Removing of cadmium ions from wet-process phosphoric acid using precipitation methods.

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²Analytical Department, Łukasiewicz Research Network - New Chemical Syntheses Institute, Puławy, 24-110 Poland, Keywords: cadmium removal, precipitation, phosphoric acid, fertilizers.
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Global phosphate industry is estimated to 60 million tons (P₂O₅) of various products per year, of which about 85-90% is used for phosphoric acid production – the base semi-product for phosphorus fertilizers production. Phosphoric acid is produced by extraction phosphates rock with mineral acid, in most cases H₂SO₄ in a wet process. Cadmium is one of the most threatening impurity of phosphates rock due to its high toxicity. In the process of phosphoric acid production this element is mostly extracted to the acid, and about 30-40% of cadmium is secreted together with phosphogypsum and deposited in post-production heaps, posing a threat to the natural environment. Due to the establishing the limits of the content of cadmium in phosphate fertilizers circulated on EU markets, the most reasonably method of cadmium removal seems to be to separate cadmium ions from wet-process phosphoric acid (WPA). Cd removal methods of industrial importance are liquid-liquid extraction, ion exchange, precipitation, flotation, electrodeposition and membrane processes. WPA contains a number of impurities, among which cadmium is present in trace amounts, compare to the content of the main impurities, such as iron, aluminum or magnesium, the concentration of whom are several hundred times higher. These impurities make it difficult to separate cadmium selectively. Using liquid-liquid extraction purification of WPA, phosphoric acid can be purified to a purity approaching that of thermally produced acid. For the production of fertilizers, the acid does not need to be purified from Fe or Al ions, therefore it is sufficient to reduce the cadmium content by selective methods, such as ion exchange or precipitation. The content of cadmium in phosphate rock varies depending on its origin. Poland does not have its own resources of phosphorites. Fertilizers are produced from raw materials imported mainly from Africa. Average cadmium contents of phosphate rocks according to country of origin are shown in Table 1.

Table 1. Average cadmium contents of phosphate rocks according to country of origin.

<table>
<thead>
<tr>
<th>Country</th>
<th>Deposit</th>
<th>Average Cd [mg/kg]</th>
<th>Range [mg/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>Kaiyang</td>
<td>&lt;2</td>
<td>-</td>
</tr>
<tr>
<td>Israel</td>
<td>Zin</td>
<td>31</td>
<td>20-40</td>
</tr>
<tr>
<td>Jordan</td>
<td>Ej-Hasa</td>
<td>5</td>
<td>3-12</td>
</tr>
<tr>
<td>Morocco</td>
<td>Bou-Craa</td>
<td>38</td>
<td>32-43</td>
</tr>
<tr>
<td>Senegal</td>
<td>Taiba</td>
<td>87</td>
<td>60-115</td>
</tr>
<tr>
<td>Syria</td>
<td>Khneifiss</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>USA</td>
<td>North Carolina</td>
<td>38</td>
<td>20-51</td>
</tr>
<tr>
<td>Russia</td>
<td>Cola</td>
<td>1</td>
<td>1-2</td>
</tr>
</tbody>
</table>

Cadmium can be precipitated from WPA mainly using sulfides in the form of insoluble CdS or other organic derivatives such as organic sulfides, especially dialkyl esters of: dithiophosphoric acid, (RO)₂PSSH; dithiophosphonate, (RO)RPSSH or dithiophosphine, R₃PSSH. Cadmium has a special affinity for diethyl(diethyldithiophosphoric ester and (diethylhexyl) dithiophosphoric ester. In this paper, the results of removal of Cd ions using sodium diethyldithiophosphinate as cadmium precipitating agent from WPA are presented. The formation of sparingly soluble deposits occurs through chemical reactions:

![Chemical reaction]

Phosphinodithioic acid, bis(2-methylpropyl)-, sodium salt (C₉H₁₈NaPS₂) manufactured by iChemical Technologies Inc. Shanghai Facility (China), was used for the tests as precipitating agent. Crude phosphoric acid produced by Grupa Azoty Zakłady Chemiczne Police S.A. (Poland) was used in the tests. The chemical composition of the tested acid is presented in Table 2.
Table 2. Composition of purified wet-process phosphoric acid.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.578</td>
<td>g/cm³</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>49.58</td>
<td>%</td>
</tr>
<tr>
<td>Cadmium</td>
<td>18.77</td>
<td>mg/dm³</td>
</tr>
<tr>
<td>Copper</td>
<td>1.28</td>
<td>mg/dm³</td>
</tr>
</tbody>
</table>

Determination of the Cd content was carried out by atomic absorption spectrometry with electrothermal atomization (ETAAS) using AA240Z/GTA120 VARIAN atomic absorption spectrometer. Studies on the influence of temperature, reaction time, DTPN to WPA ratio and acid concentration on the cadmium ion removal efficiency were carried out.

The tested phosphoric acid was previously reduced with metallic iron powder in order to reduce Fe(III) to Fe(II). Phosphogypsum was used as filtration aid. For this purpose, 2 g of phosphogypsum was weighed into a 50 ml plastic tube, then 25 ml of reduced phosphoric acid was pipetted into each of the tubes. Then, the appropriate amount of 1% DTPN water solution was transferred with an automatic pipette in the amount of 0 ml, 0.1 ml, 0.2 ml, 0.4 ml, 1.0 ml, 2.0 ml to each tube. The amounts of the reagent used corresponds respectively to 0%, 50%, 100%, 200%, 500%, and 1000% of the theoretical amount needed to precipitate cadmium. The closed tubes were placed in a laboratory shaker for 1 hour at 20°C. After the time, the acid solutions were filtered on a cellulose hard filter. Filtrates were analyzed for cadmium content. Cadmium removal efficiency was calculated as a ratio of the Cd concentration after and prior precipitation, expressed as percent. The obtained results are presented in Fig. 1.

In the second experiment, the time of the reaction was investigated. DTPN was reacted with WPA in a ratio 0.4:1000. Effect of time on Cd removal efficiency is presented at Fig. 2.

The tests carried out indicate that using DTPN as a cadmium precipitating reagent, up to 99.6% of the cadmium contained in the WPA can be removed using a five-fold excess of the reagent in relation to the amount required stoichiometrically. The reaction time should be less than 2 hours since the addition of the reagent. Studies have shown that the use of higher temperatures for the precipitation process is unfavorable. The practical consumption of DTPN is about 0.4 kg/1000 dm³ of priorly reduced phosphoric acid of 50% P₂O₅ content. Cadmium is removed in the form of a precipitate together with phosphogypsum. Some limitation of the industrial application of this method is the high cost of the DNPT, which is irretrievably lost.