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Removal of Heavy Metals and Lanthanides from Industrial Phosphoric Acid Process Liquors

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ABSTRACT

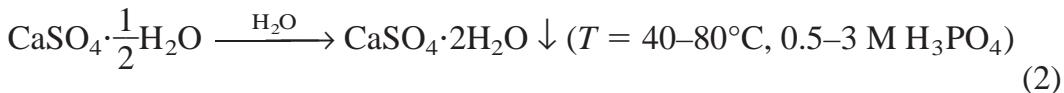
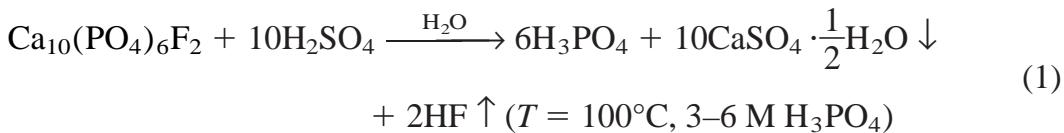
To diminish the discharge of heavy metals and lanthanides by the phosphoric acid industry, these impurities have to be removed from the mother liquor before their incorporation in the gypsum crystals. This can best be achieved by means of solvent extraction or ion exchange during the recrystallization of hemihydrate to dihydrate gypsum. Various commercial carriers and two ion-exchange resins were screened for their efficiency and selectivity. Light and heavy lanthanide ions are extracted from the recrystallization acid by didodecylphthalenesulfonic acid (Nacure 1052) and di-(2-ethylhexyl)phosphoric acid (D2EHPA), and the heavy-metal ions by bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301) and by bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302). Mercury is also extracted by the anion carriers tri(C₈–C₁₀)amine (Alamine 336) and tri(C₈–C₁₀) monomethyl ammonium chloride (Aliquat 336). Both Dowex C-500 and Amberlite IR-120 extract lanthanide and heavy-metal ions. Unfortunately, D2EHPA, Nacure 1052, and the two ion-exchange resins also show affinity for ions present in much higher concentrations, like calcium or iron ions.

INTRODUCTION

Phosphoric acid, which is used for the production of fertilizers and detergents, is primarily derived from phosphate ore and sulfuric acid (1). In the so-called HemiDiHydrate (HDH)-processes, calcium sulfate hemihydrate, formed by leaching of fluoroapatite are with sulfuric acid (Eq. 1), is recrystal-

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lized into calcium sulfate dihydrate (gypsum) in order to improve the phosphate recovery (Eq. 2):



Yearly, 100 billion kilograms of gypsum are discharged worldwide (1), and with it many tons of impurities like lanthanides and heavy metals which are incorporated in the gypsum crystals (2, 3). Although the discharge of lanthanides has not been proven harmful (4) in contrast with that of some of the heavy metals, an increase of their concentration in the environment should be avoided.

To reduce the discharge of the impurities, solvent extraction and ion exchange are investigated as potential separation processes for the removal of the impurities from the mother liquor during the production process. By either of these separation processes, the impurities can only be removed in their ionic form during the leaching of the phosphate ore (Eq. 1) or during the recrystallization of hemihydrate into dihydrate gypsum (Eq. 2). The latter step has been chosen because of the relatively mild process conditions compared with those in the leaching step. Consequently, the separation processes to be developed should be suitable for the selective removal of impurities at low concentrations ($\mu\text{g/kg}$ to mg/kg) at temperatures of at least 60°C and pH values of 0–1. Additionally, the techniques should be able to treat slurry streams with 20–40 wt% solids.

Typical concentrations of various lanthanides and heavy metals in the gypsum are listed in Table 1, but the concentrations in the production process de-

TABLE 1
Typical Concentrations of Various
Lanthanides and Heavy Metals in the
Gypsum

Element	Concentration (mg/kg)
Cd	10.0
Pb	1.3
Hg	0.1
La	110.0
Ce	220.0
Eu	4.5
Dy	6.3
Er	2.5



pend strongly on the ore used. The concentrations of lanthanides and heavy metals in the gypsum should be reduced as much as possible, but a first aim is to reach 30% of the initial concentrations.

Several carriers for application in extraction processes and two ion-exchange resins were tested on the basis of their selective affinity for lanthanide or heavy-metal ions in the presence of high concentrations of other ions, like calcium and iron ions, in industrial recrystallization acid. The affinity of a separation process for a Component A or the selective affinity for this component with respect to a Component B is represented by the distribution coefficient, K_A , or the separation factor, $\alpha_{A/B}$:

$$K_A = x_A/y_A \quad (3)$$

$$\alpha_{A/B} = \frac{x_A/x_B}{y_A/y_B} = \frac{K_A}{K_B} \quad (4)$$

where y_A is the concentration of Component A in the acid (mg/kg) and x_A is the concentration in the organic solution or in the ion-exchange resin (mg/kg), both at equilibrium.

EXPERIMENTAL

Chemicals

The industrial recrystallization acid was obtained either from a Norsk Hydro HDH process or from a Nissan-H process. Recrystallization acid from the first process contains approximately 0.8 mol/kg H_3PO_4 and 0.5 mol/kg H_2SO_4 , and that from the second process 3.9 mol/kg H_3PO_4 and 0.2 mol/kg H_2SO_4 . The concentrations of other components like lanthanides and heavy metals depend on the fluoroapatite ore.

To facilitate analysis, the concentrations of Hg, La, Ce, Eu, Dy, Er, or Cu were increased to 50 mg/kg by adding their nitrate salts to the recrystallization acid (La, Hg, Cu: Merck, pro analyse; Ce: Merck, extra pure; Eu, Dy, Er: Aldrich Chemical Company, 99.9%).

The carriers and ion-exchange resins used for the screening experiments are listed in Table 2. The carriers were diluted or dissolved in kerosene, except for Nacure 1052, which was diluted with heptane (Janssen Chimica, 99.9%) to obtain the extraction liquid.

Analyses

The concentrations of La, Ce, Eu, Dy, Er, Hg, Al, Fe, Cu, and Ca in the recrystallization acid were determined by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Spectro). The concentrations in the samples were determined by either the standard addition method



TABLE 2
Carriers and Ion-Exchange Resins Screened for Removal of Heavy-Metal and
Lanthanide Ions from Recrystallization Acids

Chemical or resin		Active group	Supplier
Di-(2-ethylhexyl) phosphoric acid	D2EHPA	(RO) ₂ P(O)OH	Alfa Johnson Matthey GmBH
Bis(2,4,4-trimethylpentyl) dithiophosphinic acid	Cyanex 301	R ₂ P(S)SH	Cytec Industries
Bis(2,4,4-trimethylpentyl) monothiophosphinic acid	Cyanex 302	R ₂ P(S)OH	Cytec Industries
Didodecylnaphthalenesulfonic acid	Nacure 1052	ROSO ₃ H	King Industries
Tributylphosphate	TBP	(RO) ₃ PO	Alfa Johnson Matthey GmBH
Dicyclohexano-18-crown-6	DC-18C6		Acros 98%
2-Hydroxy-5-nonylacetophenone oxime	LIX 84	R(OH)C(R)NOH	Henkel
Tri(C ₈ –C ₁₀)amine	Alamine 336	RNH ₂	Henkel
Tri(C ₈ –C ₁₀)monomethyl ammonium chloride	Aliquat 336	RNH ₃ ⁺ Cl [–]	Henkel
Amberlite IR-120 H ⁺ -form	Amberlite	ROSO ₃ H	Fluka Chemika
Dowex monosphere C-500 H ⁺ -form	Dowex	ROSO ₃ H	Fluka Chemika

or from a calibration line by using pure ionic solutions of 1000 mg/kg (Ca, Fe, Al, Cu, Hg: Merck standard solution; La, Ce: Aldrich Chemical Company, calibration standard; Eu, Dy, Er: Janssen Chimica atomic absorption standard solution).

The concentrations of Pb and Cd ions were determined by means of polarography (Metrohm Trace Analyser).

Procedure

Ten grams of an organic solution or various amounts of ion-exchange resin were contacted intensively with 10 g of a recrystallization acid in a shaking apparatus (Heto) with a shaking frequency of 200 times per minute at a temperature of approximately 70°C for at least 18 hours. Subsequently, the acid was separated from the organic solution in a separation funnel or from the ion-exchange resin by filtration. The concentrations of the cations in the recrystallization acid were determined before and after each shaking experiment, which enabled the calculation of the distribution coefficient:

$$K_A = \frac{y_{A,\text{initial}} - y_A}{y_A} \cdot \frac{m_{\text{acid}}}{m_{\text{organic,resin}}} \quad (5)$$



where $y_{A,\text{initial}}$ = concentration in the acid at the start (mg/kg), and m = the mass of either of the two contacted phases (kg).

RESULTS AND DISCUSSION

Extraction

Table 3 shows the results of some shaking experiments, and although the final solution compositions differ following these experiments, the calculated distribution coefficients are a good indication of the affinities of an extractant for ions from the recrystallization acid.

Table 3 shows that the heavy-metal ions are extracted from the recrystallization acid into the organic solution with Cyanex 301 as a carrier. For example, the concentration of lead in the acid decreases from 0.61 mg/kg to a value below 0.2 mg/kg, a reduction of over 67%. In agreement with Pearson's hard and soft acids and bases principle (5), Cyanex 301 and 302, which contain soft base groups (Table 2), bind with most soft and borderline Lewis acid cations such as mercury, copper, cadmium, and lead ions from acidic media (6, 7), and, as demonstrated here, from the recrystallization acid. Also in agreement with Pearson's principle is the fact that the Cyanex carriers have little or no affinity for the hard iron and lanthanide ions. Most likely, the carriers will also show no affinity for the hard calcium ions and are, therefore, very suitable for the selective removal of heavy-metal ions from a recrystallization acid that contains high concentrations of calcium and iron.

TABLE 3
Distribution Coefficients between 10 g of Recrystallization Acid and 10 g of Kerosene
Solutions with Various Carriers at 70°C^{a,b}

	Cyanex 301	Cyanex 302	D2EHPA	LIX84	DC-18C6	Aliquat 336	Alamine 336
Ce	0.15	—	—	0.02	0.06	—	0.14
Cu	238	243	—	1.2	—	—	—
Hg	5.3	5.7	0.11	0.16	5.3	6.3	7.1
Pb	>2.1	?	0.15	?	0.13	?	—
Ca	?	?	—	?	?	?	?
Al	—	—	—	—	—	—	0.04
Fe	—	—	2.4	—	—	—	—
Cd	>4.0	?	0.04	?	—	?	0.08

^a > = larger than; ? = not analyzed; — = no decrease in concentration in recrystallization acid.

^b The initial feed concentrations were approximately 50 mg/kg for Ce, Cu, Hg; 1500 mg/kg for Ca; 900 mg/kg for Fe; 0.6 mg/kg for Pb; and 4 mg/kg for Cd.



The removal of mercury by Cyanex 302 from a recrystallization acid was very efficient. After the acid had been contacted with only 0.01 wt% of Cyanex 302 in kerosene, the mercury concentration in the acid was reduced to the detection limit of the ICP-AES, which is 0.13 times the initial concentration of mercury in the recrystallization acid.

The results in Table 3 further show that mercury can also be effectively extracted with anion carriers such as Aliquat 336 and Alamine 336. This is due to the presence of chloride ions in the recrystallization acid [usually 50 to 100 mg/kg, but in some cases even higher, depending on the ore (1)], which form stable complexes with mercury (8), resulting in neutral or negatively charged complexes that can be extracted by tertiary and quaternary amines (9).

The distribution coefficients of the heavy-metal ions, except that of iron(III), for D2EHPA and LIX 84 were equal to or lower than 0.15 (Table 3). For example, the concentration of lead in the acid was reduced from 0.61 to 0.53 mg/kg if contacted with D2EHPA.

D2EHPA and alkylsulfonic acids such as Nacure 1052, which are carriers used for the extraction of lanthanide ions (10, 11), show affinity for the lanthanides from recrystallization acid as is shown in Fig. 1. The commercially used carrier TBP (12) showed no affinity for the lanthanides from recrystallization acid, and combinations of D2EHPA with TBP or DC-18C6 resulted

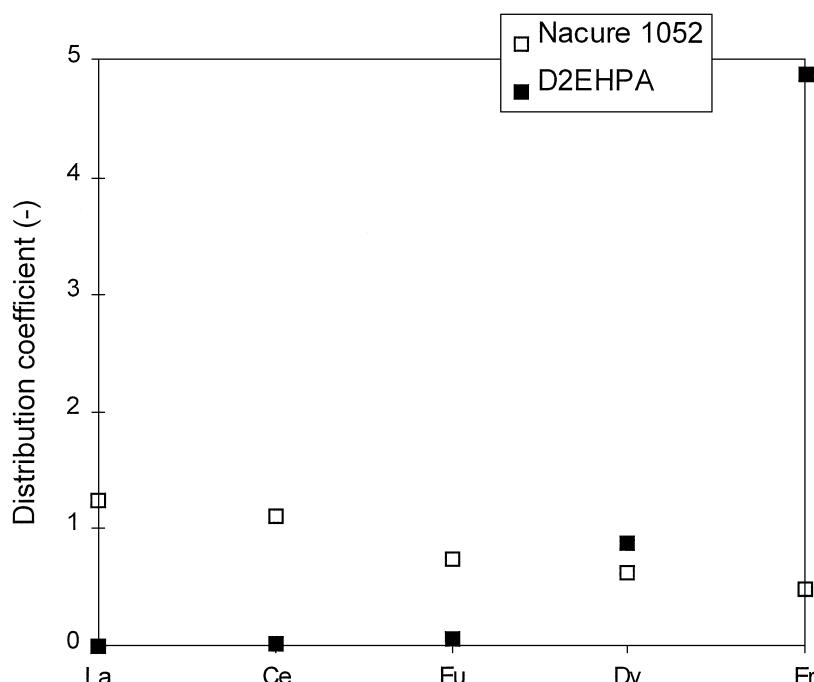


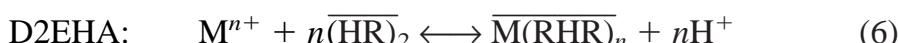
FIG. 1 Distribution coefficients, K_{Ln} (—), between a recrystallization acid and a 40 kg/kg D2EHPA in kerosene solution or a 40 kg/kg Nacure 1052 in heptane solution for five lanthanide ions with increasing atomic number at 70°C.



in lower distribution coefficients than for D2EHPA alone. Figure 1 shows that the distribution coefficients of D2EHPA increase with the atomic number of the lanthanide ions from 0 for lanthanum and cerium to 4.9 for erbium. In contrast to D2EHPA, Nacure 1052 shows a decreasing affinity with the atomic number of the lanthanide ions from 1.3 for lanthanum to 0.5 for erbium. Further, D2EHPA shows an affinity for iron(III) ($K_{Fe} = 2.4$) whereas Nacure 1052 shows an affinity for calcium ($K_{Ca} = 0.66$).

The difference in affinity between D2EHPA and Nacure 1052 can be explained by the polarizability of the functional groups as compared with that of water. Due to the polarizability sequence $POO^- > H_2O > SO_3^-$ (13), the phosphate carrier D2EHPA replaces water ligands from the cations, resulting in an increasing affinity with increasing charge density of the *bare* cation. However, the sulfate carrier Nacure 1052 does not replace water, so that the affinity increases with increasing charge density of the *hydrated* cation. This results in a reverse affinity sequence for the lanthanide ions of Nacure 1052 compared with that of D2EHPA, because of the reverse ionic radius sequence (resulting in a reverse charge density sequence) of hydrated and bare lanthanide ions. The hydrated ionic radius increases with increasing atomic number from 4.61 Å for lanthanum and cerium to 4.74 Å for dysprosium and erbium (14), whereas the bare ionic radius decreases with increasing atomic number from 1.18 Å for lanthanum to 1.00 Å for erbium (15).

The reaction equations for D2EHPA and Nacure 1052 are (15):



in which M and HR represent the metal ion and the carrier, respectively; n is the charge of the metal ion; and the overbar indicates the species in the organic phase. Taking these equations into account, it is calculated that only 3.4 mol% of D2EHPA is used for the binding of iron(III) and lanthanide ions, of which 3.2 mol% serves for binding of iron(III) ions. Only 4.8 mol% of the active component in Nacure 1052 is used for the binding of lanthanide and calcium ions, of which 4.2 mol% serves for the binding of calcium ions.

Small distribution coefficients, as were found for the heavy metals in the case of D2EHPA, and low degrees of occupation, as were found for D2EHPA and Nacure 1052, do not at all indicate that solvent extraction could not be feasible. By contacting the loaded carrier with an appropriate stripping solution, the carrier can be recovered and then reused for the extraction of the impurities. In a continuous extraction–stripping system, the impurity can be removed from the mother liquor and concentrated in the stripping solution by small amounts of carrier with only low degrees of occupation. With such a system, impurities with only little affinity for the carrier (a low distribution coefficient between mother liquor and organic solution) can be removed, but no excess of



other components with more affinity for this carrier should be present in the mother liquor.

Ion Exchange

Dowex C-500 and Amberlite IR-120 ion-exchange resins extract heavy-metal, lanthanide, and calcium ions from a recrystallization acid (Table 4). The affinity sequence for lanthanide ions of the resins is comparable to that of the carrier Nacure 1052 (Fig. 1), which is the result of the sulfonic acid functional group in these chemicals (Table 2).

Table 4 shows that the distribution coefficients are usually not constant for varying amounts of ion-exchange resin. This could be due to the fact that different amounts of resin are contacted with equal amounts of recrystallization acid, thus causing competition effects between the cations. For small amounts of resin, only the most preferred cations will be taken up, while by adding larger amounts of resin, active sites remain available for less preferred cations. This apparently results in a decrease of the distribution coefficient for the most preferred cations with an increasing amount of resin, and an increase of the distribution coefficient for the less preferred cations. In this way, the behavior of Amberlite IR-120, shown in Fig. 2, can be explained. The distribution coefficients of the most preferred cations calcium (Table 4) and lanthanum decrease, while the distribution coefficient of the less preferred cation europium increases.

TABLE 4
Distribution Coefficients between 10 g of Recrystallization Acid and 0.11
or 1.5 g of Dowex or Amberlite Resins at 70°C^{a,b}

	Dowex C-500		Amberlite IR-120	
	0.11 g	1.5 g	0.11 g	1.5 g
Ca	9.2	13	15	12
Cd	8.0	8.0	9.9	8.1
Pb	10	20	29	21
Fe	—	0.46	—	0.74
La	23	38	16	16
Ce	19	34	11	16
Eu	10	20	5.6	17
Dy	7.4	16	5.3	14
Er	7.4	15	5.0	14

^a The initial feed concentrations were approximately 50 mg/kg for Ce, Cu, and Hg; 1500 mg/kg for Ca; 900 mg/kg for Fe; 0.6 mg for Pb; and 4 mg/kg for Cd.

^b — = no decrease in concentration in recrystallization acid.



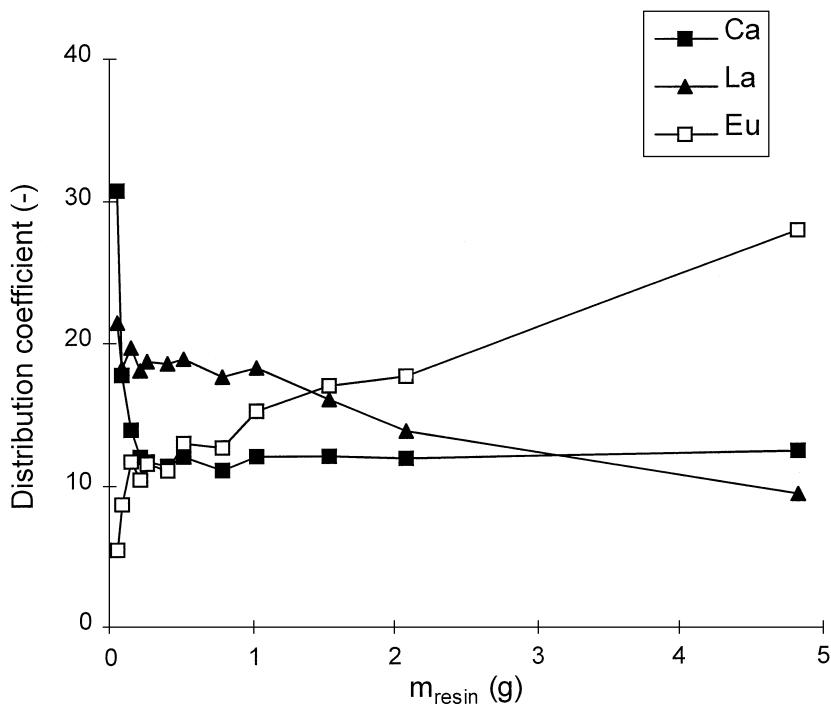


FIG. 2 Distribution coefficients, K_A (—), of calcium, lanthanum, and europium between a recrystallization acid and an increasing amount of Amberlite ion-exchange resin, m_{resin} (g), at 70°C.

Table 4 also shows that in the case of Dowex C-500 most determined distribution coefficients increase with an increasing amount of resin. This could be explained if the protons were the most preferred cations. The distribution coefficients of the protons would decrease, while the distribution coefficients of all the cations considered in this work would increase. Calculations of the ratio between the number of active sites used for the binding of calcium and lanthanides and the initial number of active sites on the resin, the degree of occupation, ε (-) (Fig. 3), supports this hypothesis:

$$\varepsilon = \frac{N_{\text{Ca}} + N_{\text{La}} + N_{\text{Ce}} + N_{\text{En}} + N_{\text{Dy}} + N_{\text{Er}} + N_{\text{Fe}}}{N_{\text{initial}}} \times 100\% \quad (8)$$

where N_x is the number of active sites occupied by component x (meq) and N_{initial} is the initial number of active sites (meq). The degree of occupation is small for Dowex C-500, indicating that most of the active sites are occupied by protons. Another explanation can be found in the presence of other cations in the recrystallization acid that were not considered in this work, such as barium or nickel. Some of these cations could be the most preferred cations, of which the distribution coefficients decrease with increasing amounts of resin.



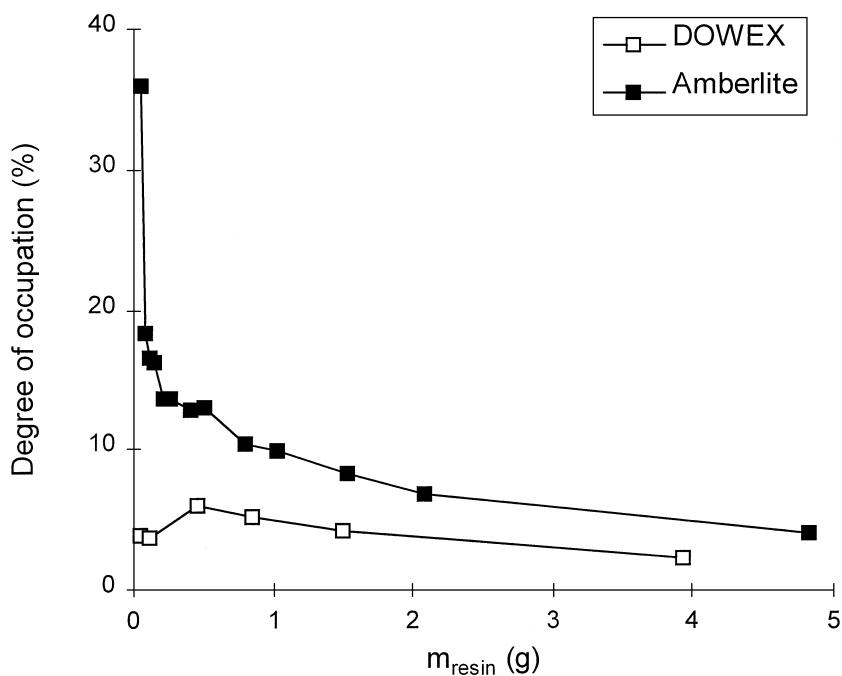


FIG. 3 Degree of occupation for increasing amounts of resin for Dowex C-500 and Amberlite IR-120, m_{resin} (g), at 70°C after shaking experiments with a recrystallization acid.

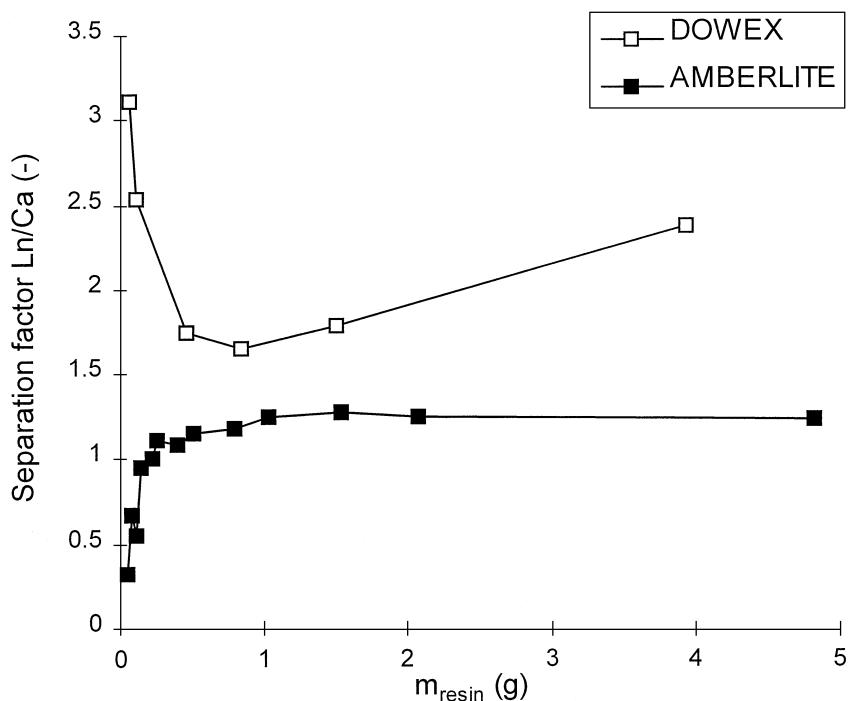


FIG. 4 Separation factor between lanthanide and calcium ions, $\alpha_{\text{Ln/Ca}}$ (—), for increasing amounts of Dowex and Amberlite resins, m_{resin} (g), at 70°C after shaking experiments with a recrystallization acid.



The differences in distribution coefficients between the lanthanide and the calcium ions yield more favorable separation factors for the Dowex C-500 resin compared with those of the Amberlite IR-120 resin for the extraction of lanthanides from a recrystallization acid, as shown in Fig. 4. For Dowex C-500, the concentration of lanthanides on the resin increases to more than twice that of calcium. Due to the much higher degree of occupation of Amberlite IR-120 as compared with that of Dowex C-500 (Fig. 3), the total amount of lanthanide ions on the resin is almost equal for both resins.

CONCLUSIONS

Some commercial carriers and resins can be applied for the extraction of heavy-metal and lanthanide ions from recrystallization acid.

The cation carriers Cyanex 301 and 302 show selective affinities for heavy-metal ions in recrystallization acid, and mercury can also be extracted from the acid by the anion carriers Alamine 336 and Aliquat 336.

D2EHPA has an affinity for the heavy lanthanide ions, increasing with increasing atomic number, whereas Nacure 1052 has an affinity for all lanthanide ions, increasing with decreasing atomic number. The disadvantage of D2EHPA is its affinity for iron ions, and that of Nacure 1052 is its affinity for calcium ions, both of which are present in the recrystallization acid at relatively high concentrations.

Both heavy-metal and lanthanide ions were extracted from recrystallization acid to low concentrations by the ion-exchange resins Dowex C-500 and Amberlite IR-120. The separation factor between lanthanide and calcium ions showed that use of Dowex C-500 is more favorable for the removal of lanthanide ions from recrystallization acids than Amberlite IR-120; however, because of a higher degree of occupation for Amberlite IR-120, the total amount of lanthanide ions on the resin is almost equal for both resins.

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