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TECHNICAL NOTE

Concentration and purification of wet industrial phosphoric acid by electro-electrodialysis

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1. Introduction

Wet phosphoric acid (WPA) produced by sulfuric acid leaching [1, 2] contains a wide range of mineral impurities (e.g., Fe, Al, Mg) which constitute part of the phosphate ore. When acid is reconcentrated with classical techniques such as evaporation, colloidal suspensions and complex salts are formed between phosphates, fluorosilicates anions and the cations previously cited. These insoluble complexes increase the acid viscosity and give rise to mud formation during stocking [3]. In industrial processes some methods such as precipitation [3], solvent extraction [4] and ion exchange resins [5] are used to remove metallic impurities. In this investigation electro-electrodialysis is used as an alternative method to generate purified and concentrated phosphoric acid.

Electro-electrodialysis (EED) is a separation technique involving the perm-selectivity of an ion exchange membrane. The electro-electrodialyser is divided into two compartments by means of an anion exchange membrane (AEM). The wet phosphoric acid to be treated, flows into the cathodic compartment in which the impurities can be retained. On the anodic side, phosphoric acid is formed with the anions crossing through the AEM and protons produced by the anodic water oxidation which permits an increase in the concentration of the acid.

Previous work has shown that the most important phenomenon limiting the current efficiency during the concentration process of sulfuric acid is proton leakage through the AEM membranes [6–8]. In the case of phosphoric acid we have selected two perfluorinated membranes because of their different grafted exchange sites: ARA 17/10 from Solvay (France) grafted with vinylpyridine and RAI 5035 from Raipore (USA) grafted with vinylbenzylamine.

In this work EED is used to study the concentration and purification of wet phosphoric acid produced in Annaba (Algeria). The concentration of this phosphoric acid is 4.11 M. The magnesium, iron, and aluminium concentration are 10, 1.8 and 1.4 g dm^{-3}, respectively.

2. Experimental details

The electro-electrodialyser comprised two Plexiglas half cells separated by an anion exchange membrane. The membrane area was 13.7 cm^2. The 2 mm thick and 16 cm^2 area rectangular titanium electrodes were platinum coated. The flow was maintained in the compartments with a two channel peristaltic pump at 4.5 dm^3 h^{-1}. The EED system was tested at ambient temperature. The constant current was supplied by a Lambda Electronic LQ 534/W generator.

2.1. *Transport number measurement*

The catholyte volume was 100 cm^3 and the anolyte volume 1000 cm^3. The larger volume on the anodic side leads to a practically constant concentration value. The tested membranes were ARA 17/10 and RAI 5035. The initial concentration of phosphoric acid (Merck) in the cathodic side was 4.05 M. A constant current density of 60 mA cm^{-2} was applied for 90 min. The H_3PO_4 concentration in the cathodic compartment was titrated before and after the electro-electrodialysis. To quantify the permeability of the membrane to $H_2PO_4^-$, the transport number is defined by the following equation:

$$t = \frac{(C_i^c V_i^c - C_f^c V_f^c)F}{Q} \qquad (1)$$

where C_i^c and C_f^c are the cathodic compartment phosphoric acid initial and final molarities respectively. V^c is the volume of the catholyte; Q is the total electrical charge transferred and F is the Faraday constant. For this calculation the first dissociation was only taken into account because the two compartments remain acidic during experiment with H_3PO_4 and $H_2PO_4^-$ as predominant species. The 3 pK_a values of the three acidities are 2.2, 7.2 and 12.3 [9]. During these experiments no noticeable volume variation was recorded.

2.2. *Concentration and purification of phosphoric acid*

For concentration and purification 500 cm^3 of filtrated industrial acid at 4.11 M were poured into the catholyte and 100 cm^3 of pure phosphoric acid 1 M into the anolyte compartment. During electro-electrodialysis, small samples of solution (0.5 or 1 ml) were withdrawn from the anolyte compartment at regular intervals. The concentration of acid and metals in the anodic side were determined respectively

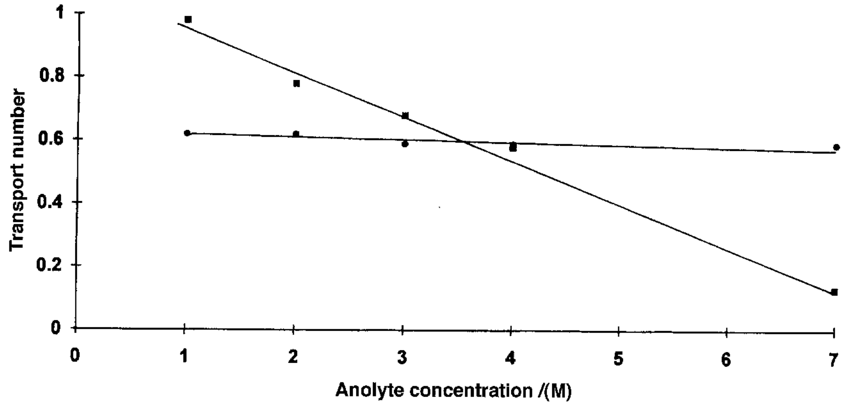

Fig. 1. Variation of transport number of $H_2PO_4^-$ against the molarity of H_3PO_4. Key: (●) ARA membrane; (□) RAI 5035 membrane.

by acid titration and atomic absorption. During these experiments a constant current density of 80 mA cm^{-2} was applied and no noticeable volume variation was recorded.

3. Results and discussion

3.1. *Selection of membranes*

The value of the $H_2PO_4^-$ transport number determined under the standard conditions already mentioned were plotted as a function of H_3PO_4 concentration for the ARA and RAI 5035 membranes (Fig. 1). This Figure shows that the variation in the transport number decreases with the increasing anolyte concentration for RAI 5035 membrane and it remains practically constant for the ARA membrane.

The decrease in the transport number of RAI 5035 is related to proton leakage through the anion exchange membrane. Anion exchange membranes are not completely impermeable to protons and, consequently, some of these ions can be transferred from the anolyte to the catholyte compartment. An increase in the acid concentration of the anolyte leads to an increase in the proton leakage and, consequently, to a decrease in the transport number of $H_2PO_4^-$.

3.2. *Concentration and purification of wet phosphoric acid of Annaba (Algeria) with ARA membrane*

Figure 2 shows the results of EED measurements. The variation of phosphoric acid molarity in the anolyte compartment is plotted versus time. Starting from 1 M of pure phosphoric acid in the anolyte and wet phosphoric acid in the catholyte, we obtained a 4 M phosphoric acid after 26 h experiment. During the experiment no generation of colloidal suspensions or insoluble salts was observed.

The concentration of phosphoric acid (4 M) in the anolyte side was obtained with good yield (63%). The purification is very high (about 95%, see Table 1).

3.3. *Effect of ammonium in the anolyte for pure acid recovery*

The concentration of phosphoric acid by electro-electrodialysis is limited by proton leakage through the AEM. To reduce this phenomenon, NH_4^+ was introduced to the anolyte. It can be assumed that the NH_4^+ ions accumulated in the anodic face of the membrane reduce the transfer of H^+ through the AEM by electrostatic repulsion (Fig. 2). In this experiment, a 4 M concentration of phosphoric acid is obtained with a better current efficiency (74%) in anolyte compartment.

The presence of NH_4^+ in the anolyte compartment is

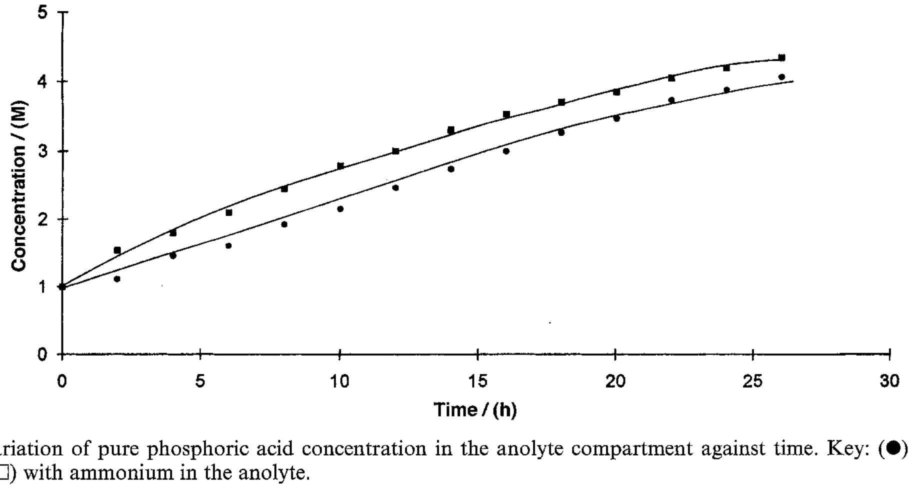

Fig. 2. Variation of pure phosphoric acid concentration in the anolyte compartment against time. Key: (●) without ammonium in the anolyte; (□) with ammonium in the anolyte.

Table 1. Elimination of metals from phosphoric acid

Element	*Initial concentration in the catholyte* /g dm^{-3}	*Concentration in the anolyte at 27 h* /g dm^{-3}	*Metal ion removal* /%
Mg	10	0.187	98.13
Fe	1.8	0.075	95.83
Al	1.4	0.000	100

not a penality for this process if the acid is destined for fertilizer production.

Conclusion

The concentration of phosphoric acid by electro-electrodialysis is limited by proton leakage through the AEM. Two membranes are studied RAI 5035 from RAIPORE (USA) and ARA from Solvay (France). With the ARA membrane, the concentrated phosphoric acid (4 M) was obtained with an interesting yield and a low concentration of metal impurities (Fe^{3+}, Al^{3+}, Mg^{2+}). The introduction of ammonium in the anolyte reduced the proton leakage and increased the current efficiency of the acid recovery.

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