_{SP}, as follows:

$$\text{Al(OH)}_3\ (pK_{SP} = 32.9) \ll \text{Cu(OH)}_2\ (19.7) < \text{Zn(OH)}_2\ (16.7) < \text{Mn(OH)}_2\ (12.7) < \text{Mg(OH)}_2\ (10.7) < \text{Ca(OH)}_2\ (5.3) \qquad (2)$$

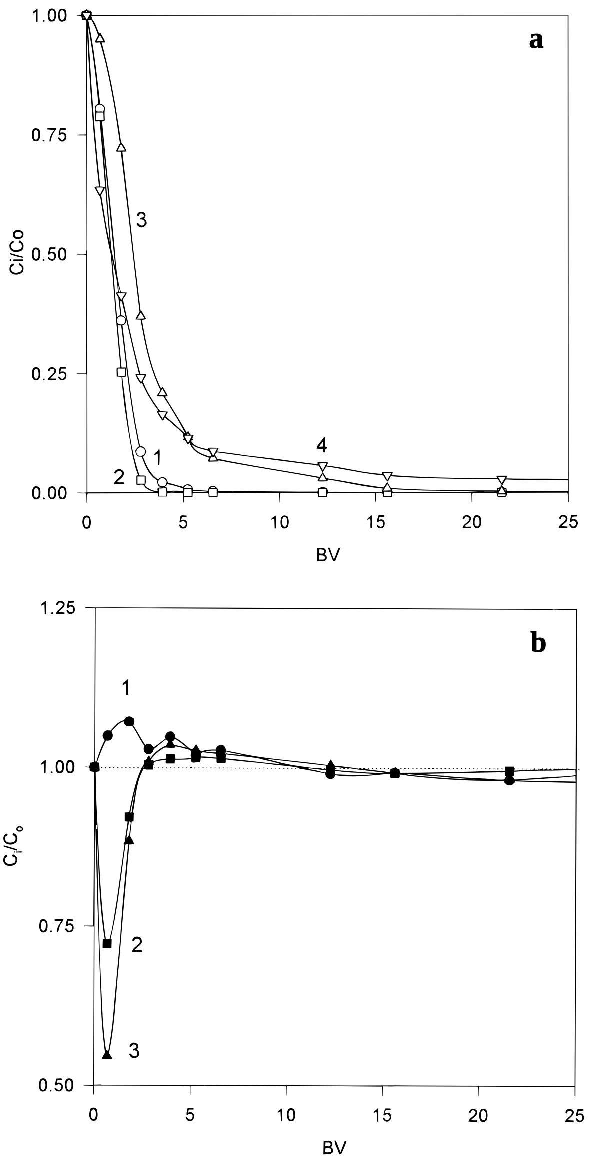

FIGURE 3. Concentration−volume histories of the regeneration of the resin with hot seawater at 80 °C: (a) Zn^{2+} (1), Mn^{2+} (2), Cu^{2+} (3), and Al^{3+} (4); (b) Ca^{2+} (1), Mg^{2+} (2), and Na^{+} (3). C_o for Ca^{2+}, Mg^{2+}, and Na^{+} is the concentration of these ions in seawater. Solution flow rate = 1.6 cm^3/min.

where $pK_{SP} = -\log K_{SP}$. In accordance with eq 2 one can expect mainly the formation of $Al(OH)_3$ precipitate, which is confirmed by the analysis of the precipitate collected from the first portions of the eluate passed through the column during the thermosorption stage. Removal of aluminium from RTW during the loading of the resin proceeds in the interbed space of the column and leads to an increase of the resin capacity toward the rest of the RTW metal ions following the sequence of the resin selectivity. The selectivity sequence of Lewatit R 250-K toward RTW cations is easily evaluated from the respective separation factor values reported elsewhere (*15*) and can be written as follows:

$$Al^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Na^{+} \qquad (3)$$

Hence, removal (at least partial) of aluminium from RTW must result in additional accumulation of copper (and some other metal ions as well) in the resin. Hence, a significant enhancing of the copper concentration is observed.

The results of thermostripping shown in Figures 1 (curve 1) and 4 have been obtained on the resin bed of 5 cm height. Increase of the bed height must result in the increase of the concentration degrees of metal ions stripped (*15*). This is clearly seen in Figure 5, where the concentration−volume

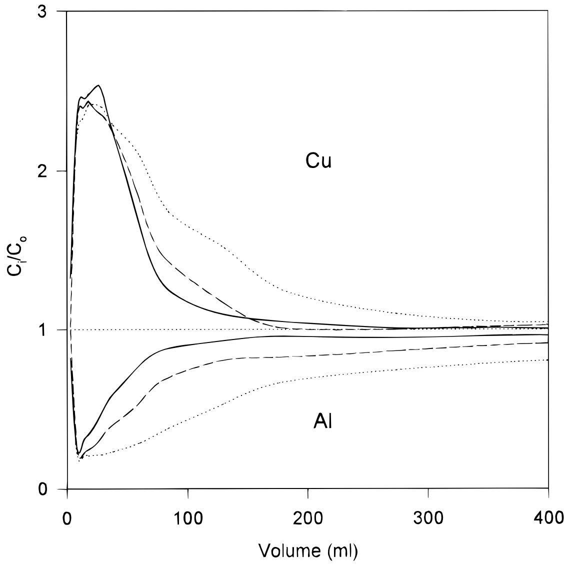

FIGURE 4. Concentration−volume histories for first thermostripping in different sequential cycles: first cycle (solid line), second cycle (dashed line), and third cycle (dotted line).

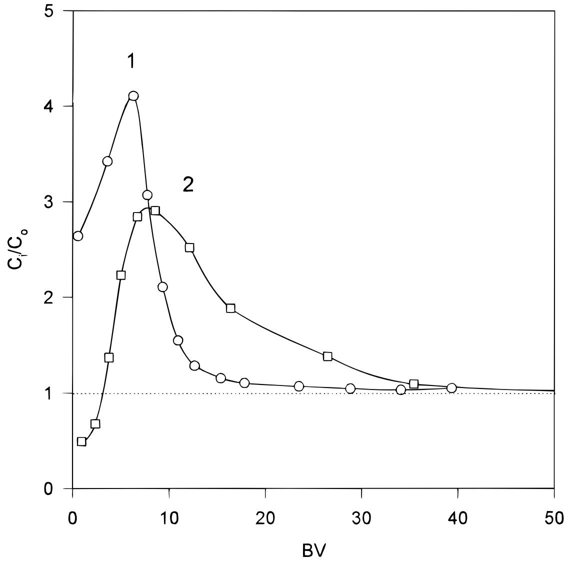

FIGURE 5. Concentration−volume histories for Cu^{2+} obtained by thermostripping from resin beds of different heights: $h = 18.5$ cm (1) and $h = 5$ cm (2). $T = 80$ °C, solution flow rate = 1.6 cm^3/min.

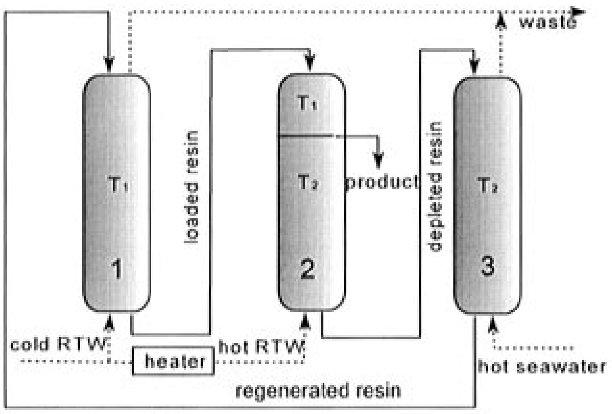

FIGURE 6. Flow sheet of the process for ion-exchange treatment of acidic mine waters in applying seawater as regenerant.

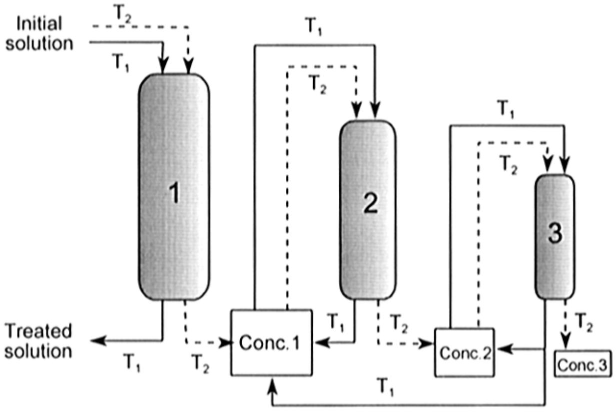

FIGURE 7. Flow sheet of the process for reagentless dual-temperature ion-exchange treatment of acidic mine waters.

histories for Cu^{2+} obtained by thermostripping from resin beds of different heights (5 and 18.5 cm) are shown.

Finally, we consider the results obtained in the present study from a practical viewpoint to propose a flow sheet of the ion-exchange process for the treatment of acidic mine waters. The block-scheme of the process is presented in Figure 6. The unit comprises three counter-current columns operating at different temperatures $T_1 = 20$ °C and $T_2 = 80$ °C. Cold RTW [after removal of iron(III) hydroxide] is treated in the first column with fluidized resin bed that has been treated with seawater. After loading with RTW metal ions, the resin bed is directed into the second (thermostripping) column, which is fed with hot RTW and produces RTW concentrate enriched with Cu^{2+}, Zn^{2+}, etc., and depleted with Al^{3+} (*20, 21*). The construction of the thermostripping column may be similar to that of counter-current ion-exchange contactors with moving packed bed (*22, 23*). The third column, where the resin underwent the final regeneration, must be of the same type as column 2 and must provide the conditions for the treatment of the resin bed with seawater at a high flow rate (see Figure 3), i.e., the column must be highly productive (*23*−*26*). The regenerated resin is returned back into column 1, and the treatment cycle repeats. The wastes produced from column 1 represent in fact the mixture of Mg^{2+}, Na^+, and Ca^{2+} sulfates at pH ∼ 6. They can be mixed with those produced by column 3 (at pH = 8.1) and discharged after elimination of sulfates content to seawater level (∼3500 ppm) with, for example, lime milk.

The results shown in Figure 2 can serve as a base for designing a flow sheet of the reagentless dual-temperature copper concentration process. The scheme of this process for the counter-current mode of operation has been proposed elsewhere (*13*).

The same process can be realized in a fixed bed mode of operation as shown schematically in Figure 7. The columns with fixed bed of Lewatit R 250-K resin are periodically treated with cold (thermosorption) and hot (thermostripping) RTW. Stripping solution (copper concentrate) obtained is collected separately and underwent further treatment in the next column. Sequential repetition of the thermostripping−thermosorption cycles leads to the accumulation of copper in the stripping solution (see Figure 2 and Table 1). Comparison of the results shown in Figure 2 with those presented in Figure 4 testify to the possibility of combining processes shown schematically in Figures 6 and 7 within one technological flow sheet. This can be done by applying the former process (Figure 6) for the final concentrating of RTW concentrates obtained at any stage of the latter process (Figure 7). As follows from Figures 4 and 5, such a combination will lead to an increase of copper concentration in the final eluate by at least a factor of 3.

In conclusion, the results of this study are the first successful demonstration of the practical possibility for designing ion-exchange treatment technology based upon the use of seawater as the auxiliary regenerating agent.

Acknowledgments

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