Physicochem. Probl. Miner. Process. 47(2011) 27-40
www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing
ISSN 1643-1049

Received March 20, 2011; reviewed; accepted April 6, 2011

Enhanced solvent extraction of cadmium and iron from phosphoric acid in chloride media

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Abstract. Cadmium and iron are common impurities in wet process phosphoric acid (WPA). These impurities should be minimized to the acceptable levels before the commercialization of the WPA. Organic extractant such as trioctylammine (TOA) will be protonated in acidic media and can act as a liquid anion exchanger for separation of anionic chloro-species of Cd^{2+} and Fe^{3+} from WPA. Synthetic solutions containing phosphoric acid, 40 ppm Cd^{2+} and 3% Fe^{3+} (calculated as Fe_2O_3) were prepared and the different parameters affecting the extraction of these metal ions with TOA were investigated. The extraction of the two metal ions was found to be neglected in absence of chloride ions and it sharply increased by increasing HCl concentration. More than 98% of Cd^{2+} was extracted with 20% TOA in kerosene from 30% H_3PO_4 in presence of 1-3% HCl. Almost complete extraction of Fe^{3+} was achieved in presence of 10% HCl at similar experimental conditions. The TOA concentration of about 10% and 30% could completely extract Cd^{2+} and Fe^{3+} at 10% HCl for 10 min, respectively. A third phase formation was observed when TOA in kerosene was contacted with acidic aqueous solutions and this was eliminated by modification of TOA with 10% n-octanol but the extraction efficiency was slightly declined. The extraction process was quite fast, where 3 minutes was found to be sufficient for equilibrium extraction of both metal ions. Increasing the H_3PO_4 concentration enhanced the extraction of Fe^{3+} but little affected that of Cd^{2+}. Most of the two metal ions can be easily stripped by contacting the loaded TOA with water but emulsion formation was observed and the phase separation was difficult. Acidic solutions such as 0.5 M HClO4 can solve the problem and strip about 90% of both metal ions. Small amount of H_3PO_4 (about 1% of the started acid) was co-extracted and stripped together with Cd^{2+} and Fe^{3+} under same conditions.

keywords: phosphoric acid, solvent extraction, trioctylammine, iron, cadmium, chlorospecies

1. Introduction

Phosphoric acid is the second most produced acid after sulfuric acid. It was used as a raw material for the production of fertilizers, detergents, food products, toothpastes and alimentary supplies for cattle. Commercial H_3PO_4 is mostly manufactured using thermal and wet processes. In thermal process, H_3PO_4 is firstly produced by reduction of phosphate rock, followed by oxidation and hydration (Slack, 1968). Phosphate rocks, depending on their origin, can contain radioactive elements like uranium, thorium and radon or heavy metals. The wet process mostly involves the reaction of phosphate rock with H_2SO_4 followed by filtration and acid concentration. The wet process phosphoric acid (WPA) is usually accompanied by a number of undesirable ionic impurities, like fluoride, iron, cadmium, copper, chromium, zinc, uranium, radioactive elements those originally present in the phosphate rocks which interfere in the technological process of phosphoric acid and/or fertilizer. These impurities also can be partially precipitated as phosphates while the acid is concentrated or stored. The removal of heavy metals from the WPA is environmentally important referring mainly to their toxicity (Schrödter et al., 1998). It is for this reason that historically, the WPA has not been used in the food, detergent and in other industries where high purity acid is necessary, only the thermal route phosphoric acid with higher purity was used. Indeed, about 95% of the WPA is directly used as a fertilizer and excluded from the use in non-fertilizer applications. Because of the large quantities of energy required to manufacture the thermal acid, its cost has risen considerably, the separation techniques have therefore been developed to purify WPA so that it can replace the thermal acid (Ennaassia et al., 2001). Although most of the precipitated sludge in the WPA can be removed in the clarification stage, a considerable amounts of impurities remained in a soluble form in the acid. Purification of WPA is the goal in the production of some industrial phosphate salts and miscellaneous applications for food, beverage, toothpaste and cleaning markets also require high purity (Kijkowska et al., 2002).

Several methods for purification of WPA were evaluated including precipitation, ion-exchange, liquid–liquid extraction (Chehid Elleuch et al., 2006, Wang et al., 2010, Kumar et al., 2009, Joshi et al., 2009 and Radhikaa et al., 2010) adsorption on activated carbon (Monser et al., 1999) and membrane technologies such as electrodialysis (ED), reverse osmosis and nanofiltration (Gonzalez et al., 2002). Cleaning the WPA from heavy metals was made by precipitation as sulfides (Qafas et al., 2001). Further purification by precipitation of cationic impurities, especially, Fe, Al, Mg, and Ca, is possible. One simple way of removing these cations is to increase the pH of the WPA until the precipitation. David, 1974, tried to remove Mg and small percent of iron and aluminum by mixing the crude H_3PO_4 with hexafluorosilicic acid. However, all precipitation techniques usually suffer from high P_2O_5 losses accompanied with the solid precipitate making the process economically infeasible.

Iron and cadmium are common impurities in WPA that is produced from phosphate rocks from some origins. Separation of these ions from WPA is difficult and need sophisticated techniques. Most of the iron content in the phosphate rock is dissolved in the WPA. Fertilizer's grade phosphoric acid of 50% P_2O_5 should contain <1.5% Fe_2O_3. Otherwise, the filtration rate of the acid will be low and the water-soluble P_2O_5 content of the prepared fertilizers will be also low. Processing of the high iron Egyptian phosphate concentrates by the dihydrate process produces 50% P_2O_5 acid with about 4 % Fe_2O_3. In our previous works, we could reduce this high iron content to the industrially acceptable limit by precipitation with K_2SO_4 (Abdel-Aal et al.,1999) and controlled the acid filtration rate using surfactants (Abdel-Aal et al., 2007). Cadmium is an extremely toxic element and cause harmful effect on plants, animals and humans. Igneous phosphate rocks contains very little cadmium (<1mg Cd/kg phosphorus) while sedimentary sources contain much higher levels of cadmium (43 to 380 mg Cd/kg phosphorus) (Gowariker 2009). Cadmium transfers from the phosphate rock to the WPA during the acid production. Cadmium as a contaminating element affects a wide variety of living organisms and is accumulated in the human body. Human exposure to Cd can affect pulmonary, kidney, gut and liver functions. Cadmium exposure can also cause common diseases, such as prostate cancer, gastro-intestinal poisoning and bone damage. Since WPA is used in phosphate fertilizers, and intended for use in the food and detergent industries, cadmium can enter the environmental cycle as well. So removal of cadmium from WPA is essential. There are various remedial processes, such as precipitation, ion exchange, solvent extraction and membrane processes which have been used to remove cadmium from WPA. Of these processes, solvent extraction has shown high efficiency (Nazari et al., 2005, Tomaszewska et al., 2007, Alguacil and Alonso 2004). A continuous micro-pilot scale mixer-settler was successfully tested for both extraction and stripping of cadmium from phosphoric acid media using D2EHDTPA in dodecane as extractant (Touati et al., 2009). Mellah and Benachour, 2006, proposed bis-(2-ethylhexyl)-phosphoric acid (D2EHPA) for the recovery of cadmium (II) and zinc(II) from phosphoric acid solution. Cadmium(II) was extracted at a higher pH than zinc(II), which suggested that the separation of zinc(II) and cadmium(II) could be attained by extraction with D2EHPA controlling aqueous pH.

In this paper, separation of Cd^{2+} and Fe^{3+} from phosphoric acid was studied with solvent extraction using trioctylamine (a tertiary amine). The latter is known to work as anion exchanger when be protonated in acidic media. Cadmium (II) and iron (III) have a common properties of formation of anionic chloro species at a specific chloride ion concentration. The main idea behind this work is the enhancement of these metals extraction through promotion of their anionic chloro species in phosphoric acid by controlling the chloride ion concentration. The different parameters affecting the extraction and stripping processes will be investigated in order to enhance the separation of these two metal ions from phosphoric acid with trioctylamine.

2. Experimental

2.1. Materials

Analytical grade phosphoric acid, H_3PO_4 (85%) and cadmium sulfate, CdSO4 (99%) were provided by Prolabo. Hydrochloric acid, HCl (35%), ferric chloride, $FeCl_3$, and potassium chloride KCl all of AR grade were provided by Merck. Trioctylamine, TOA (Henkel) was used as an active organic extractant. Pure Kerosene (El-Naser Chemical Company, Egypt) was mostly used to dilute the organic extractant. Toluene, xylene, and carbon tetrachloride were supplied by Merck and also used as solvents for the extractant. Normal octanol (Henkel) was used as a modifier. Other chemicals used in this study were of analaytical grade.

2.2. Procedures

Synthetic solutions of phosphoric acid containing heavy metals, 3% iron (estimated as Fe_2O_3) and 40 ppm cadmium, were prepared by dissolving the required weights of $FeCl_3$ and $CdSO_4$ in specific amounts of distilled water as required to dilute the concentrated phosphoric acid to concentrations ranging between 10 to 40% P_2O_5. The concentrations of chloride ion in phosphoric acid were adjusted by dissolving known amounts of concentrated HCl or KCl. The precipitated solids in phosphoric acid after one week aging were separated by filtration, washed with ethanol, dried at 40 ºC in a vacuum drier for 48 hours and then analyzed by Scanning Electron Microscope (SEM) and X-ray Diffraction analysis (XRD). The TOA solutions of different concentrations were prepared by dissolving the measured volumes of TOA in either kerosene, toluene, xylene or carbon tetrachloride.

In solvent extraction experiments, the required volume of the diluted organic extractant was placed in a 250 cm^3 cylindrical glass vessel and a specific volume of an aqueous phase of a solution containing phosphoric acid, iron and cadmium ions was added and the mixture was shacked in a water bath thermostat shaker (GFL Model 1083) for the period of time required. The temperature was set at 27 ºC. After phase separation by centrifugation, a sample from aqueous phase was withdrawn, diluted by distilled water, and used for chemical analysis of Fe, Cd ions and P_2O_5. In stripping experiments, an exact volume of the loaded organic solution was mixed with the required volume of a suitable aqueous solution and shacked in the water bath thermostat shaker. The speciation diagrams of Cd^{2+} and Fe^{3+} in acidic chloride solutions was constructed using *Stabcal* software developed by Dr. Hsin H. Huang, Department of Metallurgical and Materials Engineering, Montana Tech of the University of Montana, Butte, Montana, USA.

2.3. Measurements

Concentrations of cadmium and iron were measured after dilution with distilled water by an Atomic Absorption Spectrometer, model Perkin Elmer 3100. The crystalline phases present in the dried sample of the precipitated solids separated from phosphoric acid were identified by X-ray diffraction (XRD) on a Bruker axis D8 diffractometer using Cu-K_α radiation. The average crystallite size of the powders was estimated automatically from corresponding XRD data (using X-ray line-broadening technique employing the classical Scherrer formula). P_2O_5 content was determined spectrophotometrically between 460 and 480 nm by the known yellow method (Jeffery et al., 1989).

3. Results and discussion

3.1. Speciation of Cd^{2+} and Fe^{3+} in chloride solutions

It was important to define the forms of Fe^{3+} and Cd^{2+} ions those exist at chloride solutions. This will contribute in controlling extraction of these metals in solvent extraction experiments. Cadmium(II) forms cationic, neutral and anionic chloro-complexes depending on the choride ion concentration. The species present in equilibrium are: Cd^{2+}, $CdCl^+$, $CdCl_2$, $CdCl_3^-$ and $CdCl_4^{2-}$. The distribution of cadmium ions in chloride solutions was estimated using *Stabcal* software according to their stability constants, and the results are plotted in Fig. 1a. The cationic species Cd^{++} and $CdCl^+$ are predominant at very dilute HCl concentrations, where the fractions of neutral, $CdCl_2$, and anionic species $CdCl_3^-$ and $CdCl_4^{2-}$ are progressing with increasing the HCl concentrations. At HCl concentrations more than about 1.5 M, only the anionic species are predominant.

The speciation diagram of Fe^{3+} in acidic chloride solutions were constructed using *Stabcal* software and results are presented in Fig. 1b. It can be seen that cationic iron species such as Fe^{3+}, $FeCl^{2+}$, $FeCl_2^+$ are predominant at low HCl concentrations and the neutral species $FeCl_3$ is the main one at moderate to high HCl concentrations. Moreover, the species $FeCl_4^-$ is the only anionic form of all and formed at moderate HCl concentrations and became the main one at concentrated HCl solutions. It can be generally noticed that, the formation of anionic iron chlorocomplex, $FeCl_4^-$, exists at much concentrated HCl solutions compared with those of cadmium,$CdCl_3^-$ and $CdCl_4^{2-}$.

The variation of the form of Fe^{3+} and Cd^{2+} with concentration of HCl can suggest the corresponding variation of the extracted species with trioctylamine (TOA) in this study. The form of the predominant species at a specific Cl^- concentration can thus predict the extraction mechanism and the form of the extracted metal ions.

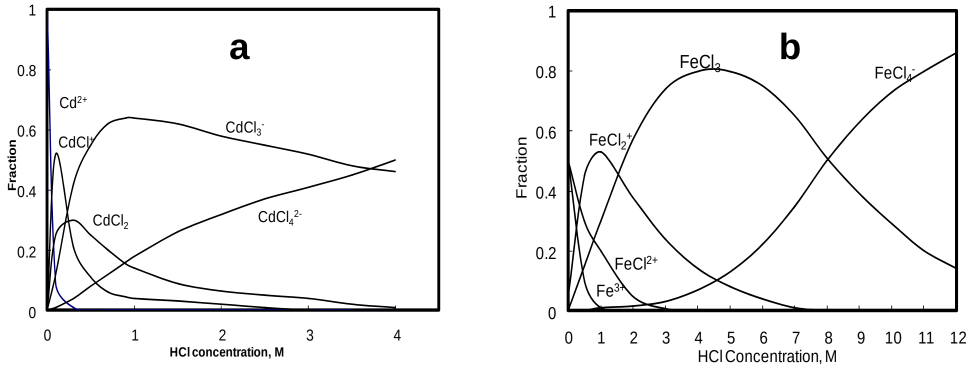

Fig. 1. Speciation diagram of Fe^{3+} and Cd^{2+} at different HCl concentrations

3.2. Effect of chloride ion concentration on extraction of Cd^{2+} and Fe^{3+} with TOA

The extraction of iron and cadmium from 30% phosphoric acid with 20% TOA in kerosene was investigated at different HCl concentrations for 10 minutes and the results are shown in Fig. 2. It is obvious from these results that the extraction of iron is very sensitive to chloride ion concentration and was continuously increasing with increasing the acid concentration. Iron forms the anionic chlorospecies, $FeCl_4^-$, that is extractable to the organic phase with the protonated TOA ($R_3NH^+Cl^-$) through anion exchange mechanism as shown as follows:

$$R_3N + HCl \rightarrow R_3NH^+Cl^-$$

$$R_3NH^+Cl^- + FeCl_4^- \rightarrow R_3NH^+FeCl_4^- + Cl^-.$$

Increasing the HCl concentration favors the formation of the extractable anionic chlorocomplex, $FeCl_4^-$, over the other existing chlorospecies those are noncharged or cationic. This can explain the continuous increase in the extraction of iron by increasing the HCl concentration. At 10% HCl, about 91% of iron was extracted while 14% HCl gave almost complete extraction.

The added amount of HCl to the contaminated phosphoric acid can be optimized to reach the acceptable limit of 1.5% Fe in phosphoric acid. For instance, about 5% HCl can reduce the Fe content to half of its initial amount, i. e., 1.5%. It is worthy to mention that presence of definite amounts of HCl is acceptable in phosphoric acid production industry. The phosphoric acid with the remaining HCl will be neutralized with NH_4OH in the next stages if it is used for production of fertilizers. This will produce mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP). Neutralization of the contained

HCl content produces NH_4Cl which can be consider as an additional source of nitrogen to the plants.

Another series of experiments was performed at similar conditions but with using KCl, as a source of chloride ions instead of HCl, and the results are also shown in Fig. 2. KCl was selected as it contains K ion which is known as a valuable plant's nutrient and its existence in phosphoric acid is an added value. In this case, the extraction was very slowly increasing with increasing Cl^- concentration (lower than 6%) and then was gradually increasing at higher Cl^- concentrations. The drop in Fe extraction with KCl, compared with that of HCl at lower range of Cl^- concentrations, may be due to the lower acid concentration where the stability of the extractable form of iron $FeCl_4^-$ is lower.

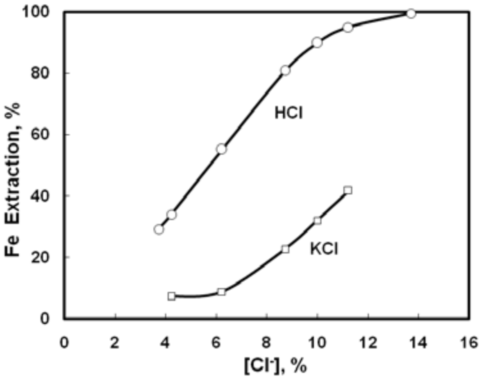

Fig. 2. Effect of HCl and KCl concentrations on extraction of Fe^{3+} from phosphoric acid

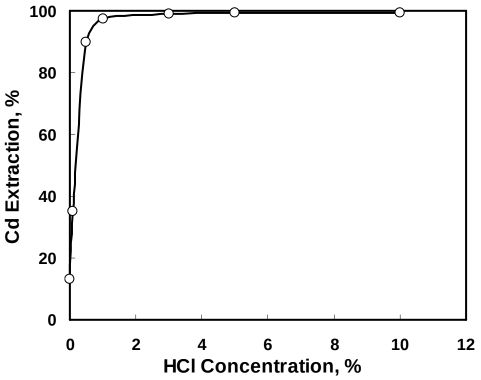

Fig. 3. Effect of HCl concentrations of extraction of Cd^{2+} from phosphoric acid

The effect of increasing HCl concentration on Cd^{2+} extraction showed a sharper increase compared with that of iron at similar experimental conditions (Fig. 3). About 98% of cadmium was extracted using 1% HCl. Only 3% HCl gave almost complete extraction of Cd^{2+}. The easier extraction of Cd^{2+} compared with that of Fe^{3+} can be explained as the anionic chlorospecies of cadmium, $CdCl_3^-$, exist at much lower chloride ion concentration compared with that of iron (see Fig. 1a and ab). That is, at very diluted HCl concentration, such as 0.1%, $CdCl_3^-$ is formed and at more concentrated HCl the form $CdCl_4^{2-}$ is more predominant. However, the only anionic species of iron, $FeCl_4^-$, is formed at much higher HCl concentrations compared to those of Cd^{2+}. The extraction of Cd^{2+} is expected to take place via the following reactions :

$$R_3NH^+Cl^- + CdCl_3^- \rightarrow R_3NH^+CdCl_3^- + Cl^-$$

$$2R_3NH^+Cl^- + CdCl_4^{2-} \rightarrow (R_3NH^+)_2\, CdCl_4^{2-} + 2Cl^-.$$

3.2.1. Identification of the precipitated solids in phosphoric acid

A brownish-black precipitated solids were found in those phosphoric acid samples containing KCl as additive after aging overnight. There was no precipitate at the start but it was growing slowly by time and its amount was found almost unchanged after about 6 days. A sample of these precipitated solids was separated after aging for one week at room temperature of around 25-30 ºC, washed, dried and analyzed by TEM and XRD. The TEM micrograph of the precipitated solids (plate 1) shows well formed hexagonal crystals. The XRD (Fig. 4) shows that the solids are a single crystalline phase of potassium iron phosphate hydrate with the formula $KFe_3P_6O_{20}\cdot 10H_2O$.

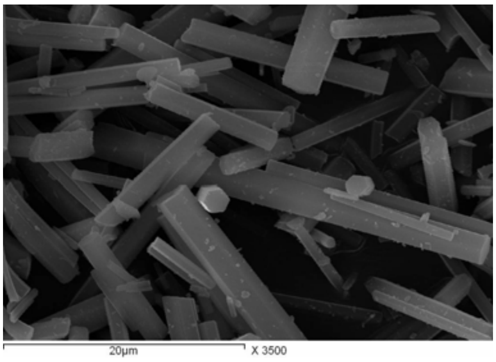

Plate 1: Scanning Electron Microscope micrograph of the precipitated crystalline solids in phosphoric acid after addition of KCl

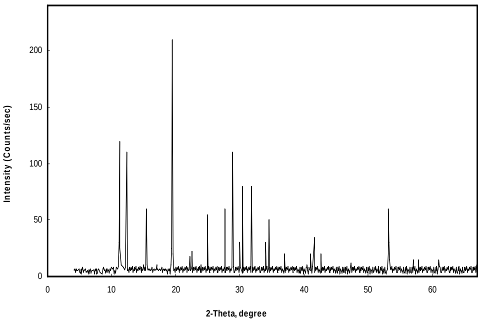

Fig. 4. X-ray diffraction analysis of the precipitated solids in phosphoric acid after addition of KCl

Table 1. EDX weight % of the precipitated solids in phosphoric acid after addition of KCl

Element	Weight, %	Weight, % as calculated from the formula $KFe_3P_6O_{20}\cdot 10H_2O$
O	58.10	53.75
P	21.57	20.82
K	3.23	4.36
Fe	17.10	18.81
H	-----	2.24

The analysis results of the precipitated particles by Energy Dispersive X-ray Spectroscopy (EDX) are given in Table 1. The EDX analysis indicated that the main constituents are phosphorus, oxygen, iron and potassium. The EDX weight percentage of the constituted elements was found close to that calculated from the structure of $KFe_3P_6O_{20}\cdot 10H_2O$. It is obvious that this precipitate, containing important elements such as P and K, is considered valuable and its discard is not applicable. Apart from the cleaning of iron from the acid, a considerable amount of P_2O_5 and K will be lost in such a precipitate. On the other hand, if the precipitate is left in the acid, it will complicate the following stages of acid concentration and subsequent neutralization for fertilizers production. In the following experiments 10% HCl will be used as a more suitable concentration from the practical point of view.

3.3. Effect of the type of solvent on extraction of Cd^{2+} and Fe^{3+} from phosphoric acid by TOA.

Several types of solvents, namely kerosene, toluene, xylene, carbon tetrachloride those belong to different organic families were tested for dilution of TOA and used for extraction of Cd^{2+} and Fe^{3+} from 30 % P_2O_5 phosphoric acid contained 10 % Cl^- added as HCl. The shaking time was 10 min with organic to aqueous phase ratio of 2: 1. The TOA was completely soluble in all tested solvents. Using different solvents had little effect on the extraction percent of Cd^{2+} and Fe^{3+}. The extraction of Cd^{2+} was ranging from 96% to about 100%, where that of Fe^{3+} is ranging from 87% to 91% for all tested solvents. Carbon tetrachloride gave the lowest extraction, 96% and 87%, where the other three solvents gave extraction ranging around 98-100% and 89-91% for Cd^{2+} and Fe^{3+}, respectively. Kerosene was selected as the suitable solvent as it gives good extraction, has high boiling point, high solubility, low toxicity and it is commercially available with low price.

3.4. Effect of TOA concentration on extraction of Fe^{3+} and Cd^{2+}

The effect of TOA concentration (from 0.1 to 30%) on extraction of Fe^{3+} and Cd^{2+} from 30% P_2O_5 phosphoric containing 10 % Cl^- added as HCl acid is shown in Fig. 5. The shaking time was 10 min with organic : aqueous phase ratio of 2: 1.

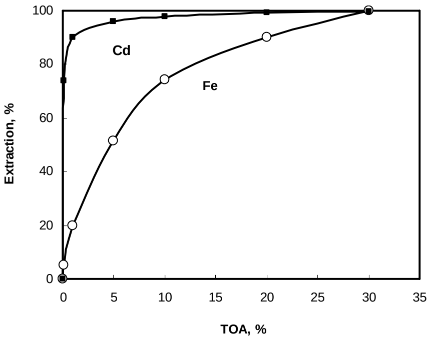

Fig. 5. Effect of TOA concentration on extraction of Cd^{2+} and Fe^{3+} from phosphoric acid

It can be noticed that increasing the TOA concentration increased the extraction percentages of both metal ions. Cadmium(II) was sharply extracted with increasing the TOA concentration at lower range (less than 1% TOA) and then gradually increased, whereas that of Fe^{3+} was gradually extracted along with the TOA concentration. At only 0.1% TOA, the Cd^{2+} extraction reached about 75% but that of Fe^{3+} did not exceed 5%. At 10% TOA the extraction percentages reached 99% and 75% for Cd^{2+} and Fe^{3+}, respectively. Almost complete extraction of Cd^{2+} and Fe^{3+} could be obtained with 30% TOA.

3.5. Effect of mixing time on extraction of Cd^{2+} and Fe^{3+} with TOA

The effect of mixing time on extraction of Cd^{2+} and Fe^{3+} with 20% TOA in kerosene from 30% P_2O_5 acid and 10% HCl is shown in Fig. 6. The extraction of both metal ions is too fast that is about 86% of $Cd^{2+}$and 77% of Fe^{3+} were extracted after only one minute of mixing time. These values increased to 99% and 89%, respectively, after 3 min and very little increased at longer mixing time. These fast kinetics support the metals extraction through the above suggested anion exchange mechanisms. In the following experiments, 10 min was chosen to ensure the maximum values of metals extraction (about 100% and 90% for Cd^{2+} and Fe^{3+}, respectively.

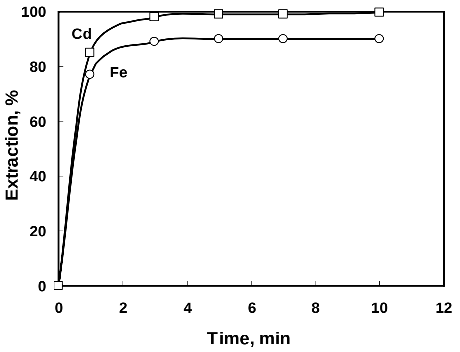

Fig. 6. Effect of mixing time on extraction of Cd^{2+} and Fe^{3+} from phosphoric acid

3.6. Effect of n-octanol concentration on extraction of Fe^{3+} and Cd^{2+}

A third phase formation was observed during the solvent extraction experiments with TOA in kerosene from acidic solutions. This may be due to the limited dissolution of the TOA after protonation when contacted with the acid in aqueous phase. In such case, a modifier can be used to enhance the solubility through a charge interaction with the protonated amine. A long chain alcohol is suitable reagent for this purpose. Preliminary investigation revealed that the third phase can be removed after addition of more than 5%

n-octanol. However, this addition can affect the extraction of Cd^{2+} and Fe^{3+} from phosphoric acid solution. Therefore, we have studied the effect of n-octanol concentration on extraction behavior of Cd^{2+} and Fe^{3+} and results are shown in Fig. 7. The experimental conditions were: 30% P_2O_5 acid, 10% HCl, 20% TOA in kerosene and 10 min mixing time. It is obvious from these results that increasing concentration of n-octanol adversely affect the extraction of both metal ions, especially at n-octanol concentrations more than 5%. This may be attributed to the interaction of n-octanol with the active sites of the TOA extractant. In presence of 10% n-octanol, the extraction reached 98% and 88% for Cd^{2+} and Fe^{3+}, respectively.

3.7. Effect of phosphoric acid concentration on extraction of Cd^{2+} and Fe^{3+} with TOA

A series of experiments was performed to study the effect of phosphoric acid concentration (from 5 to 38%) on extraction of Cd^{2+} and Fe^{3+} with 20% TOA in kerosene and 10% n-octanol for 10 min. The results given in Fig. 8 indicate that increasing phosphoric acid concentrations had little effect on metals extraction. Cadmium(II) extraction was almost unchanged, and that of Fe^{3+} slightly increased. This may be due to the higher stability of the anionic chlorospecies of Fe^{3+} at concentrated acidic solutions.

The dihydrate process firstly produces phosphoric acid of about 28% P_2O_5 (called filter acid) which is further concentrated to about 48-50% P_2O_5 (called conc. acid or commercial acid). In the hemihydrate process, filter acid of around 40% P_2O_5 is directly produced and that will be concentrated if needed. It is worthy to mention that the 50% P_2O_5 acid is viscous and needs filtration to remove the precipitated solids (sludge) before solvent extraction. Viscous liquids are not favored in solvent extraction mainly due to phase separation problems. These encouraged us to suppose that the separation of impurities could be simpler from acids with about 40% P_2O_5 as maximum concentration to avoid inconveniences. The purified acid can then be concentrated to the desired P_2O_5 concentration.

3.8. Stripping of Cd^{2+} and Fe^{3+} from Loaded TOA

It is clear from the above investigation that the key factor for the uptake of the two metal ions to the organic phase is the extent of formation and stability of their anionic chlorocomplexes in the aqueous phase. Higher concentration of acidic chloride solutions enhanced the metal ions extraction. Thus, contacting the loaded organic phase with aqueous solutions free of chloride ions may favor the release of the metal ions from the organic phase to the aqueous phase. Most of the two metal ions can be easily stripped by contacting the loaded TOA with water but emulsion formation was observed and the phase separation was difficult. In slightly acidic solutions, no emulsion phase was observed during stripping. The stripping of the two metals from 20% TOA in kerosene and 10% n-octanol was examined using stripping solutions with different nature and acidities.

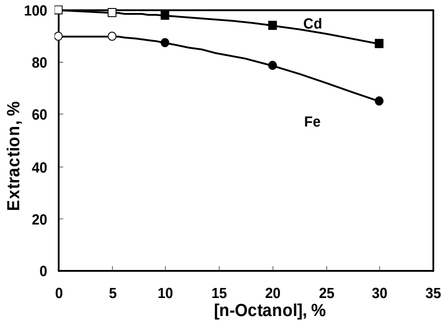

Fig. 7. Effect of n-octanol concentration on on extraction of Cd^{2+} and Fe^{3+} with TOA in kerosene from phosphoric acid. Open: third phase and closed: no third phase

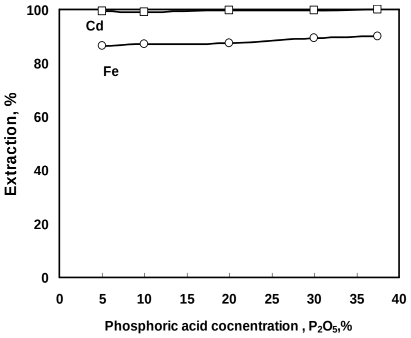

Fig. 8. Effect of phosphoric acid concentration extraction of Cd^{2+} and Fe^{3+} with TOA

Table 2. Stripping of Cd^{2+} and Fe^{3+} from TOA with different solutions and acidities

Nature of stripping solutions	Equilibrium pH	Stripping, % Cd	Fe
Hydrochloric acid	0.5	1.5	7.6
Hydrochloric acid	1.0	3.0	18.7
Hydrochloric acid	1.5	2.0	28.5
Perchloric acid	0.00	93.5	85.2
Perchloric acid	0.30	90.1	90.3
Phosphoric acid	0.50	74.3	94.2
Phosphoric acid	1.21	63.9	95.6
Water	2.39	54.5	96.2

Hydrochloric, perchloric, phosphoric, acetic acids and water were examined and results are given in Table 2. The mixing time was 10 min and the organic to aqueous phase ratio was 1: 2. Dilute hydrochloric acid solutions did not strip any significant amount of Cd^{2+}, where, the maximum stripped amount of Fe^{3+} was about 28%. In contrast, dilute perchloric acid could strip more than 90% of the two metal ions. In dilute phosphoric acid the maximum stripping were 74% and 94% for Cd^{2+} and Fe^{3+}, respectively. In distilled water, only about 55% of Cd^{2+} could be stripped and that of Fe^{3+} was 96% where the equilibrium pH reached 2.4. The P_2O_5 concentrations were analyzed in the stripping solutions after the experiments. A small amount of about 1% at maximum of phosphoric acid was found lost in the strip solutions.

4. Conclusion

Cadmium and iron are common impurities in wet process phosphoric acid (WPA). These metal ions considered undesirable in the WPA due to technological and hazardous effects and their minimization to the acceptable levels is essential. Solvent extraction is one of the very promising techniques for this purpose. Iron and cadmium can form anionic chlorocomplexes in chloride solutions. When these anions are contacted with organic anion exchanger such as protonated trioctylamine, they could be separated to the organic phase. This phenomena was investigated in this work. It was found that the extraction of both metal ions is very sensitive to the content of HCl in phosphoric acid. Increasing the HCl promoted the formation of chlorospecies of iron and cadmium and hence enhanced their extraction. The extraction parameters were optimized to achieve highest possible uptake of the two metal ions. The extraction was quite fast, that is almost complete extraction of Cd^{2+} and about 90% of Fe^{3+} was achieved within only 3 minutes.

Acknowledgement

The author wish to thank Taif University, Deanship of Scientific Research, for support of this work under Project no. 1/1431/874.

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