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A. M. Berends^a; G. J. Witkamp^a; G. M. van Rosmalen^a

^a Delft University of Technology, Laboratory for Process Equipment, Delft, The Netherlands

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EXTRACTION OF ALUMINUM FROM A PICKLING BATH WITH SUPPORTED LIQUID MEMBRANE EXTRACTION

A. M. Berends,* G. J. Witkamp, and G. M. van Rosmalen
Delft University of Technology, Laboratory for Process Equipment,
Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

ABSTRACT

Large amounts of waste are produced yearly in the galvanic and chemical surface treatment industry. Bath liquids used in the various processes lose their function due to contamination. The spent bath liquids have to be replaced and treated prior to disposal, leading to high costs and a high environmental burden. In this paper, a proposed solution to the problem is investigated: the selective removal of the contaminant with supported liquid membrane extraction. The extraction of aluminum, a contaminant at high concentrations, from a pickling bath liquid with hydrofluoric acid and phosphoric acid as its main components has been carried out with the basic extractants Alamine 308 and Alamine 336 in a flat sheet-supported liquid membrane setup. Aluminum transport rates were obtained in the order of 10^{-6} – 10^{-5} mol/(m²·s), which are normal values for this technique. The extraction was not completely selective as dissolved phosphorus was coextracted. In all experiments, precipitation took place on the surface of the liquid membrane and in the bulk of the strip phase. Increasing the stripping alkalinity from pH = 8 to pH = 13 reduced the amount of precipitation in the bulk of the strip phase but caused a substantial decrease in the aluminum flux. The precipitation prevents industrial application of the systems investigated.

INTRODUCTION

In the galvanic and chemical surface treatment industry, baths are used to treat various types of metal surfaces. The bath liquids consist of mixtures of acids, bases, or other additives and are usually very corrosive and toxic. During processing, the

* Author for correspondence: A. M. Berends@WbMT.TUDelft.NL

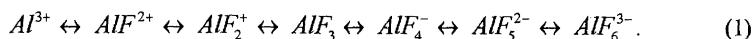
concentration of contaminants increases as they are released from the metal surfaces. After a defined period, the contaminant concentration reaches an excessive level, causing the bath liquids to lose their function. Replacement and treatment of the spent liquids lead to large amounts of waste, a high environmental burden, and high operating costs. The lifetimes of these bath liquids would increase if the contaminants that are toxic for the process were continuously and selectively removed. This can be achieved by in-line extraction techniques such as (supported) liquid membrane (SLM) extraction. In this paper, the applicability of SLM extraction for the increase of lifetimes of bath liquids in the galvanic and chemical surface treatment industry is investigated, using the chromium conversion coating of aluminum process as an example.

Chromium conversion coating of aluminum is used to provide aluminum parts intended for outdoor use with a protective layer. One of the baths used in this process is a so-called pickling bath (see Figure 1). In this bath, the Al_2O_3 layer is removed from the aluminum surface by dipping the aluminum part into a liquid with H_3PO_4 and HF as its main components, each at a concentration of 0.01–3.0 M. With repetitive use of the bath liquid, its aluminum concentration will increase. After a critical concentration is reached, the efficiency of the bath liquid declines. Every one or two months, the spent bath liquid has to be replaced. By using SLM extraction, the concentration of aluminum can be kept at an optimum level (see Figure 1). This also guarantees a constant and high quality of treated aluminum parts. The removed aluminum is intended for reuse.

The aim of our research is to develop an SLM system for aluminum removal from the pickling bath liquid. This paper describes the performance of several extractants, solvents, and strip phases in a flat-sheet SLM setup (FSSL). The focus is on the extent to which the solvent, the strip-phase alkalinity, and the addition of a modifier influence the aluminum transport rate, the selectivity of the extraction, and the duration of aluminum transport.

Selection of Suitable Extractants

Aluminum can be extracted from the pickling bath liquid in several complex forms. Aluminum dissolved in water forms $\text{Al}(\text{H}_2\text{O})_6^{3+}$, which is amphoteric. If fluoride ions are present, aluminum fluoride complexes are formed:¹



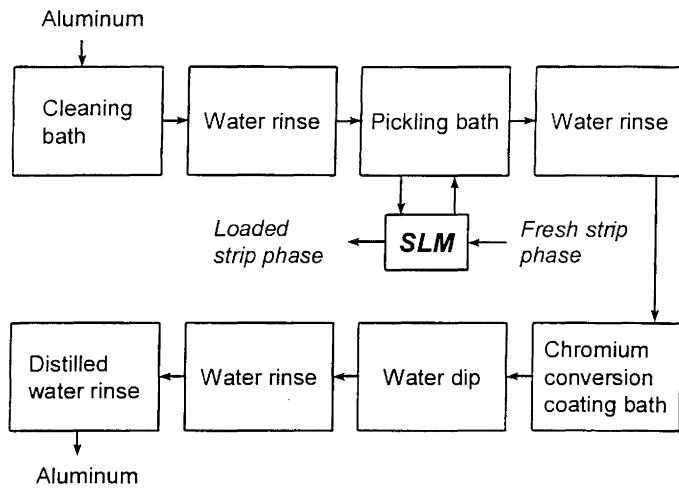


FIGURE 1. Process layout of chromium conversion coating of aluminum with an optional supported liquid membrane (SLM) extraction unit.

The (aq) after every complex in Equation (1) as well as the H_2O ligands have been omitted. The fluoride ions replace the H_2O in the first coordination sphere of Al^{3+} since F^- binds more strongly with Al^{3+} than does H_2O . The actual concentration of each of these complexes can be calculated using complex constants and activity coefficients. Figure 2 shows the results of these calculations for a phosphoric acid system with a total H^+ concentration of 1 M , using a method similar to the Nielsen method² for very dilute solutions. Aluminophosphate complexes, such as $\text{Al}(\text{H}_3\text{PO}_4)^{3+}$ and $\text{Al}(\text{H}_2\text{PO}_4)^{2+}$, can also be formed. In addition, fluoro-phosphato-aluminum complexes are formed,^{3,4} which will influence the results given in Figure 2. How the concentrations of the aluminum fluoride complexes will change is still uncertain. As all the above-mentioned complexes can be present in the pickling bath liquid, aluminum can be removed in several chemical complex forms, both negatively and positively charged.

The literature describes mostly acidic extractants for the removal of aluminum as a cation from (slightly) acidic media, such as di-2-ethylhexylphosphoric acid (D2EHPA), monononylphosphoric acid (MNPA), and sulfonic acids/organophosphorus extractant combinations.^{5,6,7,8,9,10,11,12,13} Therefore, shake tests were done on the extraction of aluminum from the pickling bath liquid as a cation with acidic extractants.¹⁴ However,

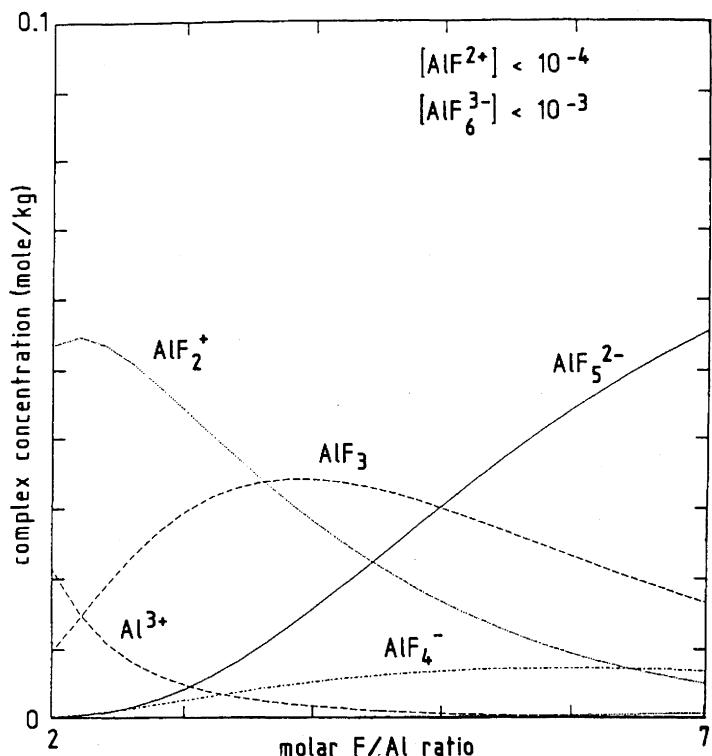


FIGURE 2. Concentrations of aluminum fluoride complexes in a phosphoric acid system with a total H^+ concentration of 1 M , calculated with a method similar to the Nielsen method (see References 1 and 2).

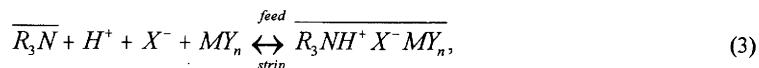
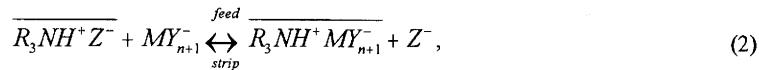
since negatively charged aluminum complexes can also be formed, basic extractants were screened as well.¹⁴ The results showed that Alamine 308 and Alamine 336 (both of which have the structure R_3N , basic extractants) were the most promising and thus selected for further study.

THEORY

Extraction Chemistry

Two relevant reaction mechanisms for the aluminum system under consideration are an anion-exchange reaction (countertransport) and an addition reaction (cotransport) as

represented by, respectively, Equations (2) and (3):

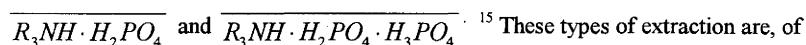


where an overbar denotes species present in the organic phase, $\overline{R_3NH^+Z^-}$ is the counter complex and $\overline{Z^-}$ is the counteranion in the case of the anion-exchange reaction, $\overline{MY_n^-}$ and $\overline{MY_{n+1}^-}$ are the metal complexes, $\overline{R_3NH^+MY_{n+1}^-}$ and $\overline{R_3NH^+X^-MY_n^-}$ are the amine-metal complexes, and $\overline{X^-}$ is the coanion in the case of the addition reaction. In practice, both reactions will take place simultaneously, with the dominating reaction type depending on the entire chemical system.^{15,16,17} The precise mechanism by which aluminum is extracted by tertiary amines is not known yet.

In addition to the above-mentioned reactions, tertiary amines can extract acids (HA) according to¹⁵⁻¹⁷



This reaction is competitive with the extraction of the metal complexes. For instance, Alamine 336 can extract H_3PO_4 , in which case the main species in the organic phase are



These types of extraction are, of course, undesirable because they reduce the selectivity of the extraction.

Apart from the above-mentioned extraction reactions, other phenomena such as aggregation can occur, even at very low amine concentrations. Aggregation can substantially hamper the extraction, but in some cases it has been reported to stimulate the extraction.¹⁸ If excessive aggregation takes place, a semisolid is formed, which can lead to a decreased transport rate. Due to these multiple effects, it is difficult to describe the mechanism of metal extraction quantitatively.¹⁶

Modifiers such as long-chain aliphatic alcohols can be added to the membrane phase to decrease the fraction of aggregated amine by increasing the amine solubility. The alcohols are capable of forming hydrogen bonds or dipole-dipole interactions with the tertiary amines or metal complexes, thus increasing their solvation in the membrane phase.^{15,16}

Mass Transfer

It is convenient to define the distribution coefficients, m_{feed} and m_{strip} , as follows:

$$m_{feed} = \frac{\overline{[M^{n+}]}}{[M^{n+}]_{feed}}, \quad (5)$$

$$m_{strip} = \frac{\overline{[M^{n+}]}}{[M^{n+}]_{strip}}, \quad (6)$$

where m_{feed} is the distribution coefficient of the metal M^{n+} between the membrane and feed phase, $\overline{[M^{n+}]}$ is the concentration of M^{n+} in the membrane phase at equilibrium (mol/dm³), $[M^{n+}]_{feed}$ is the concentration of M^{n+} in the feed phase at equilibrium (mol/dm³), m_{strip} is the distribution coefficient of M^{n+} between the membrane and strip phase, and $[M^{n+}]_{strip}$ is the concentration of M^{n+} in the strip phase at equilibrium (mol/dm³). In the earlier shake tests, m_{feed} was measured for several membrane phases.¹⁴ If, as is often the case, the diffusion of the metal-extractant complex through the liquid membrane is the rate-determining step, the flux J (mol/m²·s) for mass transfer is given by

$$J = \frac{D_{eff}}{d_{membrane}} \cdot m_{feed} \cdot c_{feed,bulk}, \quad (7)$$

where D_{eff} is the effective diffusion coefficient of the metal-extractant complex in the liquid membrane (m²/s), $d_{membrane}$ is the thickness of the liquid membrane (m), and $c_{feed,bulk}$ is the metal concentration in the bulk of the feed phase (mol/dm³). In this case, the concentration of the metal-extractant complex at the membrane phase/strip phase interface is approximately equal to zero.

The effective diffusion coefficient is proportional to the liquid diffusion coefficient $D_{liquid} \cdot D_{eff} \propto D_{liquid}$ (m²/s). Effects of the porosity and the tortuosity of the support material are considered to be constant. D_{liquid} is inversely proportional to the dynamic viscosity of the liquid membrane: $D_{liquid} \propto \frac{1}{\eta_{liquid}}$ (η_{liquid} in kg·m/s). For a given extractant and solvent combination, J has its maximum value at maximum $\frac{m_{feed}}{\eta_{liquid}}$. For this reason, the FSSLM experiments were carried out at a liquid membrane composition close to this value.

The mass balance over the feed-phase vessel in the FSSLM experiment equals

$$V_{\text{feed}} \frac{dc_{\text{feed,bulk}}}{dt} = -J \cdot A_{\text{membrane}}, \quad (8)$$

where V_{feed} is the volume of feed phase (dm^3), t is the time (s), and A_{membrane} is the liquid membrane area (m^2). J can be calculated from a measured concentration-versus-time profile in the strip phase as follows:

$$J = -\frac{V_{\text{feed}}}{A_{\text{membrane}}} \cdot \frac{\Delta c_{\text{feed,bulk}}}{\Delta t} = \frac{V_{\text{strip}}}{A_{\text{membrane}}} \cdot \frac{\Delta c_{\text{strip,bulk}}}{\Delta t}, \quad (9)$$

where $\Delta c_{\text{feed,bulk}}$ is the change in $c_{\text{feed,bulk}}$ in the time interval Δt , V_{strip} is the volume of the strip phase (dm^3), and $\Delta c_{\text{strip,bulk}}$ is the change in $c_{\text{strip,bulk}}$ (mol/dm^3) over the time interval Δt . V_{feed} and V_{strip} are approximately equal.

EXPERIMENTAL

Reagents

The pickling bath liquid was supplied by an aluminum surface treatment company. The basic extractants tested were Alamine 308 and Alamine 336 (donated by Henkel). In the calculations, each extractant was treated as if it were 100% pure, although this does not have to be the case. In most cases, kerosene was used as the solvent (Shellsol D70, Shell) but paraffin was tested as well. The modifier Exxal 13, tridecanol, was supplied by Volkers Loosdrecht. Sodium hydroxide and potassium hydroxide solutions were made by dissolving chemically pure NaOH or KOH in double-distilled water. All chemicals were used without further purification. Durapore HVHP 14250 (polyvinylidene fluoride, porosity 75%, Millipore) filter discs were used as hydrophobic membrane support material. The aqueous concentrations of aluminum and phosphorus were analyzed by inductively coupled plasma—atomic emission spectroscopy (ICP-AES) with a Spectroflame FMV – 21/016 (Spectro). The composition of the pickling bath liquid, which was the feed phase in all the experiments, was determined by ICP-AES analyses.

Apparatus

The flat-sheet apparatus consisted of two stirred, cubic perspex vessels (edge, 70 mm) with the hydrophobic, impregnated membrane sheet (effective area, 49 cm²) clamped in between (see Figure 3). The vessels were thermostated at the operating temperature (20 or 25°C) in a water bath. Stirrers were positioned in each compartment.

Procedures

Both the pickling bath liquid and the strip phase (340 mL of each) were thermostated at the operating temperature (20 or 25°C) prior to the experiment. For practical reasons, the process temperature was changed after experiment 1. The filter disc was impregnated with the membrane phase in a petri dish for 15 min, wiped off with a tissue, and clamped between the vessels. To prevent leakage, the cast flanges of the vessels were covered with high-vacuum gel and coated with a layer of paraffin wax. The bath liquid and strip phases were simultaneously poured into either of the two compartments. The vessels were thermostated; then stirrers were positioned in each compartment and rotated at approximately 300 rpm. The pH in the strip-phase compartment was kept at a constant value by addition of a NaOH solution unless stated otherwise. At appropriate time intervals, samples were taken from the feed phase (1 mL) and from the strip phase (2 mL) for ICP analysis.

RESULTS AND DISCUSSION

Composition of Pickling Bath Liquid

According to ICP-AES analysis, the major components were aluminum (0.249 M; standard deviation = 0.0045 M), phosphorus (0.340 M; standard deviation = 0.0063 M), and calcium (1.86 mM; standard deviation = 0.10 mM). The F/A1 mole ratio was greater than one, and the pH was approximately 1.35.

FSSLM Experiments

Selection of Optimum Stripping pH

The FSSLM experiments were conducted with two tertiary amines: Alamine 308 [triisooctylamine, or N(C₈H₁₇)₃]; and Alamine 336 [N(C₈H₁₇C₁₀H₂₁)₃, where C₈H₁₇:C₁₀H₂₁ ~ 2]. The liquid membrane was stable during all these experiments.

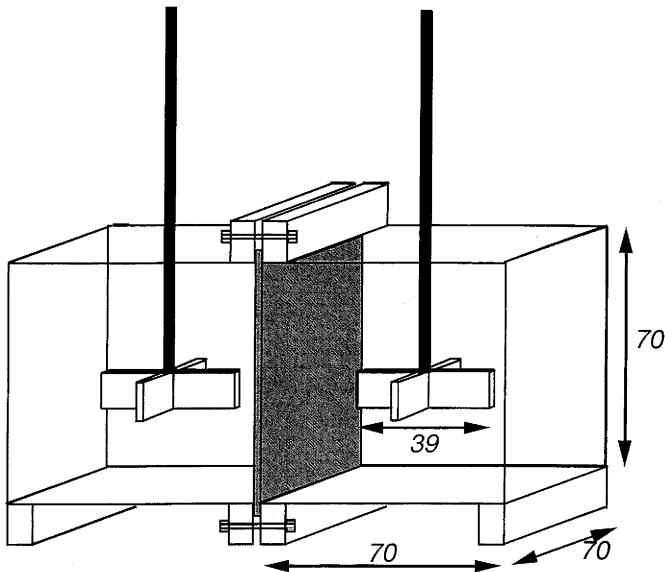


FIGURE 3. The flat sheet-supported liquid membrane (FSSLM) apparatus. The lengths of the edges are given in millimeters.

For selection of the optimal stripping pH, an experiment was conducted at 25°C with undiluted Alamine 336 as the membrane phase, pickling bath liquid as the feed phase, and a NaOH solution as the strip phase with a starting pH value of 7. During this experiment, the pH value was varied from 7 to 10 in steps of 1 pH unit. The highest flux was found at a pH value of 8, so this value was chosen for the strip phase in the experiments for both extractants. This value may not be the actual optimum pH since undesired precipitation influenced the results, as will be explained below.

Precipitation of a White Solid

Tables 1 and 2 show the conditions of the FSSLM experiments. During all of the experiments except 3 and 6, precipitation of a white solid phase took place on the surface of the liquid membrane and in the bulk of the strip phase. In experiments 3 and 6, precipitation only occurred on the liquid membrane surface. In an experiment similar to experiment 1, precipitation took place as well and this precipitate was analyzed. The

TABLE 1. EXPERIMENTAL CONDITIONS OF FSSLM EXPERIMENTS CARRIED OUT WITH ALAMINE 308

Exp.	Alamine 308			Strip phase	Temperature (°C)	Duration (ks)
	Alamine 308 (M)	Modifier (g/L)	according to $\left(\frac{m_{feed}}{\eta_{liquid}} \right)_{max}$			
1	.09	0	1.1 M	8.0	25	19
2	1.0	50	1.0 M	8.0	20	73 (20 h)
3	1.0	50	1.1 M	13.0	20	743 (206 h)

TABLE 2. EXPERIMENTAL CONDITIONS OF FSSLM EXPERIMENTS CARRIED OUT WITH ALAMINE 336

Exp.	Alamine 336			Strip phase	Temp. (°C)	Duration (ks)
	Alamine 336 (M)	Modifier (g/L)	According to $\left(\frac{m_{feed}}{\eta_{liquid}} \right)_{max}$			
4	1.19	0	1.0 M	8.0	20	14
5	1.19	0	1.0 M	8.0	20	22
6	1.19	0	1.0 M	13.0, KOH	20	20
7	1.19	0	1.0 M	8.0	20	174 (48 h)
8	1.0	50	1.0 M	8.0	20	73 (20 h)
9	2.07	0	1.2 M	8.0	20	154 (43 h)
10 ^a	0.96	50	1.9 M	8.0	20	91 (25 h)

^a Carried out with paraffin as solvent; values of $\left(\frac{m_{feed}}{\eta_{liquid}} \right)_{max}$ obtained with paraffin as the solvent were lower than those of undiluted Alamine 336 and Exxal 13 (see Reference 14).

precipitate dissolved when the pH of the strip phase was decreased to 2; however, when the pH was subsequently increased, the material precipitated again at 3.5. The white powder obtained from the strip phase by filtration at pH = 8 was analyzed by X-ray diffraction and found to be largely amorphous. The diffraction pattern showed some small peaks corresponding to Na_3AlF_6 , but no further analysis could be made. The precipitate most likely also consisted of amorphous $\text{Al}(\text{OH})_3$, which cannot be identified with X-ray diffraction. The filtrate still contained a small amount of precipitate that did not redissolve by increasing the pH above 8. This should have happened if the precipitate that remained in the filtrate was $\text{Al}(\text{OH})_3$ or Na_3AlF_6 . In addition to $\text{Al}(\text{OH})_3$ and a small amount of Na_3AlF_6 , the precipitate in the bulk of the strip phase thus also contained a third (unknown) component. If KOH is used as hydroxide in the strip phase, the potassium analog of Na_3AlF_6 is formed: K_3AlF_6 .

Precipitation (see, for example, Figures 4 and 5) is undesirable since it reduces the membrane area available for aluminum transport and decreases the fluxes. The uncontrolled nucleation and growth of the precipitate caused a spread in fluxes by roughly a factor of 2. In principle, the decreasing membrane area should be incorporated in Equation (9); however, since this decrease cannot be quantified, A_{membrane} is taken to be constant. How much time it takes for the aluminum-rich precipitate to totally block the transport of aluminum also depends on the flux; at smaller fluxes, the precipitation rate will be lower, since aluminum has to be transported to the liquid membrane first in order to precipitate.

To prevent or slow down the precipitation process, the chemical properties of $\text{Al}(\text{OH})_3$ and Na_3AlF_6 have to be considered. The $\text{Al}(\text{OH})_3$ is amphoteric and is soluble in acidic and alkaline solutions but insoluble in neutral or near-neutral solutions; Na_3AlF_6 is insoluble in acidic solutions, only slightly soluble in water, and decomposes in highly alkaline solutions.¹⁹ A strip phase with an alkalinity above pH = 8 is, therefore, expected to reduce the amount of precipitation. This was tested in experiments 3 and 6 at $\text{pH}_{\text{strip}} = 13$. These two experiments showed precipitation only on the liquid membrane surface, so increasing the alkalinity of the stripping pH reduced precipitation in the bulk of the strip phase but did not prevent precipitation on the liquid membrane surface. Probably, the pH at the liquid membrane surface was still neutral, which resulted in the precipitation of $\text{Al}(\text{OH})_3$. In addition, a large surface area such as the liquid membrane facilitates heterogeneous nucleation once supersaturation is achieved.

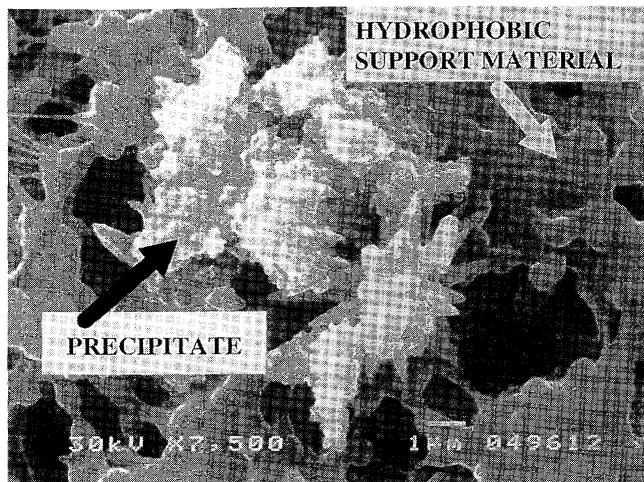


FIGURE 4. SEM view of the feed side of the liquid membrane surface after experiment 2, showing the white precipitate.

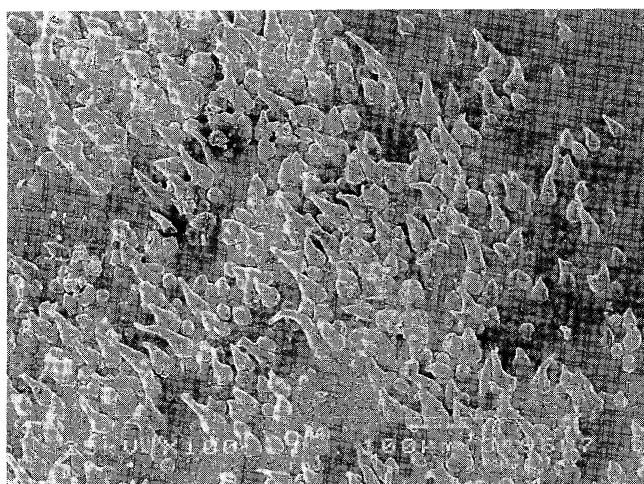


FIGURE 5. SEM view of the strip side of the liquid membrane surface after experiment 2. The entire surface of the liquid membrane is covered with the white precipitate.

Another factor that has to be evaluated in order to decrease the extent of precipitation on the liquid membrane surface is the aggregation of the extractant taking place. If excessive aggregation occurs, a semisolid is formed. This semisolid can block the pores of the liquid membrane support material as well as the surface of the liquid membrane. The precipitate on the surface of the liquid membrane is probably a combination of the precipitate formed in the bulk of the strip phase and of a semisolid formed as the result of excessive aggregation in the membrane phase.

The amount of aggregation can be decreased by adding a modifier to the membrane phase. This was tested in experiments 2, 3, 8, and 10 (see Tables 1 and 2). In all four experiments, precipitation took place on the liquid membrane surface. Even when the modifier was added to the membrane phase and the pH of the strip phase was increased to 13, as in experiment 3, precipitation still took place on the surface of the liquid membrane.

Precipitation of a white solid also occurred in several shake tests with the basic extractants. The precipitate appeared in the feed phase and/or in the membrane phase. This precipitation could be caused by excessive aggregation of the extractants, resulting in the formation of a semisolid. The precipitate present in the feed phase could consist of Al(OH)_3 , caused by an increase in the pH of the feed phase to near-neutral values. Precipitation did not take place in the shake tests with the acidic extractants; however, since it only took place to a limited extent with Alamine 308 and Alamine 336 and these extractants showed a much greater affinity for aluminum than did the acidic extractants, Alamine 308 and Alamine 336 were still chosen for further study here.¹⁴

Experiments with Alamine 308

Table 1 shows the conditions of the experiments performed with Alamine 308. All of these experiments were conducted near $\left(\frac{m_{feed}}{\eta_{liquid}} \right)_{max}$. As the concentration decrease in the feed phase was too small to be detected, only changes in the strip phase were evaluated (see Figure 6). In each experiment, phosphorus was coextracted in an approximately constant aluminum:phosphorus (Al:P) ratio; therefore, the phosphorus concentration in the strip phase is not shown in Figure 6. Table 3 shows the Al:P ratios and the aluminum fluxes. $J_{typical}$ is approximately the average aluminum flux during the

TABLE 3. RESULTS OF FSSLM EXPERIMENTS WITH ALAMINE 308

Exp.	Alamine 308 (M)	Modifier (g/L)	Strip-phase pH	J_{typical} [10^{-6} mol/(m ² ·s)]	Range of J [10^{-6} mol/(m ² ·s)]	$\left(\frac{[Al]}{[P]}\right)_{\text{strip}}$
1	0.9	0	8.0	2.0	-0.38-5.0	0.32
2	1.0	50	8.0	30	-4.2-52	0.71
3	1.0	50	13.0	4.0	-4.6-12	1.1

time period in which the transport of aluminum takes place. The range of J is given as well.

$$\text{The selectivity of the extraction is defined as } S = \left(\frac{[Al]}{[P]}\right)_{\text{strip}} \bigg/ \left(\frac{[Al]}{[P]}\right)_{\text{feed}}$$

For the pickling liquid used, $\left(\frac{[Al]}{[P]}\right)_{\text{feed}} = 0.73$. An S value higher than 1 indicates that at the given experimental conditions, the strip phase will be enriched with Al compared with the feed phase. For S values lower than 1, the strip phase will be enriched with P. For the experiments conducted with Alamine 308, S ranged from 0.44 to 1.5. This means that the strip phase could be enriched in Al, using Alamine 308 under the experimental conditions where $S = 1.5$. The selectivities are, however, not very high. This is probably due to excess acid extraction and/or the extraction of complexes consisting of both Al and P. Cotransport of P is a problem that can be resolved by adding H_3PO_4 to the pickling bath liquid.

In experiments 1-3, the focus was on the extent to which the addition of the modifier Exxal 13 to the membrane phase and also the strip-phase alkalinity influence the transport rate and the selectivity of extraction. Experiment 1 was taken as the standard, although its temperature was 25°C instead of 20°C. The amount of modifier added to the membrane phases in experiments 2 and 3 was equal to that used in each of the earlier shake tests.¹⁴

Figure 6 shows the Al concentration as a function of time for the strip phase. By adding the modifier, the Al flux was increased 15 times (compare experiments 1 and 2). The subsequent increase of pH_{strip} from 8 to 13 (experiment 3) led to a 7.5 times lower Al

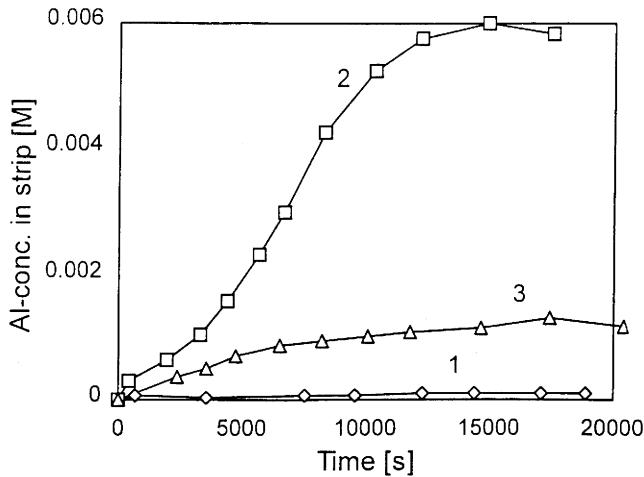


FIGURE 6. Aluminum concentration versus time in the strip phases of experiments 1, 2, and 3, carried out with Alamine 308. Experiment 1 (diamonds): no modifier, $\text{pH}_{\text{strip}} = 8$; experiment 2 (squares): with modifier, $\text{pH}_{\text{strip}} = 8$; experiment 3 (triangles): with modifier, $\text{pH}_{\text{strip}} = 13$;

flux, but the flux was still higher than that in experiments without a modifier (experiment 1). Figure 6 also shows that Al transport stopped in experiment 2 after approximately 15 ks, while transport kept taking place in both experiments 1 and 3. Because the fluxes were much lower in experiments 1 and 3 as compared with experiment 2, the precipitation rate was much lower as well and the Al transport continued after 15 ks.

The S values were 0.44 and 0.97 in experiments 1 and 2, respectively, which means that the modifier more than doubled the selectivity. Increasing the pH_{strip} from 8 to 13 increased the selectivity further by a factor of 1.5.

Experiments with Alamine 336

Table 2 shows the conditions of the experiments carried out with Alamine 336 at 20°C. Experiments 4–8 were performed near $\left(\frac{m_{\text{feed}}}{\eta_{\text{liquida}}} \right)_{\text{max}}$. The concentration decrease in the feed phase was, again, too small to be detected, and only changes in the strip phase were evaluated. Alamine 36 coextracted P with Al in an approximately

constant Al: P ratio in each experiment; these ratios are given in Table 4. This table also gives $J_{typical}$ values and the range of J . The selectivities were approximately the same as those with Alamine 308; S ranged from 0.59 to 1.5. The low values for the selectivity are probably due to excess acid extraction and/or the extraction of complexes consisting of both Al and P. The triplicate experiments 4, 5, and 7 were performed at the standard experimental conditions for Alamine 336.

Reproducibility of the FSSLM Experiments

Figure 7 shows the Al concentration-versus-time curves for the strip phases of the triplicate experiments 4, 5, and 7. This figure clearly indicates that Al reached a different concentration in each of the three experiments. The difference in Al concentrations was roughly a factor of 2, which is more than the analytical error of 5%. The transport rates $J_{typical}$ roughly differed by a factor of 2 as well. However, considering the fact that precipitation took place and that this had a profound effect on the transport rate, the reproducibility of the FSSLM experiments is quite acceptable. In all three experiments, the Al transport stopped after approximately 15 ks.

Because the results of these experiments do not coincide, the results of experiment 5 were chosen for comparison with those of experiments 6, 8, 9, and 10.

Influence of the Strip Phase

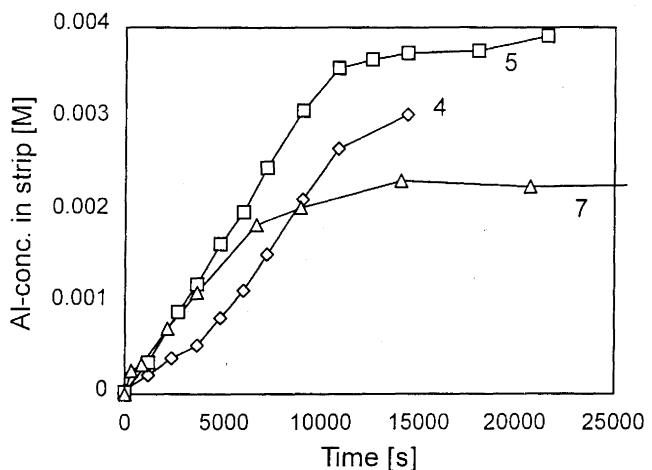
Figure 8 shows the Al concentration versus time for the strip phases of experiments 5 and 6. This figure clearly shows that increasing the pH of the strip phase from 8 to 13 and using KOH instead of NaOH (experiment 6) decreased the Al concentration by about one-half in the same period of time. The Al flux decreased by a factor of 3. The Al transport, however, continued after it had already stopped in experiment 5. Changing the strip phase did not have any influence on the selectivity of the extraction: $S = 1.4$ for experiment 5 and $S = 1.5$ for experiment 6.

Influence of the Modifier

In experiment 8, the modifier Exxal 13 was added to the membrane phase in order to decrease the amount of aggregation taking place and thereby increase the transport rate. The amount of Exxal 13 added was equal to the amount used in earlier shake tests.¹⁴ The

TABLE 4. RESULTS OF FSSLM EXPERIMENTS WITH ALAMINE 336

Exp.	Alamine 336 (M)	Modifier (g/L)	Strip-phase pH	J_{typical} [10^{-6} mol/(m ² ·s)]	Range of J [10^{-6} mol/(m ² ·s)]	$\left(\frac{[AI]}{[P]}\right)_{\text{strip}}$
4	1.19	0	8.0	16	0-23	0.94
5	1.19	0	8.0	18	0-28	1.1
6	1.19	0	13.0, KOH	6.5	0-14	1.1
7	1.19	0	8.0	12	0-57	0.86
8	1.0	50	8.0	15	-2.5-35	1.0
9	2.07	0	8.0	1.4	-2.5-7.8	0.50
10 ^a	0.96	50	8.0	1.4	-0.33-3.1	1.7

^aCarried out with paraffin as solvent.FIGURE 7. Aluminum concentration versus time in the strip phases of the triplicate experiments 4, 5, and 7, carried out with Alamine 336. Experiment 4 (diamonds), experiment 5 (squares), and experiment 7 (triangles): no modifier, $\text{pH}_{\text{strip}} = 8$.

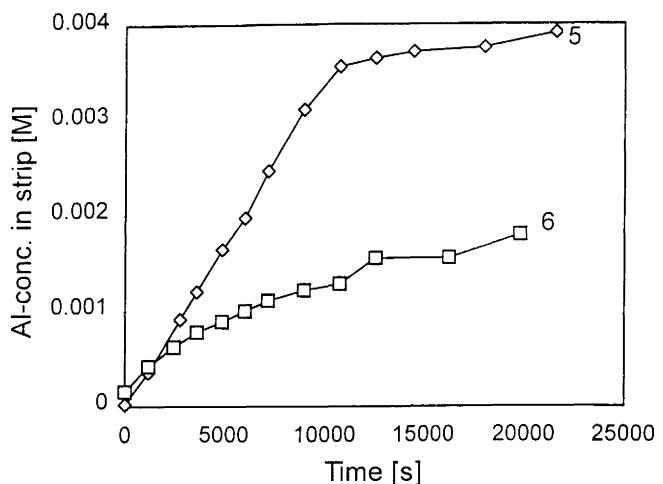


FIGURE 8. Aluminum concentration versus time in the strip phases of experiments 5 and 6, carried out with Alamine 336. Experiment 5 (diamonds): no modifier, $\text{pH}_{\text{strip}} = 8$; experiment 6 (squares): no modifier, $\text{pH}_{\text{strip}} = 13$ (KOH).

Alamine 336 concentration was slightly different from the standard condition, but this difference was only minor.

Figure 9 shows the Al concentrations in the strip phases for experiment 5 and 8. In both experiments, the transport of Al stopped after approximately 15 ks. The figure demonstrates that the Al concentrations varied in exactly the same manner over time, which shows that the addition of the modifier had no influence on the extraction or the precipitation. The values of J_{typical} confirm this conclusion. The addition of the modifier also had no influence on the selectivity of the extraction, as each experiment had an S value of 1.4.

Influence of the Solvent Kerosene

To test the influence of the solvent kerosene, the membrane phase consisted only of Alamine 336 in experiment 9. Figure 10 shows the Al concentration in the strip phase for experiments 5 and 9. Without kerosene, Al reached a concentration lower by a factor of 4 in the strip phase in 20 ks. In the absence of kerosene as solvent, the Al flux

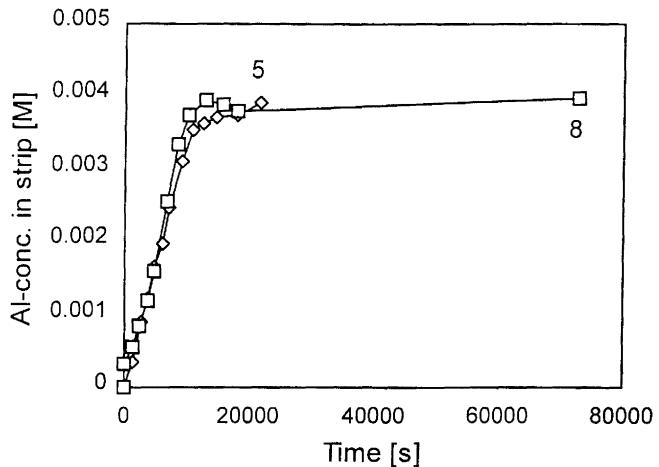


FIGURE 9. Aluminum concentration versus time in the strip phases of experiments 5 and 8, carried out with Alamine 336. Experiment 5 (diamonds): no modifier, $\text{pH}_{\text{strip}} = 8$; experiment 8 (squares): with modifier, $\text{pH}_{\text{strip}} = 8$.

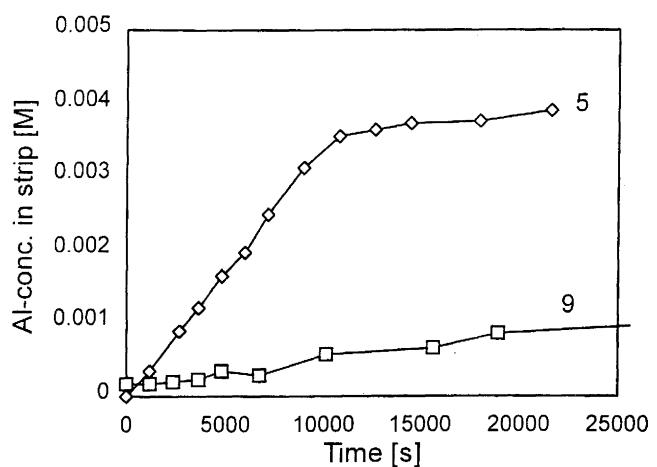


FIGURE 10. Aluminum concentration versus time in the strip phases of experiments 5 and 9, carried out with Alamine 336. Experiment 5 (diamonds): 1.19 M Alamine 336, no modifier, $\text{pH}_{\text{strip}} = 8$; experiment 9 (squares): undiluted Alamine 336 (2.07 M), no modifier, $\text{pH}_{\text{strip}} = 8$.

decreased by more than a factor of 10. This can be expected since a higher extractant concentration leads to increased aggregation and thus lowers the Al flux. The selectivity also decreased significantly; S decreased from 1.4 (with kerosene) to 0.68 (without kerosene).

Paraffin Compared with Kerosene as a Solvent

In experiment 10, paraffin was tested as a solvent. Paraffin is a mixture of linear alkanes and is very nonpolar. To compare paraffin as a solvent with kerosene, the conditions chosen for this experiment were similar to those used in experiment 8. In Figure 11, the Al concentrations in the strip phase are compared for experiments 8 and 10. As shown, Al reached a concentration twice as low with paraffin (experiment 10) as with kerosene (experiment 8). However, Al transport proceeded for a longer period with paraffin; it stopped after 15 ks in the case of kerosene and after roughly 60 ks in the case of paraffin. Using paraffin as a solvent decreased J_{typical} by a factor of 10. The selectivity dropped as well: S = 1.4 for kerosene and S = 0.59 for paraffin.

Kerosene is a much better solvent than paraffin for the extraction of Al with Alamine 336. The nonpolar paraffin has great difficulty in solvating the metal-extractant complex. The *n*-alkanes present in paraffin have no solvating power, while the naphthenic components in kerosene have solvating power due to the presence of phenyl groups. For paraffin, this resulted in excessive aggregation and in a decrease in transport rate as compared with kerosene as a solvent.

CONCLUSIONS

Aluminum is removed from the pickling bath liquid with Alamine 308 or Alamine 336 as an extractant and kerosene as a solvent. Fluxes reached are typically 10^{-6} – 10^{-5} mol/(m²· s) and are the highest when the modifier Exxal 13 is added to the membrane phase and a stripping pH of 8 is used. Phosphorus is cotransported at roughly the same flux.

During the transport of aluminum, an Al(OH)₃-containing precipitate is formed on the liquid membrane surface and in the bulk of the strip phase. This precipitate continually decreases the flux, and eventually all transport stops. Increasing the alkalinity of the strip phase reduces precipitation in the bulk of the strip phase but cannot

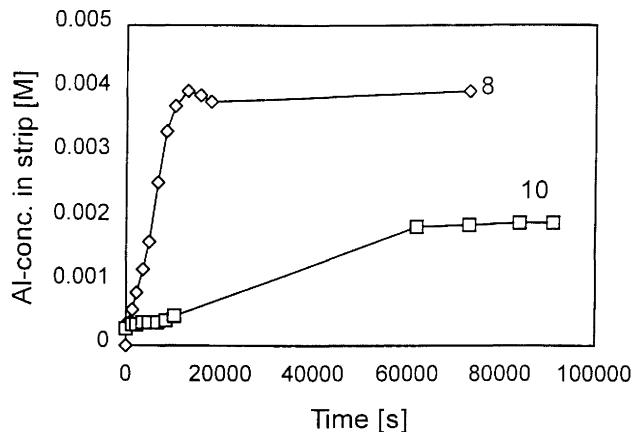


FIGURE 11. Aluminum concentration versus time in the strip phases of experiments 8 and 10, carried out with Alamine 336. Experiment 8 (diamonds): kerosene as solvent, with modifier, $\text{pH}_{\text{strip}} = 8$; experiment 10 (squares): paraffin as solvent, with modifier, $\text{pH}_{\text{strip}} = 8$.

prevent precipitation on the liquid membrane surface. Using an amine as the extractant with an alkaline strip phase is, therefore, not recommended for the removal of aluminum from the pickling bath liquid. However, SLMs can be successfully used for the selective removal of contaminants from bath liquids in the galvanic and chemical surface treatment industry if no precipitation occurs.

RECOMMENDATIONS

In order to prevent precipitation of $\text{Al}(\text{OH})_3$, an acidic strip phase should be used. This will be possible if acidic or neutral extractants are applied; therefore, these types of extractants should be investigated in the future.

If SLMs are used for the selective removal of a contaminant, care should be taken to avoid solubility problems such as the one encountered in the study discussed in this paper.

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