

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

K. Borowik<sup>1</sup>, P.Rusek<sup>1</sup>, A.Bińczak<sup>1</sup>, U.Ryszko<sup>2</sup>

<sup>1</sup>Fertilizer Research Group, Łukasiewicz Research Network -New Chemical Syntheses Institute, Puławy, 24-110 Poland,

<sup>2</sup>Analytical Department, Łukasiewicz Research Network -New Chemical Syntheses Institute, Puławy, 24-110 Poland,

Keywords: cadmium removal, precipitation, phosphoric acid, fertilizers.

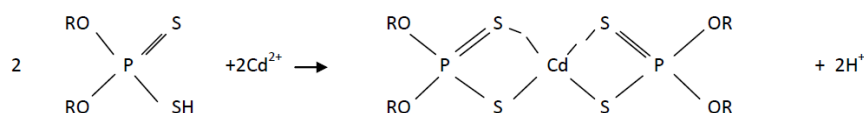
Presenting author email: [krzysztof.borowik@ins.lukasiewicz.gov.pl](mailto:krzysztof.borowik@ins.lukasiewicz.gov.pl)

Global phosphate industry is estimated to 60 million tons (P<sub>2</sub>O<sub>5</sub>) 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 H<sub>2</sub>SO<sub>4</sub> 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.

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

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)<sub>2</sub>PSSH; dithiophosphonate, (RO)RPSSH or dithiophosphine, R<sub>2</sub>PSSH. Cadmium has a special affinity for 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:



Phosphinodithioic acid, bis(2-methylpropyl)-, sodium salt (C<sub>8</sub>H<sub>18</sub>NaPS<sub>2</sub>) 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.

Parameter	Value	Unit
Density	1.578	g/cm <sup>3</sup>
P <sub>2</sub> O <sub>5</sub>	49.58	%
Cadmium	18.77	mg/dm <sup>3</sup>
Copper	1.28	mg/dm <sup>3</sup>

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.

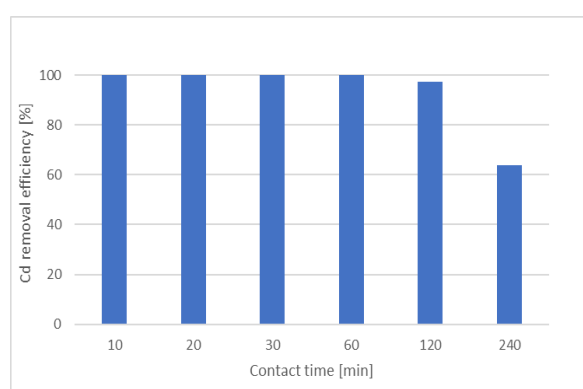
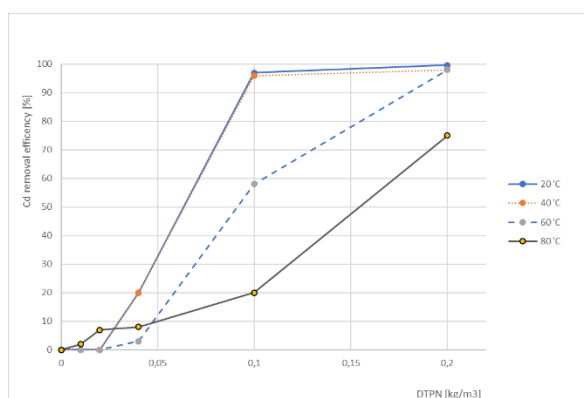


Fig.1. Effect of temperature on Cd removal efficiency.

Fig.2. Effect of time on Cd removal efficiency.

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 dm<sup>3</sup> of priorly reduced phosphoric acid of 50% P<sub>2</sub>O<sub>5</sub> 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.

- Gilmour R. *Phosphoric Acid. Purification, Uses, Technology, and Economics*; 1st ed.; CRC Press Taylor & Francis Group: Boca Raton, United States, **2013**; pp. 1-70.
- S. D. Ukeles, E. Ben-Yoseph. N. P. Finkelstein, *Cadmium removal from phosphoric acid-Israeli experience Hydrometallurgy* **1994**; pp 683–699
- Kouzbour S., Gourich B., Gros F., Vial C., Allam F., Stiriba Y. *Comparative analysis of industrial processes for cadmium removal from phosphoric acid: A review. Hydrometallurgy* **2019**, 188, 222-247.
- Roberts T.L. *Cadmium and phosphorous fertilizers: the issues and the science. Procedia. Eng.* **2014**, 83, 52–59.
- Kouzbour S., Gourich B., Gros F., Vial Ch., Stiriba Y. *Purification of industrial wet phosphoric acid solution by sulfide precipitation in batch and continuous modes: Performance analysis, kinetic modeling, and precipitate characterization. J. Clean. Prod.* **2022**, 380, 2, 135072.