Extraction of Nitric Acid from Wet-process Phosphoric Acid

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Solvent extraction of nitrates (almost all as nitric acid) from WPA produced by decomposing phosphate rock with nitric acid has been investigated using four different extractants (tributyl phosphate, methyl isobutyl ketone, n-octanol and tri-n-octyl amine) in kerosene. The results show that tri-n-octyl amine (TOA) is an effective extractant for the extraction of nitric acid from the WPA. Optimum conditions for the extraction process have also been determined. The results indicate that TOA has a good ability to extract nitric acid, while only a small amount of phosphoric acid is co-extracted. TOA can be used as an effective extractant to separate nitric acid from the WPA to produce phosphoric acid. The effect of the main impurities existing in the WPA produced by nitric acid dissolution of phosphate ore (Ca\(^{2+}\), Fe\(^{3+}\), Al\(^{3+}\), Mg\(^{2+}\) and F\(^-\)) has also been studied. The results show that the impurities have a negative effect on the extraction of nitric acid or phosphoric acid and can be partly removed in the extraction. In addition, the number of theoretical stages for extracting 99.9 % of the nitric acid is calculated by the McCabe-Thiele method.

1. Introduction

Phosphoric acid is mainly produced by the wet and furnace processes. Traditionally, the wet process involves decomposing the phosphate rock with an acid (almost always sulfuric acid as the calcium sulfate precipitate is easy to remove) [1, 2]. However, the sulfuric acid process will generate a large amount of phosphogypsum as by-product, which is harmful to the environment. Furthermore, utilization of the gypsum is difficult and expensive\(^3\text{-}^4\). However, if nitric acid is used to dissolve the phosphate ore, the main by-product is calcium nitrate, a type of nitrogen fertilizer, and this great shortcoming can be avoided. Additionally, the filtration of the phosphogypsum is very difficult but crystallized calcium nitrate is readily
filtered, so this tricky industrial production problem can also be solved by production of WPA using nitric acid.

While the general possibility and desirability of producing phosphoric acid by decomposing phosphate rock using nitric acid has been recognized in the past, it has rarely been practiced because the separation of nitric acid from WPA is very difficult. St. Paul Ammonia Products (U.S.) [2] separates 95 % of the calcium nitrate crystallization by freezing acid leach liquid and removing the residual calcium with sulfuric acid. In order to obtain high purity phosphoric acid, the residual nitric acid must be removed. Distillation and solvent extraction can be used for the recovery of nitric acid from the solutions [1, 5, 6]. However, solvent extraction is more effective and the energy consumption is much lower.

A number of organic solvents have been considered for the extraction of the acids, e.g. tributyl phosphate (TBP) [6-10], methyl isobutyl ketone (MIBK) [11], n-octanol (OT) [12] and TOA [13]. Yet few reports are concerned with the separation of nitric acid from mixed acid solutions, especially in the presence of phosphoric acid.

The aim of this work is to select a suitable solvent for the extraction of the nitric acid from the WPA to produce phosphoric acid. The optimum conditions for the extraction of nitric acid with TOA from the WPA are reported. The effect of the main impurities existed in the WPA (Ca$^{2+}$, Fe$^{3+}$, Al$^{3+}$, Mg$^{2+}$ and F$^{-}$) on the extraction of the nitric and phosphoric acids from process solution are also considered.

2. Experimental

2.1 Materials and apparatus

TBP, MIBK, OT, TOA and kerosene were provided by the Sichuan Jingcui Co., Ltd., China and were used without any further purification. Nitric acid, phosphoric acid, nitrate salts and hydrofluoric acid were supplied by the Kelong Co., China. All of these reagents were of analytical grade. Phosphate rock was provided by China Blue Chemical Ltd.. The water used in the experiments was deionized.

A constant temperature water bath oscillator (model HZS-H) was provided by Harbin Donglian Electronic Technology Development Co., Ltd, China. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, model SPS-8000) was provided by Beijing Kechuang Haiguang Instrument Co. Ltd.. The pH meter (model PHSJ-4A) was provided by INESA Scientific Instrument Co. Ltd.. The electronic analytical balance (model BSA224S) was provided by Sartorius.

2.2 Pre-treatment of the phosphate rock

The phosphate ore was first dissolved in nitric acid (about 50 % wt.), and the acid insoluble residue removed by filtration. The filtrate was cooled to -10 ºC, and approximately 90 % of the calcium nitrate was crystallized from the acid solution. The residual solution was used as the feed solution for the following extraction process. The composition of the feed solution is shown in Table 1.
Table 1. Composition of the feed solution.

<table>
<thead>
<tr>
<th>Component</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>MgO</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>F</th>
<th>NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>19.61</td>
<td>0.58</td>
<td>0.37</td>
<td>0.46</td>
<td>0.43</td>
<td>0.43</td>
<td>30.10</td>
</tr>
</tbody>
</table>

2.3 Procedures

The extraction was carried out in a conical flask with a water thermostat to control the temperature. The feed solution with known concentrations of nitric and phosphoric mixtures acid, solvents and kerosene were mixed in the conical flask. The mixture was shaken for a certain time and then completely transferred into a separatory funnel for 1 h to completely separate both phases. The aqueous phase was taken from the bottom opening of the separatory funnel. Then the organic phase was carefully collected in a jar. Both solutions were weighed and taken as the aqueous sample and organic sample, respectively. Then, the samples of both phases were analyzed. The yields (\(Y_i\)), distribution coefficients (\(D_i\)) and separation factors (\(\beta_i\)) were respectively defined as follows:

\[
Y_i = \frac{m_o \omega_i^o}{m_i \omega_i^{ia}}
\]

(1)

\[
D_i = \frac{\omega_i^o}{\omega_i^a}
\]

(2)

\[
\beta_i = \frac{D_i}{D_j}
\]

(3)

where \(m_o\) and \(m_i\) are the mass of the organic phase and the initial aqueous phase, respectively; \(\omega_i^o\), \(\omega_i^a\) and \(\omega_i^{ia}\) are the mass fraction of component \(i\) (\(I = N\) for nitric acid, \(I = P\) for P₂O₅) in the aqueous phase, organic phase and initial aqueous phase, respectively.

In the study of the effect of the impurities on the extraction process, Ca(NO₃)₂, Fe₂(NO₃)₃, Al₂(NO₃)₃, Mg(NO₃)₂ and HF are used as impurities. These agents are added to the nitric and phosphoric acid mixtures respectively, to prepare an initial aqueous phase containing one type of impurity. The concentrations of the two acids are equivalent to that in the WPA.

Phosphoric acid concentrations in both phases were determined by the quinoline phosphomolybdate gravimetric method [14]. The concentration of cations (Ca²⁺, Fe³⁺, Al³⁺, Mg²⁺) in the aqueous phase were determined by ICP-AES. The NO₃⁻ and F⁻ concentrations in aqueous phase were determined using ion-selective electrodes [15, 16]. The Ca²⁺, Fe³⁺, Al³⁺, Mg²⁺, NO₃⁻ and F⁻ concentrations in the organic phase can be determined from the material balance [17]. All of the experiments were carried out at least twice, and the average values were taken as the results. The relative deviations of all materials was within 0.5%. 

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3. Results and Discussion

3.1 Selection of the extractant

A large amount of solvents were considered for the extraction of the nitric acid such as alcohols [11, 12, 18], esters [6-11], ethers [11], ketones [11], amines [13, 19, 20] and sulfoxides [21, 22]. However, some of the phosphoric acid would inevitably be co-extracted with the nitric acid if these solvents were used as the extractants. In this study, four different common extractants (TBP, MIBK, OT and TOA) were chosen for the extraction of the nitric acid from the WPA produced by nitric acid leaching. The results are shown in Table 2.

From Table 2, it can be seen that TOA has the highest extraction yield and distribution coefficient for nitric acid. The table also indicates that the higher extraction yield of nitric acid, the lower extraction yield of phosphoric acid for the different extractants used. The distribution coefficients of the two acids also obey this law. Therefore, the separation factor of nitric acid against phosphoric acid $\beta_{P}^{N}$ using TOA as the extractant is the largest. This phenomenon can be explained because TOA is an alkaline extractant while the others are neutral extractants. As an alkaline amine extractant, the nitrogen atom in the TOA molecule has a lone pair of electrons, which can generate ammonium salts through a stable coordinate bond [23]. The anion in the aqueous phase can be combined with the ammonium salts thus transferring it from the aqueous into the organic phase. Thus, the extraction of the inorganic acids using TOA is more effective than that using the other extractants studied in this experiment. In addition, because the volume of $\text{NO}_3^-$ is smaller than $\text{H}_2\text{PO}_4^-$, the steric hindrance of $\text{NO}_3^-$ is far less than that of $\text{H}_2\text{PO}_4^-$ when they are transferred into the organic phase. So nitric acid will be extracted more easily than phosphoric acid. All of these reasons indicate that TOA is a suitable solvent to extract nitric acid from the WPA produced by nitric acid leaching.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TBP (%)</th>
<th>MIBK (%)</th>
<th>OA (%)</th>
<th>TOA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_N$</td>
<td>60.18</td>
<td>60.23</td>
<td>53.84</td>
<td>66.87</td>
</tr>
<tr>
<td>$Y_P$</td>
<td>4.13</td>
<td>5.60</td>
<td>9.61</td>
<td>1.22</td>
</tr>
<tr>
<td>$D_N$</td>
<td>0.411</td>
<td>0.314</td>
<td>0.190</td>
<td>0.792</td>
</tr>
<tr>
<td>$D_P$</td>
<td>0.021</td>
<td>0.022</td>
<td>0.043</td>
<td>0.005</td>
</tr>
<tr>
<td>$\beta_{P}^{N}$</td>
<td>19.7</td>
<td>14.1</td>
<td>4.4</td>
<td>163.8</td>
</tr>
</tbody>
</table>

3.2 Effect of the phase ratio on the extraction process

The phase ratio can greatly affect the extraction yields, distribution coefficients, separation factors of the two acids and phase separation times. Extraction with different phase ratios (O/A) from 1.0 to 4.0 was investigated in this work. The experiments were carried out under following conditions: extraction
temperature = 50 °C, shaking time = 10 min, shaking rate = 500 rpm. Figure 1 and Figure 2 show the results.

According to Figure 1 and Figure 2, with increasing phase ratio, $Y_N$, $Y_P$, $D_N$, $D_P$, the phase separation times increased, but $\beta_P^N$ decreased. Figure 1 indicates that $Y_P$ increases significantly when the phase ratio exceeds 2.0. In order to extract more nitric acid and less phosphoric acid, 2.0 is chosen as the optimal extraction phase ratio.

Figure 1. Effect of phase ratio on the extraction yield and phase separation time.
3.3 **Effect of the temperature on the extraction process**

The temperature can affect the extraction equilibrium. The extraction processes are carried out at six different temperatures from 10 to 60 °C, phase ratio (O/A) = 2.0, shaking time = 10 min, shaking rate = 500 rpm. Figure 3 and Figure 4 show the results of the experiments.
As seen from Figure 3 and Figure 4, both the extraction yields and the distribution coefficients of nitric acid increase with increasing extraction temperature. Yet this trend is just the opposite to that for phosphoric acid. Since the increase in $Y_N$ and $D_N$ become less marked as the temperature increases, 50 °C is
chosen as the best extraction temperature.

3.4 Effect of the shaking time and rate on the extraction process

Whether extraction equilibrium has been reached depends on the extraction time and shaking rate of the extraction system. The extraction processes with different shaking times (1, 3, 5, 10, 20, 30, 45 and 60 min) and shaking rates (200, 300, 400, 500 and 600 rpm) have been investigated under the following conditions: phase ratio (O/A)=2.0, extraction temperature=50 °C. Figure 5 and Figure 6 show the results of the experiments. The intersections of dashed lines and extraction yield curves represent the points at which the extraction system has reached equilibrium.

![Figure 5. Effect of the shaking time on the extraction yield of nitric acid.](image)

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From Figure 5 and Figure 6, with increasing extraction time, it can be seen that $Y_N$ initially increases rapidly, but then the rate of increase is sharply reduced when the extraction approaches equilibrium. The faster the shaking rate, the earlier equilibrium is reached. Phosphoric acid extraction shows the same features but at a much lower level. Figure 5 and Figure 6 also indicate that equilibrium for the extraction of nitric acid is reached in less time than that of phosphoric acid. Because the short extraction time is beneficial to the industrial production, 500 rpm shaking rate and 5–10 min shaking time are chosen as the preferred extraction process conditions.

### 3.5 Effect of the impurities on the extraction process

The impurities existed in the WPA can be divided into two types: cation impurities and anion impurities. In WPA produced by nitric acid leaching of phosphate ore, the cation impurities are mainly Ca$^{2+}$, Fe$^{3+}$, Al$^{3+}$, Mg$^{2+}$ and the anion impurity is mainly F. All of these impurities can affect the distribution of the nitric and phosphoric acids. Also, the distributions of these impurities themselves in both phases are very important for this work. The experiments, wherein the concentrations of the impurities range from 0 to 1.0 %wt., were carried out under the following conditions: phase ratio (O/A) = 2.0, extraction temperature = 50 °C, shaking time = 10 min, shaking rate = 500 rpm. The results are shown in Figure 7, Figure 8 and Figure 9.

From Figure 7, it can be seen that the nitric acid distribution coefficient decreases when the concentration of the impurities increases and the effect is in the order Ca$^{2+} >$ F $>$ Fe$^{3+} >$ Al$^{3+} >$ Mg$^{2+}$. The
cause of this phenomenon can be attributed to the salting-in effect of the cations, that is, the cations in solution increase the total concentration of the ions and the electrostatic attraction between H\(^+\) and NO\(_3^-\) is decreased. Since the HNO\(_3\) is extracted into the organic phase in the form of an ion pair, the extraction becomes more difficult when the cations are present in the aqueous phase. For the anion, it can be interpreted that part of the NO\(_3^-\) in the organic phase is replaced by F\(^-\).

Figure 8 indicates that \(D_P\) first increases and then decreases after reaching a maximum value when the concentration of the impurities increases. The reason for this phenomenon can be explained because at the low range of concentration, the salting-out effect of the impurities plays a leading role in the extraction process, that is, part of the water in the solution is used to hydrate excess ions and the repulsive force between H\(^+\) and H\(_2\)PO\(_4^-\) is reduced. As a result, the concentration of the H\(_3\)PO\(_4\) molecule increases and the extraction of the H\(_3\)PO\(_4\) becomes easier. However, at high concentrations, the phosphoric acid can react with the metal cations and form dihydrogen phosphates. Further ionization can be caused by phosphate complexation, which has a negative effect on the extraction of the phosphoric acid.

As seen from Figure 9, the distribution coefficients of the metal cations decrease with their increasing concentration in the initial aqueous phase while opposite effect is found for the F\(^-\). The results indicate that all types of impurities existing in WPA can be partly removed by extraction with TOA.
Figure 8. Effect of the impurities on the distribution coefficient of phosphoric acid.

Figure 9. Effect of the concentration of the impurities on their own distribution coefficients.

3.6 Determination of the extraction stages

The equilibrium data of nitrate extraction with TOA from the WPA was investigated. The data are used
to calculate the theoretical stages of a counter-current extraction process by the McCabe-Thiele method [24-26], to achieving a 99.9 % yield of nitric acid at 50 °C. The concentration of the nitric acid in the raffinate and feed acid are 0.01 % and 34.10 %wt., respectively. The volume ratio of the organic to aqueous phase is 2.0. In order to verify the reliability of the calculated number of theoretical extraction stages, a 3 stage count-current cascade experiment was performed. The results are shown in Figure 10 and Table 3. Each of the data presented herein is the average value of the analysis of at least two samples collected during stable operating conditions.

The results in Figure 10 indicate that, under the conditions given above, the required theoretical stages will be 2 to 3 in order to extract 99.9 % of the nitrate. Table 3 shows that 3 stages will be required to achieve a 99.9 % extraction yield of nitric acid. The calculated theoretical extraction stages are reliable. In addition, the co-extraction of phosphate cannot be neglected when the number of extraction stages exceeds 2. Additionally, since the TOA is an alkaline extractant and the extract of nitric acid with TOA involves production of an acid-base salt, an alkali such as ammonia can be used to strip the loaded organic phase.

<table>
<thead>
<tr>
<th>Stage</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_N$ (%)</td>
<td>65.11</td>
<td>95.73</td>
<td>99.96</td>
</tr>
<tr>
<td>$Y_P$ (%)</td>
<td>1.67</td>
<td>4.86</td>
<td>19.03</td>
</tr>
</tbody>
</table>

Table 3. Extraction yield of nitric and phosphoric acids in the count-current cascade experiment.

![Concentration of nitric acid in the aqueous phase (\%)](Image)

Figure 10. Theoretical stages for the extraction of nitric acid with TOA.

4. Conclusions

1) TOA can be used as an effective solvent for the extraction of nitric acid from the WPA produced by leaching the phosphate rock with nitric acid.

2) The optimum operation conditions for the extraction of nitric acid have been determined as follows: phase ratio (O/A) = 2.0, extraction temperature = 50 °C, shaking rate = 500 rpm, shaking time = 5-10
3) The effect of the impurities on the distribution coefficient of nitric acid is in the order Ca$^{2+} > F^- > Fe^{3+} > Al^{3+} > Mg^{2+}$. The impurities have a negative effect on the extraction of nitric acid or phosphoric acid and can be partly removed in the extraction with TOA.

4) The number of theoretical stages for extracting 99.9 % of the nitric acid has been calculated. The verification experiment shows that the calculation is reliable.

References