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Extraction of heavy metals from industrial phosphoric acid in a transverse flow hollow fiber membrane contactor

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EXTRACTION OF HEAVY METALS FROM INDUSTRIAL PHOSPHORIC ACID IN A TRANSVERSE FLOW HOLLOW FIBER MEMBRANE CONTACTOR

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ABSTRACT

Phosphoric acid is produced mainly in the so-called wet processes, in which phosphate ore reacts with sulfuric acid to form phosphoric acid and calcium sulfate solids. With the phosphate ore, impurities enter the production process. Some of these impurities mainly end up in the product acid, others mainly in the calcium sulfate. The aim is to develop an in-line technique for the removal of impurities from the product acid, and simultaneously avoid their incorporation into the calcium sulfate solids. This paper describes the treatment of industrial phosphoric acid in transverse flow hollow fiber membrane contactors and the feasibility of these contactors for the treatment of a phosphoric acid/calcium sulfate slurry.

Mercury, copper, lead, and cadmium were extracted from an industrial phosphoric acid by Cyanex 302 (bis(2,4,4-trimethyl-

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pentyl)thiophosphinic acid) in kerosene in a contactor. The permeability was 3×10^{-6} m/sec. With the same contactor, erbium, and dysprosium were extracted by di(2-ethylhexyl)phosphoric acid in kerosene. The permeability was $2-6 \times 10^{-8}$ m/sec.

Experiments had to be terminated, because of leakage of organic phase into the aqueous phase. Vibrations due to pulsation of the tube pumps are thought to be the main reason for this leakage. Problems with respect to organic phase leakage due to e.g., the formation of eddies caused by the transverse flow could not be determined.

The feasibility of hollow fiber membrane contactors to remove impurities from the slurries depends strongly on the particle size of the solids and the required pitches to avoid clogging.

INTRODUCTION

In the so-called wet processes, phosphate ore (fluoroapatite ore) reacts with sulfuric acid to yield the product phosphoric acid and a byproduct calcium sulfate according to

$$Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + xH_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \cdot xH_2O + HF$$

Depending on the process conditions, either calcium sulfate hemihydrate (HH, $x = 1/2$), dihydrate (DH, $x = 2$), or anhydrite (AH, $x = 0$) is formed. The calcium sulfate, which is formed, depends on the process conditions, like the temperature and the acid concentration. In the HemiDiHydrate (HDH) processes, first HH is formed. This is recrystallized in a second step to DH to recover the incorporated phosphoric acid. During this solvent-mediated recrystallization, HH dissolves including all incorporated impurities and DH crystals are formed from the solution. Due to the recrystallization step, the process efficiency becomes $>99\%$. The HDH processes can be operated in different ways. This is shown in Fig. 1 by the phase diagram of the $CaSO_4-H_3PO_4-H_2O$ system (1). In the two-filter process, the HH is separated from the product acid and contacted with a phosphoric acid solution with lower acid strength and temperature to effect the recrystallization, route C–D in Fig. 1. In the one-filter process, the temperature of the product acid/HH slurry is lowered and HH recrystallizes to DH in the product acid, route A–B in Fig. 1.

With the phosphate ore also, impurities enter the production process. Some of these impurities mainly end up in the product acid, like nickel; others mainly end up in the DH, like lead and mercury. The aim is to develop in-line techniques to remove the impurities from the production process to avoid their dispersion in the environment. Potential separation techniques that are investigated are ion-

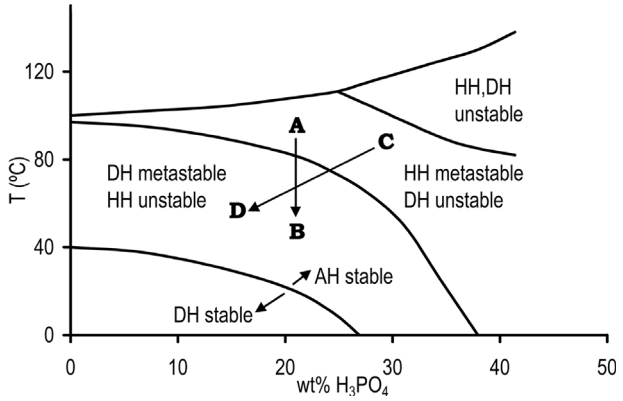

Figure 1. The thermodynamic (metastable) equilibrium lines of AH, HH, and DH for the system $CaSO_4-H_3PO_4-H_2O$ with the indication of the process conditions in the one-filter HDH process (A–B) and the two-filter process (C–D).

exchange extraction and liquid membrane extraction, because these techniques can separate elements selectively in the presence of high concentrations of other elements.

BACKGROUND

To remove the impurities with ion-exchange extraction or liquid membrane extraction, they have to be present in a solution in their ionic form. For the impurities, which are incorporated mainly in the calcium sulfate solid phase, this is only the case during the reaction of the phosphate ore with sulfuric acid and during the solvent-mediated recrystallization. Due to the milder process conditions, as indicated in Fig. 1, the recrystallization step was chosen as the potential process step to remove the impurities. To be able to remove the impurities, which are dissolved in the HH solids, the recrystallization and extraction should be performed simultaneously to prevent the impurities to become incorporated again into the DH solids. The removal of the impurities from the phosphoric acid will result in both, a decrease in the concentration of the acid as well as a decrease in the concentration of the DH, because the concentrations are related by a thermodynamically determined distribution, K_{DH} [−]. For impurity ion M, this relation is

$$K_{DH,M} = \frac{[M]_{DH}}{[M]_{acid}} \tag{1}$$

For the removal of the impurities from the phosphoric acid, liquid carriers, and ion exchange resins had to be found with a selective affinity towards the impurities. In an earlier paper (2), it was described that Cyanex 302 and 301 (bis(2,4,4-trimethylpentyl)thiophosphinic acid and bis(2,4,4-trimethylpentyl)-dithiophosphinic acid) selectively bind mercury, lead, cadmium, and copper from industrial phosphoric acid and D2EHPA (di(2-ethylhexyl)phosphoric acid) binds the heavy lanthanides, dysprosium, and erbium selectively. It was also proven that the addition of Cyanex 302 during the recrystallization of HH to DH resulted in a decrease in the concentration of zinc and cadmium in the newly formed DH (3). The latter results were obtained by contacting the organic extraction phase intensively with the recrystallizing slurry by stirring. The disadvantage of such a process is the emulsification of the organic phase in the phosphoric acid solution and its possible incorporation in the newly formed DH crystals.

To avoid this emulsification, liquid membrane extraction is thought to be a potential separation technique. In a hollow fiber membrane contactor, the organic phase is immobilized in a porous polymeric support, like a polypropylene hollow fiber, preventing emulsification of the organic phase in the feed solution. This is shown in Fig. 2.

In a transverse flow contactor, the feed slurry flows straight down from the top to the bottom of the module. When applying a top angle with a maximum of 8° and a bottom angle with a maximum of 25–30°, the solution follows the module wall (4) and no dead areas occur, in which settling of solids can develop. In ordinary parallel flow contactors, the feed solution enters and leaves the module with an angle of 90°, resulting in dead areas. In these areas, the settling of solids will occur resulting eventually in clogging. The transverse and parallel flow modules are shown in Fig. 3.

Another advantage of the transverse flow when compared to the parallel flow may be the extra turbulence on the shell side of the fibers, which will result in a thinner diffusion layer.

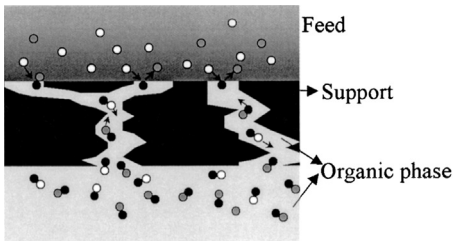

Figure 2. The extraction process using porous hollow fibers to separate the aqueous feed solution/slurry physically from the organic solution (white, gray, and black dots represent the impurity ion, the counter ion, and the carrier, respectively).

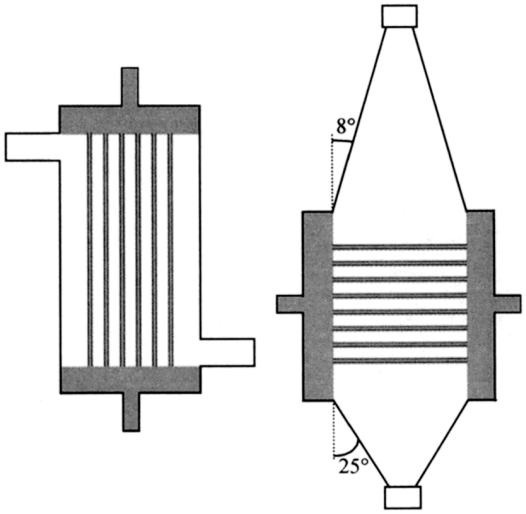

Figure 3. A parallel flow hollow fiber module (left) and a transverse flow hollow fiber module (right).

Membrane contactors have also disadvantages. The layer, through which the ion–carrier complex has to diffuse, is thick. This layer is at least as thick as the wall thickness of the hollow fiber, in which the organic phase is immobilized. Another disadvantage is the instability, i.e., the loss of organic phase from the pores of the fiber (5). Another disadvantage of the transverse flow contactor when compared to the parallel flow contactor may be the extra instabilities due to the transverse flow. An additional disadvantage for the treatment of a slurry stream is that the contact area between the two phases is small, because the pitches between the fibers must be large enough to avoid clogging in the module by the solid particles. This in contrast to membrane contactors used for the treatment of liquids, which can contain large contact areas.

The aim of this work is to get an insight into the feasibility of the transverse flow hollow fiber membrane contactor for the treatment of industrial phosphoric acid during the recrystallization of HH to DH. Therefore, the transverse flow hollow fiber membrane contactor is tested for the removal of impurities from industrial phosphoric acid. From the results gained with the membrane contactor for the treatment of industrial phosphoric acid, a feasibility study for the extraction with these kinds of modules during the recrystallization of HH to DH in the phosphoric acid process will be discussed at the end of this paper.

THEORY

Extraction in a Membrane Contactor

For solvent extraction, ions are taken up by the organic phase from the feed phase until thermodynamic equilibrium is reached. At equilibrium, the distribution coefficient, $K_{org,A}$ [−], is calculated by

$$K_{org,A} = \frac{[A]_{org}}{[A]_{acid}} \tag{2}$$

For a batch process (as is the case in the experiments described here), the flux of component A, J_A [mol m^{-2} sec^{-1}], equals

$$J_A = -\frac{d[A]_{acid}}{dt}\frac{V}{A} \tag{3}$$

with V the volume of the slurry [m^3], A the contact area [m^2], and t the time [sec]. The flux can be corrected for the feed concentration, resulting in the permeability, P [m/sec], defined as

$$P = -\frac{1}{[A]_{acid}}\frac{d[A]_{acid}}{dt}\frac{V}{A} = -\ln\frac{[A]_{acid,t=2}}{[A]_{acid,t=1}}\frac{V}{A}\frac{1}{t_2 - t_1} \tag{4}$$

Instability Mechanisms

The instability mechanisms of the membrane contactor, in which an organic phase is contacted with a feed phase, will have the same origin as those in supported liquid membranes (SLM). In SLMs the organic phase does not flow through the hollow fibers as it does in the studied membrane contactor, but is only present in the pores of the porous polymer support. A stripping solution, which receives the impurity ions from the organic phase, flows on the other side of the fiber wall than the feed solution. In this way, extraction of impurities and recovery of the carrier is performed in one apparatus.

The instability of the SLMs has been investigated widely. Kemperman (5) made an extensive survey of the instability mechanisms. It was found that many factors influenced the stability of the membranes. This paragraph aims at giving an insight into the additional instability mechanisms in the transverse flow modules compared to the parallel flow modules. This will also give an insight into the most dominant instability mechanism in transverse flow hollow fiber membrane contactors.

Instability of SLMs may be the result of pressure differences, emulsification of the organic phase in the aqueous phase or/and degradation of the fiber materia.

Pressure Differences

If the pressure difference between the shell and inner side of the fiber wall, the transmembrane pressure, exceeds the critical pressure, the organic phase will be pushed out of the most susceptible pores of the support. The system is unstable and the aqueous feed solution will get contaminated with the organic phase. The critical pressure, P_c [Pa], for cylindrical pores is given by the Laplace equation:

$$P_c = \frac{2\gamma \cos\theta}{r} \tag{5}$$

with γ the interfacial tension between the organic phase and the aqueous phase [N/m], θ the contact angle between the support pore wall and the organic phase [−], and r the pore radius [m]. The dependence of the critical pressure on the interfacial tension and the contact angle indicate that the support material, the composition of the aqueous solution, the organic solvent and carrier influence the stability strongly.

In a transverse flow membrane contactor, pressure differences, which are negligible in a parallel flow contactor, may result in higher transmembrane pressures and thus promote instability of the system. In a transverse flow membrane contactor, a pressure difference already occurs around the fibers. The transverse flow is shown in Fig. 4.

The pressure on the fiber is highest at point A. At this point, the feed velocity equals 0 and according to Bernoulli's equation, the pressure, P_A [Pa], becomes equal to

$$P_A = \frac{1}{2}\rho v_\infty^2 + P_\infty \tag{6}$$

with ρ the density of the feed solution [kg m^{-3}]. The pressure at point B is the lowest around the fiber. This pressure depends on the velocity between the fibers. The velocity between the fibers, v [m/sec], is determined by

$$v = v_\infty \frac{s/d}{s/d - 1} \tag{7}$$

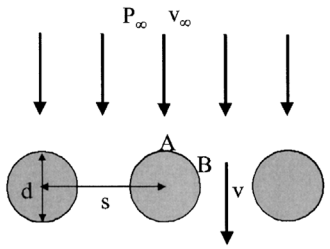

Figure 4. A schematic representation of the transverse flow in the hollow fiber module.

with s the longitudinal pitch [m], and d the fiber diameter [m]. The pressure is the lowest when we assume that there is no friction and is given by

$$P_B = -\frac{3}{2}\rho v^2 + P_\infty \tag{8}$$

Due to the transverse flow, a pressure drop also occurs in the contactor due to drag forces. The pressure drop is a function of the geometry (transversal pitch, longitudinal pitch, fiber diameter), the number of fiber rows in the module, the feed velocity, and the physical properties of the feed. It is assumed that the flow pattern around a fiber is not influenced by former rows of fibers, because the distance between the fibers is large in a contactor, in which a slurry stream is treated. For low Reynolds numbers when the flow field behind a cylinder is small, this will be a good assumption. The pressure drop over one fiber, P_w [Pa], is calculated as

$$P_w = C_w\left(\frac{1}{2}\rho v^2\right) \tag{9}$$

with C_w [−] the drag coefficient. The drag coefficient depends on the Reynolds number.

Emulsification of the Organic Phase

Emulsification is thought to be an important cause of SLM instability. Local deformations of the organic phase meniscus in the support pores combined with the Marangoni effect are probably the causes of the emulsification. These local deformations can have several origins, of which the most important are

- Kelvin–Helmholtz instabilities, two phases move with different velocities parallel to the interface creating waves,
- vibrations of the organic phase in the pores, small deformations on the organic phase meniscus due to pulsation of the aqueous phase resulting in the formation of ripples.

Once waves or ripples are formed on the organic phase meniscus, concentration differences can cause surface tension gradients on the organic/aqueous interface causing interfacial turbulence. This effect is called the Marangoni effect. The Marangoni effect is shown in Fig. 5. The interfacial turbulence may result in emulsification of the organic phase.

The presence of the Kelvin–Helmholtz instabilities depends on the velocity difference between the two phases and on the density difference between

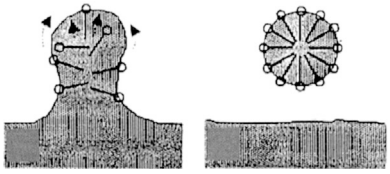

Figure 5. The Marangoni effect.

these phases. The critical velocity difference, Δv_c, at which Kelvin–Helmholtz instabilities occur can be estimated by (6)

$$\Delta v_C = \left(\frac{2(\rho_1 + \rho_2)}{\rho_1 \rho_2}\right)^{0.5} (\Delta \rho g \gamma)^{0.25} \tag{10}$$

The effect of Kelvin–Helmholtz instabilities can be more severe for the transverse flow than for the parallel flow. In the transverse flow, velocity gradients occur around the fiber, which is not the case in parallel flow. At point B in Fig. 4, the velocity along the fiber surface is higher than the superficial velocity. The critical velocity difference between the aqueous and organic phase is reached therefore at lower superficial velocities.

Especially the vibrations of the organic phase in the pores may be more severe in transverse flow than in parallel flow resulting in a less stable system. Due to transverse flow, eddy formation at the rear of the fibers may cause additional turbulence (4). An increasing turbulence will result in more violent vibrations of the organic phase in the pores. The formation of eddies depends on the Reynolds number, Re [−],

$$Re = \frac{\rho v d}{\eta} \tag{11}$$

with η the viscosity [kg m^{-1} sec^{-1}]. In a laminar flow, $Re < 1$, the stream lines follow the form of the fiber and no additional turbulence occurs. At $1 < Re < 70$, the flow at the rear becomes more turbulent and eddies are formed. At higher Re, $70 < Re < 150$, the eddies are dragged along with the flow and swirl away from the rear of the fiber. This is known as the Von Karman effect. At $150 < Re < 10$ (5), the turbulence behind the fiber increases further. The swirls become irregular and the turbulence area behind the fiber is large. Further increase in Re results in turbulence in the boundary layer of the fiber, whereas the turbulence area behind the fiber becomes smaller.

EXPERIMENTAL

Procedure and Experimental Set-Up

The extraction of heavy metals with Cyanex 302 (Cytec Industries) was performed with 175 g clear phosphoric acid from an industrial one-filter HemiRecrystallization (HRC) phosphoric acid process (3.8 mol H_3PO_4/kg, 0.2 mol H_2SO_4/kg) using 35% Jordan and 65% Kovdor ore. The density of the acid was determined to be 1280 kg m^{-3}, and the viscosity (1) 8.3×10^{-4} kg m^{-1} sec^{-1}. By adding analytically pure mercury nitrate the mercury concentration in the acid was increased by 0.25 mmol/kg resulting in a starting concentration in the acid of 0.29 mmol/kg. The acid was pumped round the hollow fibers with a superficial velocity of 0.4 cm/sec. The organic solution (130 g) of 1.18 mol/kg of Cyanex 302 in kerosene was pumped through the hydrophobic polypropylene fibers with a velocity of 1.2 cm/sec.

In the same module, the extraction of lanthanides with D2EHPA was performed with 560 g clear phosphoric acid from an industrial two-filter HemiDiHydrate (HDH) production process (0.8 mol H_3PO_4/kg, 0.5 mol H_2SO_4/kg) using 100% Jordan ore. The concentration of lanthanum, cerium, europium, dysprosium, and erbium was increased by adding their nitrate salts to starting concentrations of 0.27 mmol/kg lanthanum, 0.39 mmol/kg cerium, 0.31 mmol/kg europium, 0.34 mmol/kg dysprosium, 0.32 mmol/kg erbium. The concentrations were determined by analysis (see "Analysis" section) after addition. The density of this acid is 1120 kg m^{-3}. The organic phase of 0.35 mol/kg D2EHPA in kerosene (110 g) was pumped through the fibers with 1.2 cm/sec.

A laboratory set-up was built with a small module, in which dead areas were avoided by using feed tubes with the same diameter as that of the membrane compartment. The transverse flow module (XTO, The Netherlands) has a compartment of 8 mL, which contains four rows with 31 fibers (Oxyphan 50/280) each. The outer diameter of the fibers is 0.38 mm, the inner diameter 0.28 mm, and they have a pore size of 0.2 μm. The fibers have a total contact area of 29.8 cm^2. The transversal pitch between the fiber rows is 4000 μm and the longitudinal pitch is 650 μm. This is schematically shown in Fig. 6.

Analyses

Copper, mercury, and the lanthanides were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Spectro), whereas cadmium and lead were analyzed by polarography (stripping voltametry with hanging mercury drop electrode) (Trace Analyser, Metrohm). The organic solutions could not be

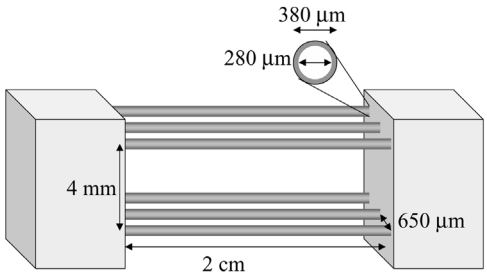

Figure 6. Schematic illustration of the distances in the transverse flow hollow fiber module used.

analyzed by ICP-AES, because after digestion the concentration in these solutions dropped below the detection limit.

The sizes of the industrial calcium sulfate hemihydrate and calcium sulfate dihydrate particles were determined by laser light scattering (Malvern Mastersizer) and scanning electron microscopy (SEM) (Jeol).

RESULTS

Extraction

Contacting the industrial phosphoric acid feed solution with Cyanex 302 in kerosene in a transverse flow hollow fiber membrane contactor resulted in the extraction of mercury, lead, and cadmium. The concentration decrease of mercury is shown in Fig. 7 as a function of time. Lead and cadmium were only determined before and after extraction. The concentration of lead was reduced from 1.6 to 0.5 μmol/kg, and that of cadmium from 8.0 to 1.8 μmol/kg.

Only the concentration of mercury was determined as a function of time. After 25×10^3 sec no more mercury was extracted. Apparently, thermodynamic equilibrium between the feed solution and the organic phase was reached with respect to mercury. Calculation of the distribution coefficient confirmed this. The calculated distribution coefficient was 5.1. This value is comparable to that determined after equilibration. At equilibrium, a distribution coefficient of 5.7 was found (2).

The average flux of mercury between 0 and 25×10^3 sec was calculated to be 2×10^{-7} mol m^{-2} sec^{-1} corresponding to a permeability of 1×10^{-6} m/sec. These fluxes and permeabilities have the same order of magnitude as those found in literature for SLM extraction (7,8).

Also copper was transported. The average copper flux was found to be 2×10^{-7} mol m^{-2} sec^{-1}, which corresponds to a permeability of 1×10^{-6} m/sec.

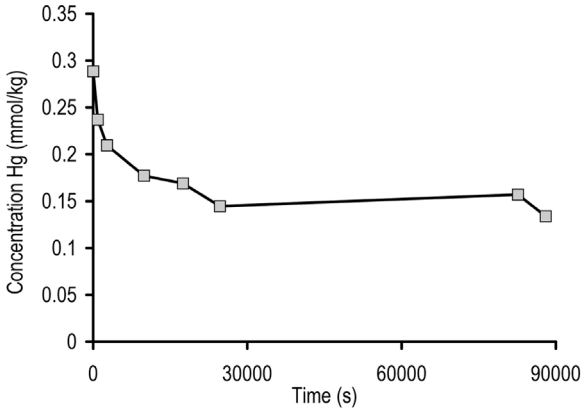

Figure 7. The concentration of mercury during the treatment of industrial phosphoric acid with Cyanex 302 in a transverse flow hollow fiber membrane contactor.

Similar extraction experiments were performed with the carrier D2EHPA in kerosene to remove lanthanides from the phosphoric acid. As expected from the results of equilibration tests (2), the light lanthanides lanthanum, cerium, and europium were not extracted at all. The heavier lanthanides dysprosium and erbium were extracted, as is shown in Fig. 8.

The fluxes of the trivalent lanthanides were lower than those of the heavy metals during extraction with Cyanex 302. The average flux of erbium was 2×10^{-8} mol m^{-2} sec^{-1}, which results in a permeability of 6×10^{-8} m/sec. The permeability of dysprosium was lower. The average dysprosium flux was 6×10^{-8} mol m^{-2} sec^{-1} and the permeability was 2×10^{-8} m/sec. The lower permeability is the result of the lower affinity of D2EHPA for this ion.

Instability

Experiments had to be terminated due to leakage of the organic phase, which flows through the hollow fiber, to the inorganic phosphoric acid phase, which flows around the fibers.

Pressure Differences

For polypropylene fibers with a nominal pore diameter of 0.2 μm, the critical pressure difference increased with the wall thickness of the fiber. For

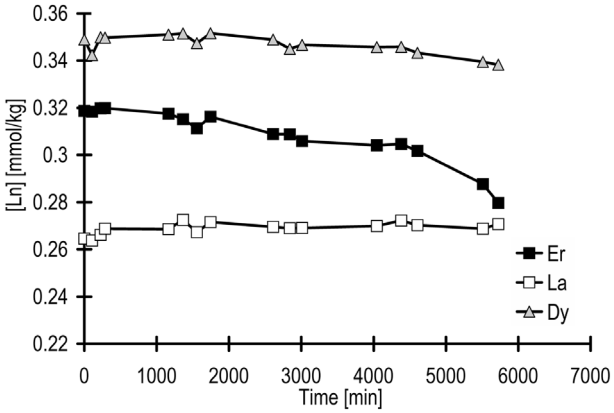

Figure 8. The concentration of lanthanum, dysprosium, and erbium in the acid during the treatment of industrial phosphoric acid with D2EHPA in kerosene in a transverse flow hollow fiber membrane contactor.

fibers with wall thicknesses of 150, 200, and 500 μm, the critical membrane pressures were found to be 0.72, 1.13, and 1.36×10^5 Pa, respectively, for the system kerosene/water (9,10). The fibers in the used membrane contactor have a wall thickness of only 50 μm. So, the critical pressure is thought to be lower than 0.72×10^5 Pa, but with the lack of a clear relation between the wall thickness and the critical pressure, it cannot be estimated precisely.

Equation (5) shows that the critical pressure depends strongly on the interfacial tension. The above-mentioned critical pressures were determined for a kerosene/water system. For extraction, a carrier is added to the kerosene phase. Generally, the addition of a carrier reduces the interfacial tension. This was illustrated for D2EHPA (11), which reduced the interfacial tension between water and *n*-dodecane from 52 to 14 mN/m, and LIX84 (11) (2-hydroxy-5-nonylacetophenone oxime), which reduced the interfacial tension between water and kerosene from 42 to 20 mN/m. Complexation of the carrier with an impurity ion may either decrease the interfacial tension further (nickel/D2EHPA) or may result in an increase of the interfacial tension (copper/LIX84) (12). Equation (5) shows that the reduction in the interfacial tension results in a decrease in the critical pressure. If assuming the same effect of D2EHPA in kerosene as in *n*-dodecane, the interfacial tension becomes 12 mN/m instead of 42 mN/m. The critical pressure of 0.72×10^5 Pa of the kerosene/water system would become 0.21×10^5 Pa for D2EHPA/ kerosene/water.

With Eqs. (6)–(8), it was calculated that with a superficial velocity of 0.4 cm/sec of phosphoric acid, the maximum pressure difference around the fiber is only 0.2 Pa. Comparing this with the critical pressure, it is clear that this is no reason for an increase in instability compared to the parallel flow. At a velocity of 1 m/sec, the pressure difference around the fiber becomes 0.1×10^5 Pa. So, only at very high velocities around the fiber, the pressure difference will contribute to the instability of the system.

The Reynolds number during the experiments equals 5. At this low Reynolds number, the resistance coefficient (12) used for the pressure drop of Eq. (9), is 4. The pressure drop becomes 0.2 Pa per fiber. With four rows of fibers, the total pressure drop in the contactor becomes 0.8 Pa. So, at these low velocities, the pressure drop will not cause significant additional stability problems. At a velocity of 1 m/sec, Reynolds number becomes 500 and the resistance coefficient then equals 1.2. Neglecting the influence of former rows of fibers on the flow pattern, the pressure drop becomes 675 Pa over a fiber. With this high velocity, the pressure drop equals 0.21×10^5 Pa after 31 rows of fibers. In that case, the extraction in the transverse flow membrane contactor cannot be operated anymore without instability problems due to the pressure drop.

It is concluded that at the low velocities used during the experiments, additional pressure differences due to transverse flow are not significant enough to reduce the stability of the system. Only at higher velocities, the pressure differences will cause stability problems that do not occur in the parallel flow contactors.

Emulsification

The D2EHPA has a density of 974 kg m^{-3}. With the density of 790 kg m^{-3} for kerosene, the density of the organic phase becomes 807 kg m^{-3}. With Eq. (10) and an interfacial tension that was estimated to be 12 mN/m for the D2EHPA/kerosene/water, it was calculated that the critical velocity difference for Kelvin–Helmholtz instabilities equals 16 cm/sec. With an interfacial tension of 42 mN/m for the kerosene/water system, this critical velocity difference becomes 22 cm/sec. With a velocity of 0 for the organic phase in the pores, the velocity of the aqueous phase may become as high as 16 cm/sec before Kelvin–Helmholtz instabilities occur. During the experiments, the velocity around the fibers had a maximum of 1 cm/sec and Kelvin–Helmholtz instabilities are not expected to have played a role in the instability of the membrane.

The vibrations of the organic phase in the pores cannot be quantified. However, it is expected that these vibrations are the cause of the instability problems. For pumping of the aqueous and organic phases, tube pumps were used. Although double tubing was used to reduce the pulsation, it is expected that

the pulsation causes vibration of the organic phase and thereby instability. Additional instability problems due to the formation of eddies, which do already occur at a Reynolds number of 5, cannot be determined. More research should be performed to compare parallel and transverse flow operation to eliminate the effect of pumping pulsation.

Swelling

Swelling of the fibers may result in other stability problems, although these problems will also occur in parallel flow membrane contactors. Due to swelling, the fibers become longer and meander in the module and they will connect. In a membrane contactor, an organic film layer may be formed between the hydrophobic fibers. This organic layer on the surface of the fibers may be dragged along with the aqueous phase resulting in a continuous loss of organic phase to the aqueous phase.

TRANSVERSE FLOW CONTACTORS FOR TREATMENT DURING RECRYSTALLIZATION

The described transverse flow hollow fiber membrane contactor is not suitable for the treatment of slurry streams, like the phosphoric acid slurry during the recrystallization of HH to DH. The longitudinal pitch of only 650 μm (270 μm between the outsides of the fibers) is too small to avoid clogging. However, increasing the pitches would make it possible to treat a slurry, but due to this increase the contact area per volume in the contactor will decrease.

In the two-filter HDH process, the average particle size of the HH crystals is 50 μm with a maximum particle size of 260 μm. The DH particles are larger with an average size of 80 μm and a maximum of 530 μm. No design parameters were found in literature with respect to the size of the pitches needed to avoid clogging. For a first feasibility calculation, a distance between the fibers of 10 times the maximum particle size was chosen.

During recrystallization, the impurities in the phosphoric acid are redistributed between the acid and the newly formed crystals. To achieve a lower concentration in DH, the concentration in the phosphoric acid should be reduced. To maintain a low concentration of impurities in the acid, the ions that enter the recrystallization section with the phosphoric acid and those that are released from the HH crystals have to be extracted.

To illustrate the feasibility of the membrane contactor to remove impurities during the recrystallization, lead is taken as an example. The industrial

recrystallization is performed in stirred vessels with a volume of 1000 m^3 and a residence time of 210 min. So, the flow rate equals 0.08 m^3/sec. The relative amount of $CaSO_4$ solids in the input flow and in the recrystallizer equals about 40%. The concentration of lead in the acid is 0.54 mmol m^{-3}, resulting in a supply of lead to the reactor with the acid of 2.6×10^{-5} mol/sec. The conversion of HH to DH in the first recrystallizer is about 86%. With a concentration of lead in HH of 16 mmol m^{-3}, it can be calculated that 0.44 mmol Pb/sec is released from HH into the acid. The total supply of lead becomes 0.47 mmol/sec.

For a reduction of 70% of lead in the acid and in DH, the concentration in the acid should become 0.16 mmol m^{-3}. Assuming a permeability coefficient of 3×10^{-6} m/sec, the flux through the membrane can be calculated with

$$J = P[\mathrm{A}]_{\mathrm{acid}} \tag{12}$$

with $[\mathrm{A}]_{\mathrm{acid}}$ the concentration of lead in the acid [mol m^{-3}]. The flux becomes 4.9×10^{-10} mol m^{-2} sec^{-1}. To remove 70% of the input amount of lead, 0.33 mmol/sec, a contact area of 6.7×10^5 m^2 is required.

For a contactor with pitches of 5.38 mm (5 mm distance between the fibers, about 10 times the maximum particle size of the crystals) and fibers of 380 μm, the contact area per volume is 41 m^2 m^{-3}. To gain the required contact area of 6.7×10^5 m^2, a contactor of 1.6×10^4 m^3 should be available. Taking into account that the recrystallizer has a volume of 1000 m^3, even a contactor, in which extraction and recrystallization are performed simultaneously, is not suitable to achieve the desired extraction efficiency. If the recrystallizer is used as a contactor, in which the recrystallization and the extraction are performed simultaneously, only 12% of the lead input can be removed with these pitches and fibers.

If smaller pitches could be applied, the contact area would increase significantly in the contactor. For a distance of 0.95 mm between the fibers (pitches of 1.33 mm), the contact area per volume of contactor increases to 675 m^2 m^{-3}. With this contact area, 70% of the lead input can be extracted when using the 1000 m^3 recrystallizer as a contactor.

It is concluded that the feasibility of treating slurry streams in a membrane contactor depends strongly on the required pitches. It is important to search for the smallest pitches possible. More research should be performed on the clogging behavior of slurries passing beds of tubes.

CONCLUSIONS

Mercury, copper, lead, and cadmium were removed from clear industrial recrystallization acid in a transverse flow hollow fiber membrane contactor by Cyanex 302 in kerosene. The permeability of mercury and copper was 1×10^{-6} m/sec, which is comparable to that of SLM extraction.

With the same module, erbium was extracted also from the phosphoric acid solution by the extracting agent D2EHPA in kerosene. The permeability of erbium was calculated to be 6×10^{-8} m/sec and that of dysprosium 2×10^{-8} m/sec.

Experiments had to be terminated, because of leakage of the organic phase into the feed solution. Transverse flow may result in additional instabilities compared to parallel flow. However, additional pressure differences and Kelvin–Helmholtz instabilities will only be significant at velocities higher than used in this research. Vibrations due to pulsation of the tube pumps are thought to be the main reason for instabilities. Additional instability problems due to the formation of eddies could not be determined.

The feasibility of a membrane contactor to remove impurities from a slurry depends strongly on the particle size of the solids and the required pitches to avoid clogging.

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