

Research Article

Electrodialysis of Phosphates in Industrial-Grade Phosphoric Acid

J. J. Machorro,¹ J. C. Olvera,¹ A. Larios,¹ H. M. Hernández-Hernández,²
M. E. Alcantara-Garduño,³ and G. Orozco¹

¹ Centro de Investigación y Desarrollo Tecnológico en Electroquímica S.C. Parque, Tecnológico Querétaro, 76703 Sanfandila Pedro Escobedo, QRO, Mexico

² Universidad Tecnológica de Querétaro, 76148 Querétaro, QRO, Mexico

³ Universidad del Mar, Ciudad Universitaria, Puerto Ángel, 70902 Distrito de San Pedro Pochutla, OAX, Mexico

Correspondence should be addressed to G. Orozco; gorozco@cideteq.mx

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The objective of this research was to study the purification of industrial-grade phosphoric acid (P_2O_5) by conventional electro-dialysis. The experiments were conducted using a three-compartment cell with anion and cation membranes, and industrial acid solution was introduced into the central compartment. The elemental analysis of the diluted solution indicated that the composition of magnesium, phosphates, and sodium was reduced in the central compartment. The ratios of the concentration of the ions and the phosphates were essentially unchanged by the process. Consequently, electro-dialysis could not purify the acid in the central compartment, and the migration of phosphate ions to the anolyte produced a highly concentrated phosphoric acid solution containing sulfates and chlorides as impurities. However, the migration of the phosphate ions across the membrane consumed a large amount of energy. Detailed speciation diagrams were constructed in this study. These diagrams showed that metal-phosphate complexes were predominant in the industrial phosphoric acid solution. This result explains why the ratios of the concentrations of the ion metals and the phosphates did not change in the purification process. The energy consumed in the electro-dialysis indicated that the metal-phosphate complexes were less mobile than the free-phosphate ions. The speciation diagrams explained the experimental results satisfactorily.

1. Introduction

The annual global phosphorus consumption is approximately 20,764 million metric tons [1]. Phosphoric acid and phosphate salts have several applications. For example, phosphoric acid fuel cells use liquid phosphoric acid as an electrolyte [2, 3]. Industrial-grade phosphoric acid is produced from phosphate rock and consequently has a high content of mineral impurities, which lower the acid quality for commercial use. This industrial-grade phosphoric acid (52–54% P_2O_5) is also named as merchant-grade acid. Phosphoric acid purification is a major challenge, and a variety of methods have been used to eliminate the impurities in the industrial-grade phosphoric acid [4–18]. These methods which are described in the

literature are enumerated in Table 1. In addition, Table 2 shows electro-dialysis process for concentrating industrial-grade phosphoric acid [19–27]. These studies in Table 2 provided more comprehensive and consistent information on the energy requirements for the process. Comparing these methods is very difficult for the following reasons: (a) there is a wide variation in the types of the impurities in industrial-grade acid because ores of similar grades can originate from different mines; (b) consequently, the studies investigated different metal impurities; (c) the studies were neither consisted nor complete in their description of the acid purity; and (d) the studies used dissimilar efficiency criteria. Therefore, the methods described in Table 1 cannot be ranked in terms of their relative efficacies. Nonetheless,

TABLE I: Studies of industrial-grade phosphoric acid purification.

Process	Efficiency/energy requirements/power consumption (kWh/kg)	Reference
Selective precipitation	63% of Pb and As was precipitated from the phosphate solution. Purification was carried out at 49°C	[4]
Selective precipitation	Mg was removed by mixing the crude acid with SiF_6^{2-} to form $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$. Also, 25% Fe and 10% Al were removed. Filtrate had 0.37–0.51% of MgO in 72% P_2O_5 . The temperatures range was 20 to 30°C	[5]
Selective precipitation	Ammonia was added to crude acid. Iron precipitates as $\text{Fe}_3(\text{K}, \text{NH}_4)\text{H}_8(\text{PO}_4)_6 \cdot \text{H}_2\text{O}$. The concentrations of Al, Fe, and Mg were decreased by ten times their initial values. The process was continued for 8 h at 70°C	[6]
Solvent extraction	The purified acid contained between 50 and 60% phosphate and approximately 1% SO_4^- and 0.2% F^- . The concentration of the cation impurities was approximately 0.2%. Crude phosphoric acid (P_2O_5 52%) was fed at rate of 19.1 mL/min at temperature of 65°C. The process produced 37.5% phosphoric acid, and the impurities were extracted by solvent extraction at 110°C	[7]
Solvent extraction	The process removed approximately 95% of Cd after 260 h of operation. The method used three hydraulic pumps, an extraction module (1.4 m ²), and a back-extraction module at pressure of 4 psi	[8]
Flotation and selective precipitation	95% of the Cd and metals impurities (M^{n+}) were removed by neutralizing the solution to pH 1.4–2.0 and cooling it to 5–40°C. The metals were precipitated as metal xanthates (<i>MXan</i>). The xanthate having the longest and most branched organic part produced the best results	[9]
Nanofiltration by membranes	The filtering process operated at a temperature of approximately –1°C to about 30°C and at a pressure between 600 and 1000 psig. The feed solution was filtered through a nanofiltration membrane to remove approximately 90% of the metal ion impurities	[10]
Solvent extraction	Resin impregnated with extractants was put into contact with phosphoric acid for 24 h using a reciprocal shaker (150 rpm) at 25°C. Solvent extraction removed approximately 90% of the Cd from concentrated phosphoric acid solutions. The presence of cations strongly decreased the Cd removal efficiency.	[11]
Reverse osmosis and nanofiltration	Nanofiltration was more efficient than reverse osmosis. The permeate flow was 13.5 L/m ² h at 1800 psi. The acid permeation was 46.3%, and 99.3% of the cationic impurities were globally rejected. The concentration of the impurities was reduced by approximately 100 times the initial value. However, the acid concentration was reduced to half its original value.	[12]
Selective precipitation	This method produced an acid solution with an As concentration of less than 1 ppm. The purification method produced P_2O_5 concentration of at least 72.4%. The temperatures range was 130 to 150°C. Examples of the method produced concentrations of impurities in industrial 84–85% phosphoric acid were as follows: Fe (0.2–1.6%), Cr (0.1–0.8%), Ni (0.1–0.6%), Mo (<0.5%), and Na (0.1%)	[13]
Nanofiltration by membranes	An 8 M acid solution was filtrated at 1000 psi for different periods of time. For periods longer than 120 h, the rejection of impurities decayed considerably. The acid permeation at 25°C was approximately 90% and the metal impurities' retention was approximately 97%	[14]
Solvent extraction	Phosphoric acid was purified using solvent mixtures at 30°C. The most efficient P_2O_5 recovery was obtained using 55% methyl isobutyl ketone and 45% tributyl phosphate. A phase diagram was created for the ternary system of H_3PO_4 -water-optimal phosphate solvent. The concentration of impurities decreased 1000 times from their initial values. Mg^{2+} purification was higher than that for the other impurities	[15]
Complex formation and zeolites as adsorbents	Bentonite and potassium amyl xanthate were used to remove organic impurities and Fe from crude phosphoric acid. The efficiency of potassium amyl xanthate in reducing the iron content was 79.19% and was accompanied by a small decrease in the P_2O_5 concentration. Bentonite clay was used to remove the organic impurities. Na_2SiO_3 and Na_2CO_3 reduced the F^- content at 70°C at a defluorination efficiency of 90.56%. The Fe content was reduced to 0.52% of its initial value at a P_2O_5 loss of 3%. Cd and Cu were removed at a P_2O_5 loss of 1.70%. The Fe minimizing efficiency was 10.95–52.38% at the temperatures of 25 to 70°C	[16]
Selective precipitation	Precipitation occurred at 60°C. The process produced 85% acid with 200 ppb of Sb. The impurities were removed by adding H_2S . However, the S_2^- content was 220 ppb	[17]
Solvent extraction	The phosphoric acid was purified using n-butanol, n-hexanol, and n-octanol. Octanol was the most efficient alcohol. The final concentration of H_3PO_4 was 9.2 M. 98% of F^- was removed and the final concentration of Fe was 10 ppm. The Cu, Cd, Mn, and Zn concentrations were too low to be determined. The temperature (5°C and 60°C) had a small effect	[18]

TABLE 2: Electrodialysis (ED) studies of industrial phosphoric purification (54% P₂O₅ or 74.5% H₃PO₄).

ED process characteristics	Energy	Reference
Phosphoric acid was concentrated using a combination of apatite Ca ₅ (PO ₄) ₃ (F, Cl, OH) digestion by sulfuric acid and aluminum production from alunite KAl ₃ (SO ₄) ₂ (OH) ₆ . The catholyte (H ₃ PO ₄) was separated from the middle compartment (K ₂ SO ₄) by a CEM, and the anolyte (water) was separated by AEM. The products were KH ₂ PO ₄ (catholyte), a diluted solution of K ₂ SO ₄ , and H ₂ SO ₄ (anolyte)	A cell voltage of 6 V and a current of 4.5 A were used. The current efficiency was approximately 96%. Electric power consumption was 1.27 kWh/Kg of P ₂ O ₅ at 2.5 weight % P ₂ O ₅	[19]
This method concentrated phosphoric acid by ED using membranes typically used to desalinate water. The stack assembly consisted of 20 cell pairs sandwiched between two electrode compartments. A CR-61 cation-transfer membrane and an AR-I03 anion-transfer membrane were used to concentrate the acid from 0.1 to 1.0 M by electrodialysis. The diluted compartment was fed with 0.10 M, 0.20 M, 0.29 M, and 0.45 M reagent-grade acid solutions and the compartment concentrate had 1 M of industrial-grade acid	The total effective membrane area was 2300 cm ² . The electrical currents applied were 8, 10, 12, and 14 A. The voltages varied from 10 to 43 V. This method concentrated reagent-grade H ₃ PO ₄ from 0.1 to 1.0 M. The energy requirements ranged from 1.73 to 2.50 kWh/Kg of P ₂ O ₅	[20]
A cell (13.3 cm ²) was divided into two compartments by an AEM. The cathode was graphite and the anode was platinized titanium. The volume of the catholyte (4.11 M industrial-grade acid, supplemented by ammonium ions) was 100 cm ³ and the volume of the anolyte (pure 1 M H ₃ PO ₄) was 1000 cm ³ . The impurities were retained in the catholyte compartment. In the anolyte compartment, H ₃ PO ₄ was formed with the anions crossing through the AEM and protons produced at the anode. AEM ARA 17/10 from Solvay (France) and RAI 5035 from Raipore (USA) were used	A constant current of 60 Am ⁻² was applied for 90 min. The acid concentration changed from 1 M to 4.11 M with a 63% of yield. A 4 M acid solution was obtained for a current efficiency of 74% in the anolyte compartment. Mg, Al, and Fe were removed at 95–100%. The efficiency was limited by the migration of protons across the anion membrane (proton leakage)	[21]
Cell with two compartments was divided by a membrane. The catholyte was industrial phosphoric acid 10 to 55% percent P ₂ O ₅ and anolyte was 1 to 40% P ₂ O ₅	The electrical current density ranges from 100 to 3000 (A/m ²)	[22]
An electrodeionization cell (36 cm ²) with a central compartment (industrial 11% P ₂ O ₅ or 15.2% H ₃ PO ₄) was delimited by AEM/textile membrane and CEM/textile membrane. Catholyte and anolyte were 2 M H ₃ PO ₄ solutions placed in the other compartments	Very low current efficiencies for both cations and anions were observed after 5 h of treatment. This method produced 11% phosphoric acid with low concentrations of impurities: Mg (1.4 gdm ⁻³), Fe (0.9 gdm ⁻³), Zn (0.4 gdm ⁻³), Cd (0.01 gdm ⁻³), and SO ₄ ²⁻ (16.5 gdm ⁻³). The highest current efficiency for cations was found for Mg ²⁺	[23]
Cell with liquid membrane of amyl alcohol with the addition of a trialkylamine. The catholyte was H ₃ PO ₄ 1.0 M and anolyte was H ₂ O. The cathode was made of stainless steel and anode was made of platinum or titanium coated with ruthenium dioxide	Extraction of phosphate ions from the starting solution was 95%	[24]
The raw material was H ₃ PO ₄ containing mainly calcium phosphate. A low concentration of acid was fed into alternate partition chambers formed cation transfer membranes. H ₃ PO ₄ was introduced on the anode sides of the partition chambers. Process is carried out under acidic conditions, avoiding precipitates of the impurities such as iron and aluminum	No data	[25]
Cells with a large number of anion and cation membranes were alternately arranged. Industrial phosphoric acid and diluted pure phosphoric acid (10–44% P ₂ O ₅) were supplied to the anode and to the cathode compartments, respectively	The current density was 100–2000 A/m ² . The energy requirement ranged from 3.95 to 15.78 kWh/Kg of P ₂ O ₅	[26]
Electro-electrodialysis with laboratory-scale cell. The cathode was graphite and the anode was platinized titanium. There were three compartments divided by anionic and cationic membranes. The industrial H ₃ PO ₄ was introduced into the central compartment	The cell voltage was 4 V and current of 10 A. A 28% H ₃ PO ₄ was removed from central compartment and impurities decrease. Also, Food-grade H ₃ PO ₄ at 25% was produced in anolyte after 21 h at 3-4 V and 11 A	[27]

AEM: anion-exchange membranes; CEM: cation-exchange membranes.

the studies of electrodialysis show that concentrated phosphoric acid with a low concentration of metal impurities can be obtained by electrodialysis; see Table 2.

Table 1 serves to display the great importance of the acid purification. Although a variety of problem-solving techniques have been identified, there are a limited number of studies with acceptable results. The production of food-grade phosphoric acid is a difficult business.

A significant factor for elucidating the purification process is the speciation of the metals in the concentrated acids. However, the studies presented in Tables 1 and 2 do not address this issue. Therefore, in this study, speciation diagrams were constructed to more thoroughly analyze the purification process.

The goal of this work is to evaluate the viability of electrodialysis for the production of high-value chemicals from raw materials that are abundant in the central region of Mexico and therefore these would be feasible resources for mass production. Other studies are also being conducted in our laboratory on a different highly pure raw material. The current study will serve as an important benchmark for our future research.

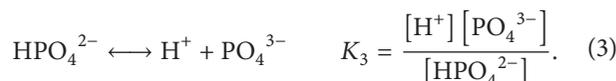
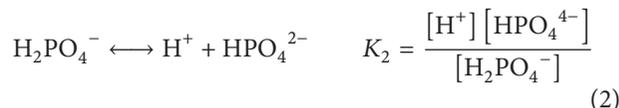
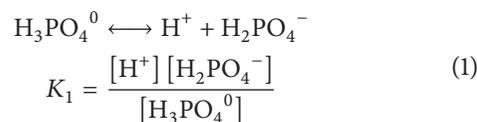
2. Materials and Methods

2.1. Materials and Reagents. Two samples of industrial-grade phosphoric acid (also called wet-industrial phosphoric acid) were obtained from Fertinal S. A. (Mexico). These raw materials were produced by the acid digestion of phosphate rock. Pure phosphoric acid 86% was purchased from J. T. Baker (ACS Grade). All other reagents were of analytical grade and were obtained from commercial sources and used without further purification. The high ionic strength of industrial phosphoric acid can produce a layer of precipitates of metal-phosphates, metal-sulfates, and so forth, on the membrane surface. Thus, a dilution solution of industrial acid at 5% w/w was used to prevent membrane fouling.

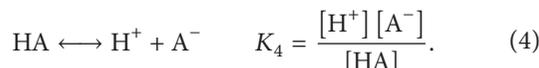
A trace element mineral analysis was performed by inductively coupled plasma mass spectrometry (Perkin Elmer, USA, model Optima 3300 DV) and by flame atomic absorption spectrophotometry (Perkin Elmer, USA, model AAnalyst 200). The presence of sulfate, fluoride, and phosphate was identified by UV-Vis spectrometry. Samples taken from a phosphoric acid production site were analyzed by potentiometric titration with a NaOH solution.

The membranes were purchased from Ameridia (the US representative of Tokuyama Corporation, Japan). The main characteristic of these membranes is their excellent exchange capacity (mequiv g⁻¹ of ion in the dry membrane form). An AMX-Neosepta anion exchange membrane was used with an exchange capacity of 1.25 mequiv g⁻¹. A CMX-Neosepta cation exchange membrane was used with an exchange capacity 1.62 mequiv g⁻¹. Neosepta-AMX contains quaternary ammonium groups as fixed charges, and Neosepta-CMX contains sulfonic acid groups as fixed charges [28]. These membranes were equilibrated with 1 M KCl solution for 12 h before each experiment.

2.2. Speciation Calculations. The speciation diagrams predict the value of α , the fraction of ions that are free or associated, at a given pH value. The dissociation equilibrium for the phosphate-containing species in the diagrams is given by



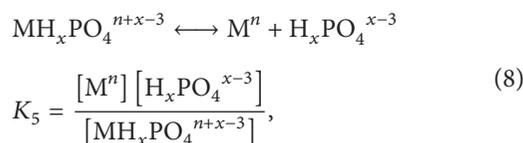
The HA acids were HF, HCl, and H₂SO₄, and the respective anions were F⁻, Cl⁻, HSO₄⁻, and SO₄²⁻. The general dissociation acid reaction is given by



Note that the silicon concentration is related to the fluoride concentration. That is, during industrial phosphoric acid production, fluoride is produced in the form of fluorosilicic acid. However, this acid and the SiF₆²⁻ ion dissociate into Si(HO)₄ and HF. The dissociation reactions are as follows:



Therefore, Si(HO)₄ and SiF₆²⁻ were also included in the speciation diagrams. In addition, 18 metal-phosphate complexes or ion-pairs, that is, NaHPO₄⁻, AlHPO₄⁺, and so forth, were included with their respective simple cations, that is, Na⁺, Al³⁺, and so forth. The general equation of the chemical equilibrium for the metal-phosphate complexes is



where x equals 1, 2, or 3, depending on the partial deprotonation of the phosphoric acid and n can vary between 1 and 3. Values derived from the literature [29–31] were used for the equilibrium constants K_1 to K_5 . The quantity α is defined by the following equation:

$$\alpha_A = \frac{[A]}{C_t}, \quad (9)$$

where $[A]$ is the concentration of species A and C_t is the total concentration of all the species that contain A. Material

balances must be formulated to determine the fraction α . The total quantities of the metal impurities (M_t), the acids (C_{H_nA}), and the phosphates (P_t) are fixed in a closed system; therefore, the following set of equations holds:

$$P_t = [\text{H}_3\text{PO}_4^0] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}], \quad (10)$$

$$M_t = [\text{M}^+] + [\text{MH}_2\text{PO}_4^0] + [\text{MHPO}_4^-] + [\text{MPO}_4^{2-}], \quad (11)$$

$$C_{H_nA} = [\text{H}_n\text{A}] + [\text{H}_{n-1}\text{A}^-] + \dots + [\text{A}^-]. \quad (12)$$

Equations (10), (11) or (12) can be combined with the equilibrium constants (1)–(5) and (8) and (9) to obtain a set of α -fractions as functions of $[\text{H}^+]$. The α -fraction for the $\text{H}_x\text{PO}_4^{x-3}$ species is defined by the following equation:

$$\begin{aligned} \alpha_{\text{H}_x\text{PO}_4^{x-3}} &= \frac{[\text{H}_x\text{PO}_4^{x-3}]}{P_t} \\ &= \frac{1}{[\text{H}^+]^n + [\text{H}^+]^{n-1}/K_1 + [\text{H}^+]^{n-2}/K_1K_2 + \dots}, \end{aligned} \quad (13)$$

where $[\text{H}^+]$ denotes the proton concentration which was related to the pH and K_n denotes the equilibrium constants K_1 to K_3 . The α -fractions of the metal-phosphate complexes were directly related to the α -fraction of $\text{H}_x\text{PO}_4^{x-3}$ species and their equilibrium constants; for example

$$\begin{aligned} \alpha_{\text{Ca}^{2+}} &= \frac{[\text{Ca}^{2+}]}{M_t} \\ &= 1 \times \left(1 + \frac{\alpha_{\text{P}_2\text{O}_4^{3-}}}{10^{-6.5}} + \frac{\alpha_{\text{HPO}_4^{2-}}}{10^{-2.7}} \right. \\ &\quad \left. + \frac{\alpha_{\text{H}_2\text{PO}_4^-}}{10^{-1.4}} \right)^{-1}. \end{aligned} \quad (14)$$

The speciation diagrams were calculated for solutions at 25°C and zero ionic strength. The ionic strength varied during the experiments; however, the equilibrium constants have been reported to depend weakly on the ionic strength (0.40/value) [32]. The temperature increased by 10°C during the experiments. However, only a small variation with temperature has been reported for the equilibrium constants for complex formation (0.045/deg) [32]. Thus, the concentration fractions in diagrams were representative of the actual values.

2.3. Experimental Apparatus. The system consisted of an electro dialysis cell from Asahi Glass Co., DS-0 (Japan), three storage tanks, three hydraulic pumps and a DC power source. The electrodes (each with an effective area of 0.02 m²) were made of titanium coated with platinum and stainless steel. The solution flowed through a plastic schedule 40 polyvinyl chloride pipe. Hydraulic pumps, propelled the electrolyte solution from the storage tank to the electro dialysis cell, through the pipe and back to the storage tanks. A bypass was introduced to control the flow rate (at 5 L/min) at each inlet.

TABLE 3: Average composition of two industrial phosphoric acid samples.

Species	Concentration	Milliequivalents of solute per liter
P ₂ O ₅	54% w/w	—
SO ₄ ²⁻	13.4480 g/L	(-) 274.0
CaO	8.4116 g/L	(+) 299.9
SiO ₂	18.0240 g/L	(SiO ₄ ⁴⁻) (-) 1199.9
Fe ₂ O ₃	7.9843 g/L	(+) 149.9
Al ₂ O ₃	8.1567 g/L	(+) 239.9
MgO	4.8364 g/L	(+) 239.9
Na ₂ O	3.0989 g/L	(+) 99.9
K ₂ O	3.7678 g/L	(+) 79.9
HF	3.4196 g/L	(-) 170.9
HCl	0.1773 g/L	(-) 93.7

The phosphoric acid concentration is typically expressed in terms of the P₂O₅ concentration. The conversion formula is as follows: $[\text{H}_3\text{PO}_4] = [\text{P}_2\text{O}_5] \times 196/142$. Thus, 54% P₂O₅ concentration corresponds to an acid concentration of 74.5%.

Figure 1 is a schematic of the experimental apparatus for phosphoric acid demineralization. The two membranes were separated by 1.5 mm, and the gap in the anolyte and the catholyte compartments was 2.25 mm.

Prior to each experiment, the three compartments were fed with a 0.01 M NaCl solution (for 30 min), which was replaced a posteriori with the respective solutions (for 30 min), and finally with fresh solutions for demineralization. The central compartment was filled with the solutions shown in Figure 1. Then, the central compartment contained a 0.1 M NaCl solution in 5% w/w analytical-grade phosphoric acid. Also, solutions of 5% w/w industrial-grade acid were introduced into the central compartment, and the behavior of the solutions was compared.

The current-voltage curves were obtained in a galvanodynamic mode, and the limiting current density was obtained from the electrical resistance (R) versus 1/electrical current (I) plots, as described by Sorensen [33]. The temperature, the conductivity, the flow rate, the electrical voltage, and the electrical current were measured during the experiments. More details of the apparatus are provided in our previous work [34]. The Toroidal Conductivity Sensor (Model 226, Rosemount Analytical, USA) was calibrated with KCl solutions. The experiments were performed in triplicate.

3. Results

3.1. Speciation Diagrams. The industrial-grade phosphoric acid was chemically analyzed for eleven components (see Table 3). The concentration of the impurities was 71.33 g/L, which was representative of the raw material produced by Fertinal (Mexico). The pH of the industrial phosphoric acid was approximately 1; consequently, the speciation diagrams (Figure 2) were concentrated in the acidic region.

During the manufacture of industrial-grade phosphoric acid by treating the rock with acids, fluoride was volatilized and lost in the residues and approximately 3 g/L of fluoride remains in the phosphoric acid. Figure 2(a) shows that

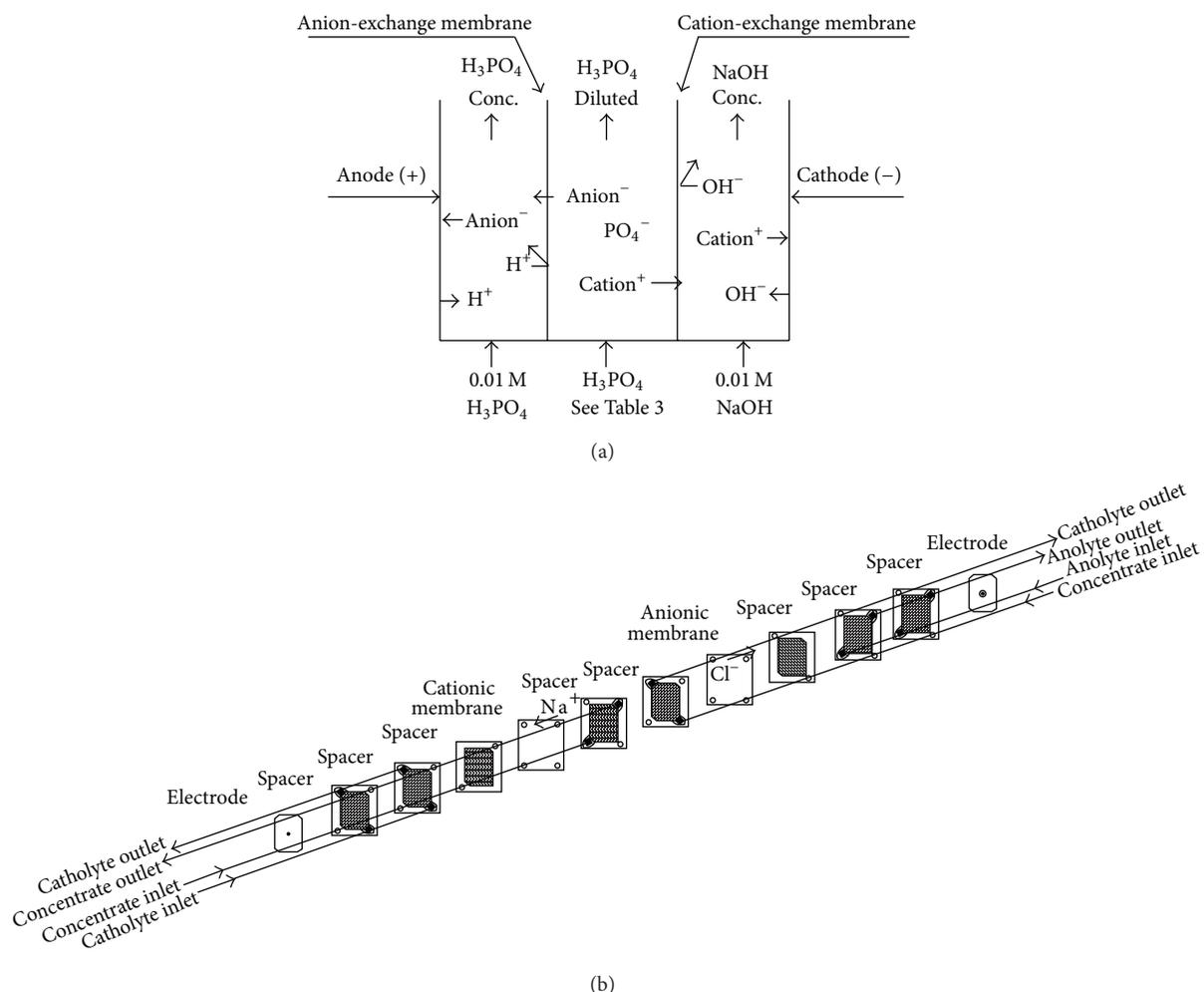


FIGURE 1: (a) Schematic of phosphoric acid demineralization apparatus, (b) classical electrodiolysis; cation-exchange and anion-exchange membranes, fed solutions and products.

hydrogen fluoride (HF) and siliceous acid $\text{Si}(\text{OH})_4$ were the predominant species in the industrial acid. The speciation diagrams show that electrodiolysis cannot be used to remove fluoride and silicon because the Coulombic attraction was lowered considerably. To be precise, electrodiolysis only can remove ionic impurities from industrial acid by using an electric current to pull these ions across the membrane. For HF and $\text{Si}(\text{OH})_4$, there is no net driving Coulombic force to produce a migration; that is, nonionic compounds did not migrate when an electric field was imposed. Figure 2(b) shows eight negatively charged species; however, only two ions (sulfates and chlorides) have high concentrations. Therefore, elevated migration can only be expected for these ions. Figure 2(c) shows the seven positively charged species in the pH region that was studied. However, only a few ionic species (K^+ , Na^+ , and Mg^{2+}) have high concentrations and consequently will migrate abundantly. Moreover, only about 40% of Ca^{2+} ions can migrate. Figures 2(d) and 2(e) predict that metal-phosphate complexes or ion-pairs, such as FeHPO_4^+ , can form for most metal impurities. Although included in the mathematical analysis, the amounts of the ion-pairs of

sodium or potassium were always negligible in our solutions, for example, NaPO_4^{2-} ; see Figure 2(f). Migneault and Forcé [35] and Pethybridge et al. [36] found lower ion-pair association constants of sodium or potassium.

These complexes or ion-pairs are essentially larger ions with lower effective electric charge density. The implication of this lower charge is an increase in the electrical resistance; to be precise, their positive charges allow the complexes to migrate near to the membrane, when electric field is applied across the cell. However, their large size prevents their passage abundantly through the membrane. Consequently, these charged molecules tend to accumulate on the dilute side of membrane and result in a buildup of membrane electrical resistance.

The industrial-grade phosphate had high concentration of phosphate and consequently the metal-phosphate complexes and ion-pairs were formed copiously. However, the studies presented in Table 1 did not address this issue because the speciation diagrams were not consulted. The implication of this is that studies cannot comprehensively analyze their purification process. On the other hand, the construction of

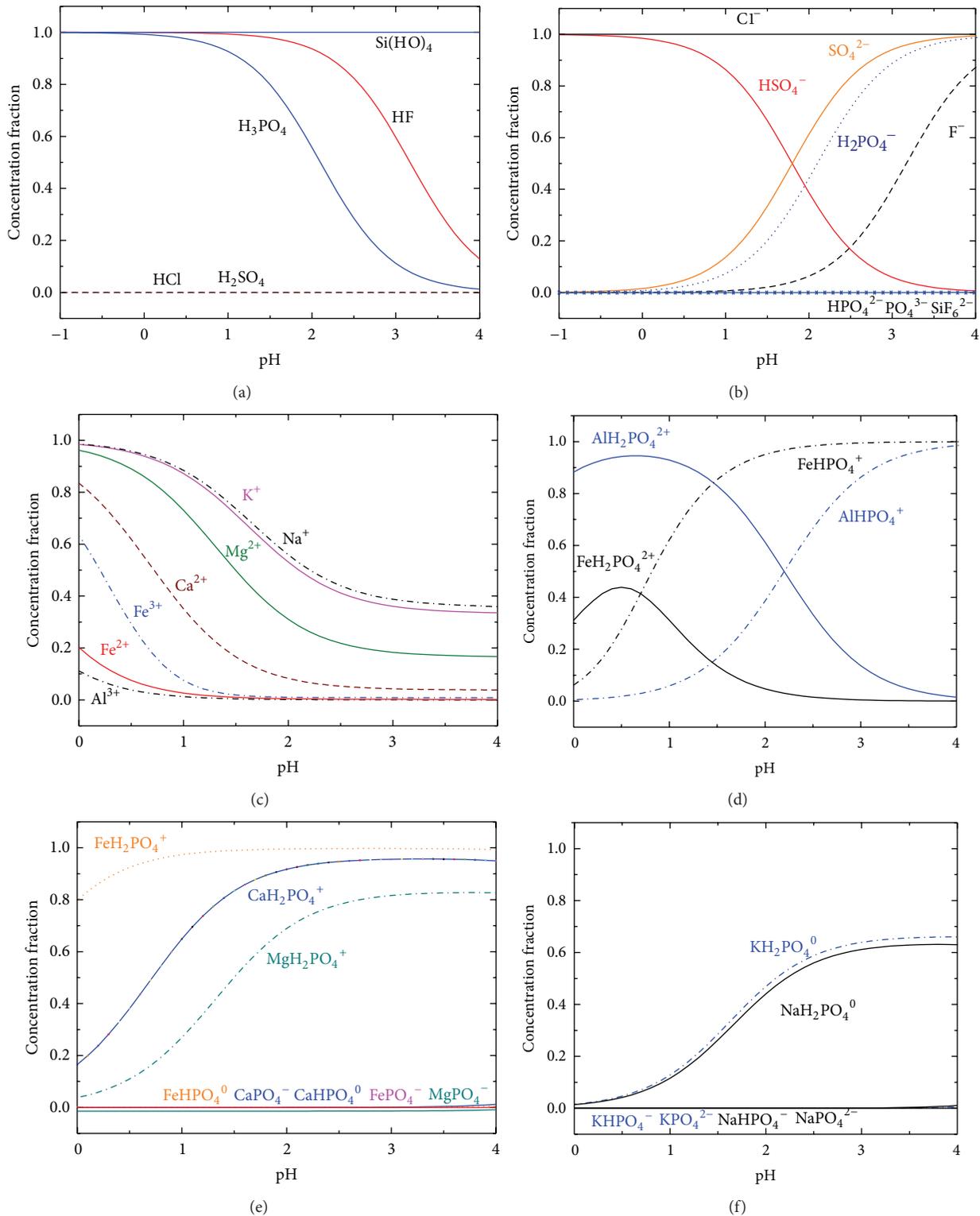


FIGURE 2: Speciation diagrams for (a) acids; (b) anions; (c) cations; (d) phosphate-metal (III) complexes; (e) phosphate-metal (II) complexes; and (f) phosphate-metal (I) complexes.

the speciation diagrams implied very time-consuming calculations. However, there are software can easily constructed the diagrams. For example MEDUSA with its thermodynamic constants database HYDRA [37] is able to draw the diagrams. The database HYDRA is incomplete for the metal-phosphate complexes and ion-pairs constant, but it is possible added data. The diagrams constructed using the software MEDUSA and our diagrams were compared. The results are not shown for the sake of brevity. The computational software can be applied to create efficiently the speciation diagrams.

Azaroual et al. [38] recently show preliminary results for quantifying the undesirable mineral impurities from phosphate ores using a computation tool (SCALE2000 software). However, it is not possible yet to compare the estimated diagrams of aqueous speciation of phosphoric acid.

Figure 3 shows that the conductance of the industrial phosphoric acid was higher than that of the analytical-grade acid. The low conductivity of the pure acid was because the H_2PO_4^- ion comprised only 6% of the phosphate concentration. However, the conductance of the industrial acid was related to the high ion concentration. The industrial phosphoric acid viscosity has also been reported to increase with the phosphoric acid concentration [39]. Note that pure H_3PO_4 consists of tetragonal groups that are linked by hydrogen bonds [40]. This structure results in a high viscosity fluid, especially at high phosphoric acid concentrations. The dimeric anion ($\text{H}_5\text{P}_2\text{O}_8^-$) has been found at high acid concentrations, but has not been observed in dilute solutions at room temperature [41, 42]. For solutions below 50% phosphoric acid, there are more bonds between the phosphate ions and water than between the phosphate ions themselves [40]. These larger anions pass scarcely through the positively charged anion exchange membrane. Therefore, electro dialysis was conducted in dilute acid solutions to prevent the formation of phosphate dimeric anions.

3.2. Limiting Current Densities. The limiting current densities (Table 4) were obtained from the current-potential curves (Figure 4). These limiting currents were obtained directly from plots of the electrical resistance versus the reciprocal of the electrical current (which are not shown for brevity), using a method that has been described elsewhere [33, 34]. The inflexion point in the curve for the solution of NaCl in the analytical-grade acid was produced at steady state; that is, the numbers of ions entering the membrane equaled the number of ions entering the diffusion zone. The limiting currents of the industrial-grade phosphoric acid were difficult to obtain, whereas the limiting currents of the analytical-grade acid solutions were straightforward to determine. In addition, the limiting current was also selected to avoid damage to the membrane. Therefore, the limiting current values for the solutions of NaCl in analytical-grade phosphoric acid were selected for the electro dialysis of the industrial-grade phosphoric acid. These current-potential behaviors were affected by the electrical resistance of the electro dialysis cell, which was given by the sum of the solution and membrane resistances. In addition, the formation of the polarization layers adjacent to both sides of the membranes produced a great contribution to the electrical resistance of the cell.

TABLE 4: Limiting currents of the experimental three-compartment electro dialysis cells; dilute, central compartment: experimental solution; anolyte: 0.01 M HCl; catholyte: 0.01 M NaOH.

Experimental solution	Limiting current (A)
Wet industrial phosphoric acid diluted at 5% (w/w)	indeterminate
Wet industrial phosphoric acid diluted at 1% (w/w)	indeterminate
Solution of 6.27 g/L of NaCl and 54% analytical-grade phosphoric acid diluted at 5% (w/w)	0.20
Solution of 1.254 g/L of NaCl and analytical-grade phosphoric acid diluted at 1% (w/w)	0.15

* 0.15 A was the average current level during the electro dialysis process.

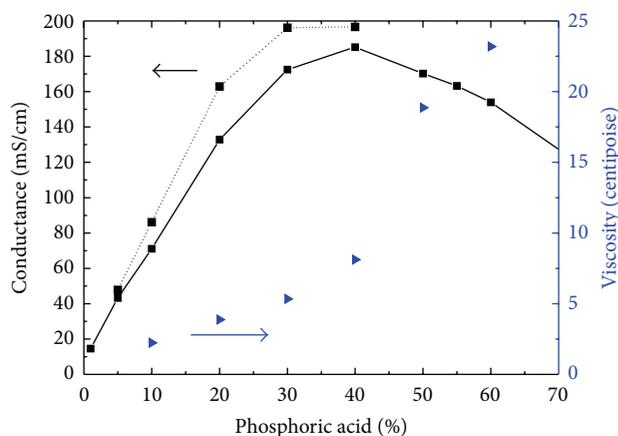


FIGURE 3: Conductance values for industrial phosphoric acid (---) and analytical-grade phosphoric acid (—); phosphoric acid viscosity data (►), as reported by Lobo [39].

The electrical resistances of the solution are discussed first. The solution of NaCl in the analytical-grade acid produced the highest electrical current. This behavior was observed because the sodium and chlorine ions were moving faster than the metal-phosphate complexes. More precisely, the motion of these ions was unimpeded by attachment to phosphates. Metals, such as aluminum, would have to drag their phosphate ligands along, resulting in a high electrical resistance for the complex. Similar results were obtained by Diallo et al. [43], who observed that the electrophoretic mobility of ions was proportional to the ion charge/size ratio. Diallo et al. [43] observed that ion mobility in an electric field range could be ranked in descending order as follows: $\text{Cl}^- > \text{H}_2\text{PO}_4^- > \text{H}_3\text{PO}_4^0 > \text{Fe}(\text{H}_2\text{PO}_4)_4^-$. Therefore, the complexes decreased the electrostatic interactions resulting in a low electrical current (Figure 4). The phosphate-free ions (see Figures 2(b) and 2(c)) had more mobility than the acids (Figure 2(a)) and the metal-phosphate complexes (Figure 2(d)). The membranes electrical resistances are discussed next. Pismenskaya et al. [44, 45] reported a low electrical conductivity for an anionic-exchange membrane in contact with a phosphate solution. Koter and Kultys [46]

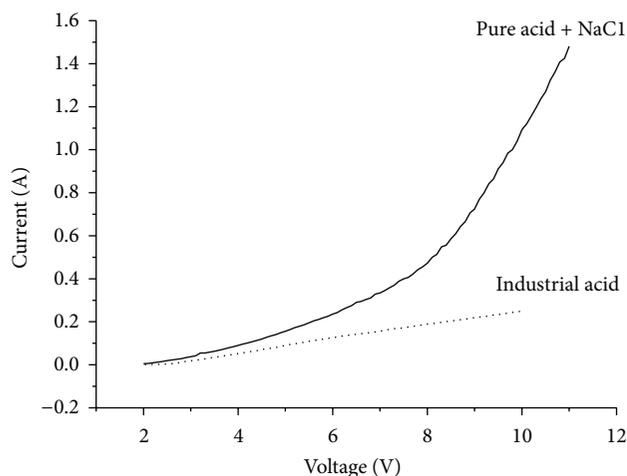


FIGURE 4: Current-potential curves for the electrodiagnosis cell at a flow rate of 5 L/min for industrial phosphoric acid (---) and analytical-grade phosphoric acid with 6.27 g/L NaCl (—).

observed a low efficiency for phosphoric acid removal by electrodiagnosis with anionic membranes. Koter and Kultys [46] theoretically calculated an association equilibrium constant between H_2PO_4^- and the fixed charges of the anionic membrane. This association diminished the efficacy of the separation process because the H_2PO_4^- neutralized the fixed charges in the anionic membrane. In a previous study, we observed a similar association between nitrate ions and the fixed charges in an anionic membrane using Raman spectroscopy and electrochemical impedance spectroscopy [34]. The excessive potential drop across the cation exchange membrane was because only the protons and the phosphate-free cations were able to migrate effectively. The metal-phosphate complexes had large ionic radii and low charge densities, which decreased their electrostatic interactions and mobilities inside the membrane. This increase of the electrical resistance was explained in Section 3.1. The speciation diagrams clearly show that most positive ions migrated with a very low efficiency because of their reduced ionic charge. However, proton transfer across the membrane increased at the highest electrical currents, depleting the proton concentrations inside the membrane. Therefore, the internal membrane resistance increased.

3.3. Demineralization of Industrial- and Analytical-Grade Acids. The conductance of the acids decreased during the electrodiagnosis process, as shown in Figure 5. The pH decreased slightly during the demineralization, while the temperature increased by 10°C. These changes did not alter the chemical composition of the solutions and the transport of ions was negligibly affected by the small temperature change.

Hannachi et al. [15] observed that the highest cation removal occurred for the Mg^{2+} species; see Table 1. This result is supported by the speciation diagrams (Figure 2), which clearly show that the Mg^{2+} and phosphate can migrate independently of each other. It is known that Mg^{2+} and phosphate do not form a covalent complex; for example, Raman

TABLE 5: Ion concentrations in the central compartment before and after demineralization for 450 min; the cell potential was approximately 7.4 V and the average electric current was 0.15 A.

Initial concentration		Final concentration	
MgO	H_3PO_4	MgO	H_3PO_4
0.0192 M	0.707 M	0.0072 M	0.206 M

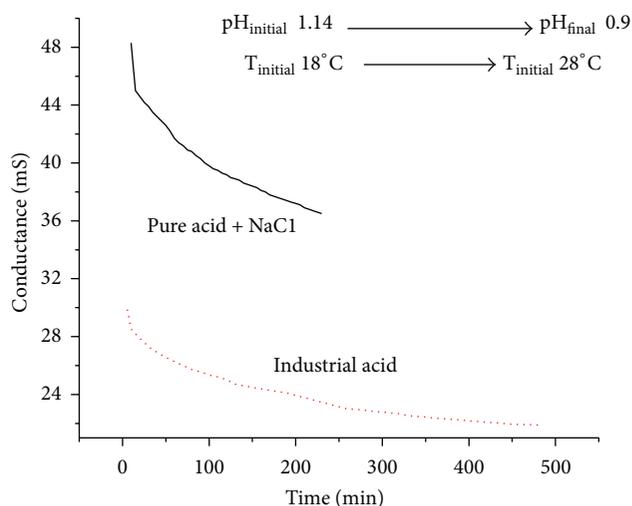


FIGURE 5: Variation in the conductance of the central compartment during electrodiagnosis; a constant electrical current of 0.15 A was applied to the conventional electrodiagnosis cell containing industrial phosphoric acid at 5% (—) and analytical-grade phosphoric acid at 5% with 6.27 g/L NaCl (---); the initial and final temperatures and pH values are also reported.

spectroscopy has been used to show that the intermolecular Mg–O–P bonding in phosphate salts is more ionic than for other metal–O–P bonds [47]. These ions were selected as a representative species to determine the electrodiagnosis efficiency. The initial and final concentrations of these species are listed in Table 5. The Mg^{2+} concentration decreased by approximately 63% on average of its initial value, whereas approximately 70% of the phosphates migrated, which was more than expected. However, the ratio between the concentration of the Mg^{2+} ions and that of the phosphoric acid was the same before and after the demineralization process (see Figure 6). The same behavior was observed for the ratio between the concentration of the Na^+ ions and that of the analytical-grade phosphoric acid. These results show that electrodiagnosis cannot be used to purify the acid in the central compartment. The migration of phosphates could produce a highly concentrated phosphoric acid solution in the anolyte; however, the sulfates and chlorides would also migrate. Consequently, electrodiagnosis would produce an anolyte solution containing anionic impurities. The low migration of free cations could be used to produce a catholyte containing cationic impurities.

The energy consumed in the migration of the Na^+ and Cl^- species was compared with the energy consumption for the electrodiagnosis of the industrial-grade acid (see Table 6).

TABLE 6: Energy consumption of the electro dialysis cell*.

Process characteristics	Energy
The central compartment contained a 0.1 M NaCl solution in 5% analytical-grade phosphoric acid. The cell current was constant at 0.2 A, and the average potential was 8.5 V. The NaCl was diluted from 6.27 g to 1.03 g and approximately 40% of the acid was removed	1.57 kWh/kg
The central compartment contained industrial-grade phosphoric acid. The cell current was constant at 0.2 A, and potential was approximately 8.8 V	7.8 kWh/kg
The concentration changes are reported in Table 5	

*The volume of the feed tank was 10 L. The flow rate was at 5 Lmin⁻¹; average temperature was 24 ± 2°C. The duration of the experiment was 230 min.

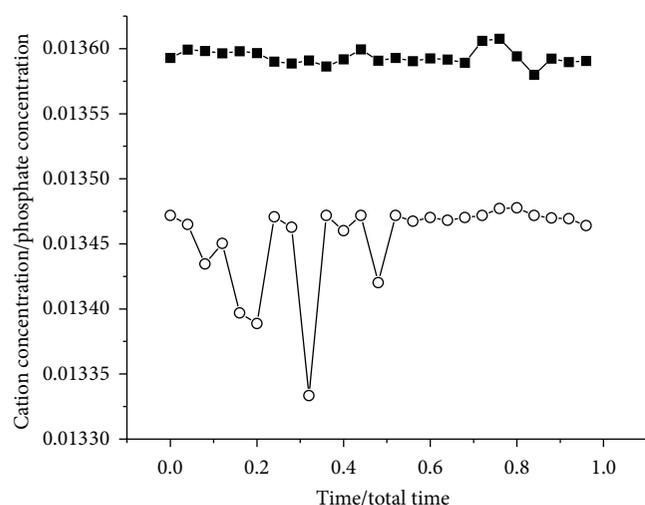


FIGURE 6: The ratio between the concentration of Mg²⁺ ions and that of H₃PO₄ acid (■-■-) and the ratio between the concentration of Na⁺ ions and that of H₃PO₄ acid (-o-o-) during the demineralization process.

The energy consumption for the migration of the Na⁺ and Cl⁻ ions was ten times more effective than the industrial-grade acid demineralization. That is, the energy consumed in Cl⁻ migration (1.57 kWh/kg) was lower than the energy consumed in H₂PO₄⁻ migration (7.8 kWh/kg). This result can be explained by the mass transfer limitations at low H₂PO₄⁻ concentrations. The discussion on the electrical resistances of the solution and the membrane, which was previously presented in Section 3.2, can also explain this result.

There is insufficient energy consumption data to compare the studies in Table 1 with the present study. On the other hand, the data in Table 6 show that electro dialysis produced phosphoric acid concentrations that were similar to those reported by the studies in Table 2. Hanley et al. [20] reported lower energy consumption, and this author also reported a higher acid concentration than that was observed in the present study; but did not report the final concentration of impurities; see Table 2.

The energy consumption for the Na⁺ and Cl⁻ migration showed that the membranes performed acceptably for electro dialysis; however, the energy consumption for the industrial-grade acid showed that phosphate ions could not migrate efficiently across the membranes.

4. Conclusions

Many methods have been evaluated in the literature for the purification and concentration of merchant-grade phosphoric acid (52% P₂O₅); see Table 1. However, these methods cannot be ranked in terms of efficacy because speciation diagrams have not been considered. The speciation diagrams in this study showed that the formation of metal-phosphate complexes decreased electrostatic interactions because of the lower mobility of the complexes. This observation was in fair agreement with the electro dialysis results. The speciation diagrams predicted that the low resistance of sodium and chloride ions relative to the other ions can facilitate phosphoric acid removal, which was verified by the observed energy consumption in the electro dialysis process. The results of the studies in Tables 1 and 2 must be reexamined in light of the speciation diagrams that were constructed in the present work. For example, Mg²⁺ purification was higher than that for the other metal impurities as speciation diagrams predicted.

A dilute industrial phosphoric acid solution was used to prevent membrane fouling. The three-compartment cell produced a highly concentrated phosphoric acid solution with ionic impurities in the anolyte. In the central compartment, the acid concentration decreased without purifying the acid. Previous electro dialysis studies [20, 21] have assumed that phosphate ions can efficiently migrate across membranes; however, our results show that such a migration process consumes a large amount of energy and would therefore be extremely costly. In addition, the voltages of the ED process were sufficient to damage the membrane. Our results show that electro dialysis is not commercially viable for purifying industrial-grade phosphoric acid. Nevertheless, in future research, our group will test another phosphate raw material, Na₃PO₄, by the electro dialysis technique, using this study as a benchmark.

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