Summary

Due to significant restrictions on cadmium content in fertilizers introduced by European Union legislation on June 5, 2019, by Regulation (EU) 2019/1009 of the European Parliament and Council and Sustainable Development programs such as Resource-efficient Economy and Circular Economy, the dissertation aims to develop technology for the removal of cadmium from phosphate ore and from phosphoric acid obtained by the wet method by decomposing phosphate ore with sulfuric acid.

The new legislative rules are effective from May 2020. EU Regulation 2019/1009 introduced a limit on cadmium content in inorganic phosphate fertilizers at 60 mg Cd/kg P_2O_5. This limit is much stricter than previous limits set in most European Union member countries. Due to increasing difficulties with the quantity and quality of available phosphate ore, the new regulations threaten the continuity of production and profitability of the fertilizer industry. The aforementioned problems are the reason why the research community and the phosphate fertilizer industry are looking for new ways to remove cadmium.

Cadmium compounds, in small amounts, always accompany phosphorus compounds in natural phosphate ore. Their content is usually in the range of 1-100 mg Cd/kg of raw material (0.0001-0.01 wt% Cd). Phosphate ore are the main industrially used raw material for the production of phosphate fertilizers and phosphate salts. Technologies for the manufacture of these products use methods based on the direct use of phosphate ore or indirectly through wet-process phosphoric acid. The chemical nature of these processes means that most of the contaminants contained in the raw materials, including cadmium and other heavy metals, are found in the final products, and as a result are introduced into the environment mainly with phosphate fertilizers, feed additives and household chemicals.

The dissertation consists of an introduction, a theoretical part, the aim of the work, an experimental part and a summary.

The theoretical part presents a brief history of the development of the phosphate industry in the world. The chemical and technological basics of the industrial methods used to obtain fertilizers, phosphoric acid and selected phosphate salts are characterized. Considerations include the requirements of the Best Available Techniques (BAT) for manufacturing, environmental and economic aspects. The legal situation regarding the limit of cadmium content in phosphate fertilizers is presented, and its toxicity and effects on human health and the natural environment are described. An important part, from the point of view of potential industrial use as well as the innovative nature of the scientific research carried

out, is a detailed review of the scientific literature of existing methods for removing cadmium from streams containing phosphorus compounds. Due to the utilitarian nature of the proposed technical solutions, a detailed review of current patents and patent applications was performed.

Conclusions from the literature and patent studies and applicable legal requirements formed the basis for the formulation of the dissertation aim. The main objective of the dissertation was to perform basic research and develop concepts and technological assumptions for:

- evaluation of the possibility of cadmium removal from phosphate ore by calcination,
- evaluation of the possibility of cadmium removal from wet-process phosphoric acid by extraction with organic solvents.

In the experimental part of the work, the choice of analytical methods used in the experiments was made. Flame atomic absorption spectrometry (FAAS), thermal analysis by differential scanning calorimetry (DSC) coupled with thermogravimetry (TG) and mass spectrometry (MS), spectrophotometric methods, Karl-Fischer coulometric method and other basic methods used in chemical analytics were used to evaluate chemical operations and processes. The experiments were carried out on a laboratory scale.

For studied methods, parameters that can affect processes were selected and tested. Experiments were carried out to remove cadmium from streams containing phosphorus compounds by:

- calcination of phosphate ore and calcination of phosphate ore with the addition of inorganic salts (NaCl, KNO_3, Na_2CO_3),
- extraction of cadmium from phosphoric acid solutions using organic solvents as extractants: isopropylacetone, methylcyclohexane and tributyl phosphate.

The research was preceded by the development of the relevant experiment matrices using the Design Of Experiment (DOE) methodology. For studies related to the calcination of phosphate ore, a three-level complete plan including two independent variables was performed. For studies related to cadmium extraction from phosphoric acid with organic solvents, a D-optimal three-level fractional plan including five independent variables was performed. After conducting the planned experiments, the statistical analysis of the obtained results was carried out and the corresponding mathematical models of the studied dependent variables were determined. Statistica software was used to prepare the matrix of experiments, statistical analysis and mathematical modelling.

For calcination studies of phosphate ores, the degree of transition of phosphorus compounds from raw material to calcinate was similar for all samples (90-99%), depending on the calcination temperature. The degree of transition of cadmium from raw material without the addition of inorganic salts to the calcinate was in range 80-90%, depending on the calcination temperature. Addition of inorganic salts to phosphate ore allows to reduce it – for Na_2CO_3 by about 40%, for NaCl by about 50-70%. This makes it possible to obtain calcinates with a more favourable (lower) relative cadmium content (mg Cd/kg P_2O_5).

For solvent extraction studies of cadmium from phosphoric acid solutions, phosphoric acid extraction efficiencies of 0.5-13%; 7-39%; 13-61% and cadmium extraction efficiencies of 31-68%; 37-95%; 9-90% were obtained using isopropylacetone, methylcyclohexane and tributyl phosphate as extractant, respectively. Observations and relationships determined from experiments with model phosphoric acids were confirmed in experiments with industrial wet-process phosphoric acids. The extraction efficiencies of individual chemical entities were lower by 1-5% due to the complex matrix of the wet-process phosphoric acid.

Using the determined mathematical models, the optimal process parameters were selected and based on them four perspective technological concepts for cadmium removal from phosphate raw materials and wet-process phosphoric acid possible for implementation in the phosphate industry were developed. They take into account the technological conditions of the phosphate industry and the legal requirements of Regulation (EU) 2019/1009. For the developed processes, conceptual diagrams are presented along with sample material balances. Material balance calculations were performed using the Polymath program.

The proposed solution for the removal of cadmium from phosphate ore with the addition of inorganic salts by calcination was claimed by patent application No. P 442462 dated 07/10/2022.