Waste Minimisation and Utilisation in Phosphoric Acid Industry

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The EC supported FP6 INCO Project ECOPHOS involves the development of a new research and innovation strategy for the waste minimisation and utilisation in the phosphoric acid industry. It targets the development of environmentally friendly, resource and energy saving process technology for the production of a wide class of phosphorus containing substances. The research focuses on new technologies for (a) production of useful phosphorous salts (fodder, food and pharmaceutical phosphates), phosphorous acid and phosphates in a cost efficient and ecologically sustainable way, (b) improvement of existing methods in the phosphoric acid production for the drastic minimisation of waste, (c) utilisation and processing of industrial solid waste from the production of phosphoric acid and (d) production of a new generation of phosphoric fertilizers. The new methodology targets an efficient and sustainable operation of the production systems with key objectives the reduction of cost, waste and energy.
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1. Introduction

The technology of waste minimisation and utilisation in phosphorus industry is to large extent outdated and unable to face the environmental problems. The wide class of new sustainable production technologies would bring significant changes in the environmental impact of relevant industries and furthermore increase their competitiveness. Within ECOPHOS project analysis of literature data on interaction of white phosphorous (main component of phosphorus sludge) with hydroxides brought the following results: 1) Data on interaction of white phosphorous with hydroxides solutions are contradictory and not sufficiently proved; 2) Data on specifics of interaction of phosphorus sludge (waste of phosphoric acid production) with hydroxides are practically absent; 3) Correct quantitative data on interaction reactions kinetics are obtained only for reaction of hypophosphite oxidation with phosphite formation (Zeng

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and Zhou, 1999) under conditions making these data inapplicable to the systems of interest. Kinetics of sodium phosphite synthesis from phosphorus-containing sludge has never been studied. Comprehensive collection of new experimental data is necessary for sodium phosphite (SD) synthesis development and optimisation. The reliable data are also required to for environmentally friendly and cost effective SD production process.

The literature analysis of methods of phosphorous acid production has proved that despite extensive application of phosphorous acid (as a stabilizer in polyester production, inhibitor of salt deposition in oil processing, inhibitor of salt deposition in boilers, etc) the data on phosphorous acid synthesis kinetics are practically absent. The most commonly used reaction for phosphorous acid production is phosphorous tri-chloride hydrolysis at 150-200°C (Melhem and Reid, 2006). The practical application of this reaction is limited because of high corrosion and environmentally hazardous toxic activity of the feed and reaction products. Produced acid contains impurities which are predominantly phosphoric and hydrochloric acids.

The alternative method of phosphorous acid production is based on reaction of phosphorous with iodine with formation of phosphorous tri-iodide, which is further hydrolyzed resulting in formation of phosphorous acid and hydrogen iodide (Lide, 2004-2005). HI is then oxidized to molecular iodine, which is recycled as a feed to the first stage of the process. The use of phosphorus sludge instead of expensive white phosphorous in the latter case is evidently advantageous and besides provides a solution of the phosphorus sludge utilization problem. The research carried out by the some of the project participants has extended the knowledge of kinetics of interaction of phosphorus sludge with iodine. Those data will be necessary for the achievement of environmentally friendly phosphorous acid production and waste minimisation.

Data for the kinetics of synthesis of dibasic lead phosphite-stabilizer of polymeric materials (Associated Additives, 2006) are very limited. Previous research has shown that the production of dibasic lead phosphite synthesis from sodium phosphite (produced in its turn from phosphorus sludge) is an excellent example of waste utilisation and environmental protection technology development.

Mathematical models reflecting physicochemical essence of processes of production of sodium phosphite and hypophosphite, phosphorous acid, dibasic lead phosphite are essentially absent in the literature. Such models are essential in the evaluation of alternative process flowsheets with respect to economic, environmental, sustainability and safety criteria and the rigorous calculation of the optimal conditions for cost effective production of phosphorus-containing products from phosphorus sludge. The use of accurate mathematical models with the direct implementation of advanced CAD tools for the synthesis, design and optimisation of processes would enable the achievement of the key objectives in the minimisation of waste generation and energy consumption. Those models are being developed by ECOPHOS and are incorporated into the information system. The results will become available as deliverables of potential industrial users. Practically all existing methods of sodium hypophosphite and phosphite production are patented by in the EC countries, but all these patents deal with sludge containing 30-50% phosphorous, whereas Russia and Kazakhstan possess primarily rich 50-80% sludge, thus making the patent conditions (prescribing molar ratio of reagents, feeding mode in semibatch process, etc.) inapplicable to this sludge. These conditions dictate the need for different approaches to waste minimisation and production technologies for the relevant components.

Within ECOPHOS project, a detailed quantitative description of processes under phosphates interaction with sulphuric and phosphoric acids are performed. This enables the development of accurate mathematical models covering a large variety of the developed process mechanisms. The production technology with the least consumption of resources such as energy and water and the minimisation of emissions and waste could be developed.

Environmental aspects of phosphates production are significant. Presently an effective and environmentally friendly phosphates processing is restricted by content of some admixtures influencing the processes or changing products quality. Presence of magnum, iron and some other substances typical for phosphate ores of Russian Federation, EU Baltic countries, Kazakhstan, Uzbekistan and etc. (Kijkowska et al, 2002; Potapova et al 1983) complicates phosphates decay processes and requires solution of an acute problem – the of methods which would combine enrichment phosphate raw materials with application of physical and chemical methods. This solves this challenging task. At the other side Russian Federation ores contain less cadmium than ores elsewhere. The World Health Organization indicates of inadmissibility of cadmium presence in the fertilizers and salts IPCS INCHEM (2006) . They highlight the health safety aspects of phosphorus production.

More than 60 % of phosphorus containing fertilizers are produced on the basis of extraction phosphoric acid, the main methods of its production being dihydrate and dihydrate-hemihydrate methods (Jansen et al., 1984). This Project develops technology for production of phosphoric acid from low grade raw material (phosphorites) with a large amount of impurities with new combined dehydrate-hemihydrate method without intermediate filtration. This provides more concentrated phosphoric acid yield with comparison of widely spread industrial dihydrate method. The industrial dihydrate method requires significant energy supply on 22% P_2O_5 weak acid concentration by evaporation. The proposed method also provides a clean α-hemihydrate of calcium sulphate product, which can be used in the construction as a binding material.

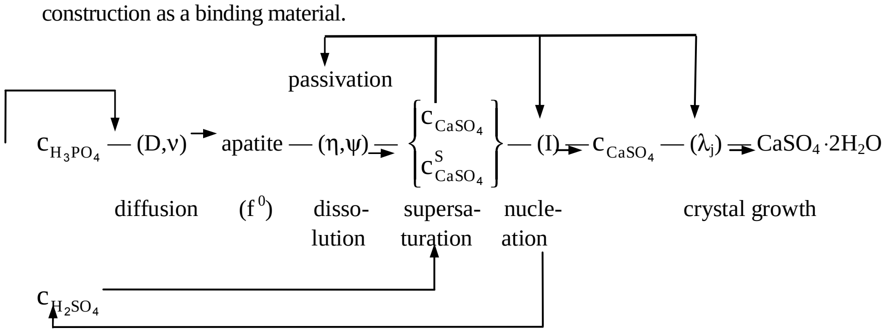

Figure 1. Scheme of physical-chemical phenomena interaction in the combined mathematical model of phosphates dissolution and calcium sulphate crystallisation processes.

2. Dihydrate Method of Phosphoric Acid Extraction

The initial part of ECOPHOS project concentrates on analysis and optimisation of dehydrate method of phosphoric acid extraction. Acidic methods of phosphorus-containing ores treatment are the main for phosphoric fertilizers obtaining. More than 60 % of phosphorus containing fertilizers all over the world is produced on the basis of extraction phosphoric acid, the main methods of its production being dihydrate method. The growing demand in high-grade fertilisers, resource and energy saving requirements result in the increase of phosphoric acid production by the wet processes compared with thermal processes (Koltsova et al., 1999).

There are two major types of wet processes: (i) single stage and (ii) recrystallization processes. Single-stage processes involve one reaction–recrystallization step. Their advantage is reliability and flexibility and they are widely applied in the industry. The most common technologies of the single-stage processes are the dihydrate (provides higher recovery of P_2O_5) and the hemihydrate processes (lower grinding requirements but P_2O_5 recovery is lower) see e.g. Samir et al (2001).

The process of phosphoric acid extraction is a concurrent process including both natural phosphates dissolution in sulphuric acid solutions and crystallization of calcium sulphate modifications (calcium sulphate dihydrate or calcium sulphate hemihydrate) depending on dihydrate, hemihydrate or dihydrate - hemihydrate methods carried out under different temperatures conditions.

The overall chemical reaction involved in the wet process is represented by Eq (1)

$$Ca_5(PO_4)_3F + 5H_2SO_4 + nH_3PO_4 + mH2O \rightarrow (n+3)H_3PO_4 + 5CaSO_4{\cdot}mH_2O + HF\uparrow \qquad (1)$$

where *n* can be 0, 1/2 or 2, depending on the hydrate form in which the calcium sulphate crystallises, *m* can be 0, 1/2 or 2.
For the calcium sulphate crystallisation description the mechanism of a homogeneous nucleation and crystals growth in the kinetic area is accepted. Scheme of the processes interaction, described by the mathematical model, is shown in the Fig. 1.

Taking into account that both processes (phosphorite dissolution and calcium sulphate crystallization) are described within the framework of ideal mixing isothermal reactor models the following equations for velocities of the main processes were developed: for phosphorite particles dissolution rate η and passivation filming rate ψ, for calcium sulphate nucleation rate I, for average rate of calcium sulphate crystal growth λ_j on linear parameters L_j.

For the description of sulphate calcium mass crystallisation and polydispersed phosphorite dissolution the equations for the particles size distribution functions were used. The particles evolution of phosphorite was examined in two-dimensional phase space with co-ordinates: l - size of phosphorite non-dissolved grain, h - thickness of the passivation film. For the crystallisation process two characteristic linear sizes of crystal L_1 and L_2 were selected as phase space co-ordinates. For description of dissolution process experimental data, received by the method of radioactive isotopes on laboratory installation were used.

The mathematical model of extraction phosphoric acid production under the periodic conditions for dihydrate process is being developed on the basis of mentioned above equations. As result of mathematical modelling the dissolution rate of polydispersed composition phosphorite, the rate of nucleation and the crystal growth rate were calculated and kinetic constants were found.

For industrial continuous process of phosphoric acid extraction the rectangular ten-sectional reactor with the working capacity of 740 m^3 was chosen as the most widely spread type of reactors used in phosphoric acid production. Taking into consideration a number of assumptions, this type of reactor can be described as the model consisting of five units of ideal mixing with the following process flow diagram (Fig. 2):

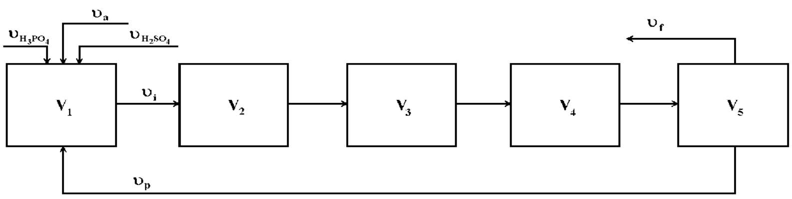

Figure 2. Process flow diagram for continuous industrial process integration

where $u_{H_2SO_4}, u_{H_3PO_4}$ - volume flow rates of the sulphuric and phosphoric acids; u_a, u_f, u_p - volume flow rates of apatite, pulp on stage of filtration and circulation; $\mathbf{V}_{1\text{-}5}$ - capacities of units, corresponding to the capacity of two adjacent sections of simulated reactor; υ_i - pulp flow into i unit of reactor model that is equal to the amount of loaded reagents.

3. Results and Future Work

As result of mathematical modelling the dissolution rate of polydispersed composition apatite, the rate of nucleation and the crystal growth rate for each unit of reactor were calculated. It has been shown that in the industrial reactor all the processes practically are over in the fifth-sixth sections (in the third unit of the model) and approximately 65% of reactor working capacity provides the theoretical capacity. This is why is important to develop extraction phosphoric acid production method which would provide the full occupation of reactor working capacity to increase the productivity and to rise P_2O_5 extraction factor. It will result in saving of raw materials and power conservation.

Within ECOPHOS project (www.ecophos.org), the phosphoric acid production method in the non-steady state technological conditions has been developed. As a control parameter for these conditions the sulphuric acid flow rate in the reactor was chosen. The developed method allows us to create two sulphate levels, corresponding to the optimum conditions of dissolution and crystallisation processes during the stay time in the reactor zone. With the help of the mathematical model the optimal values of amplitude and frequencies of sulphuric acid flow rate periodic oscillation have been obtained.

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