ECOΦOS

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ECOPHOS

Waste utilization in the phosphoric acid industry through the development of ecologically sustainable and environmentally friendly processes for a wide class of phosphorous containing products

Specific targeted research or innovation project

Specific measures in support of international cooperation – Russia and the other NIS

Publishable Final Activity Report

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1. Introduction

Project ECOPHOS involves the development of a new research and innovation strategy for the waste minimisation and utilisation in the phosphoric acid industry. The main aim is the development of ecologically sustainable, environmentally friendly, resource and energy saving industrial process technology for the production of a wide-class of phosphorous-containing substances. The project focuses on new technologies for (a) the production of useful phosphorous salts (fodder, food and pharmaceutical phosphates), phosphorous acid and phosphates in a cost efficient and ecologically sustainable way, (b) the improvement of existing methods in the phosphoric acid production for the drastic minimisation of waste, (c) the utilisation and processing of industrial solid waste from the production of phosphoric acid, and (d) the production of a new generation of phosphoric fertilizers. Mathematical models and computer-aided process engineering tools guarantee the efficient and sustainable operation of the production systems with key objectives the reduction of cost, waste and energy. The new technological advancements will be accommodated in an information system for easy access and utilisation. The newly developed production systems will be classified with respect to both the waste properties and the environmental and sustainability potentials. An expert system will assist the user to select the appropriate production scheme according to the needs and particular specifications.

The consortium is consisted of two Research Institutes, seven Universities, two engineering consulting SME, one industrial SME, and one large industrial partner from eight different countries as shown on the table below.

No	Partner name	Partner ID	Country
1	Centre for Research and Technology – Hellas / Chemical Process Engineering Research Institute	CERTH.CPERI	Greece
2	University of Manchester	UOM	United Kingdom
3	Universidad Politechnica de Catalunya	UPC	Spain
4	Firth Executive, Ltd	FE	United Kingdom
5	Phosphoric Fertilizers Industry S.A.	PFI	Greece
6	Universitaet Dortmund	UNIDO	Germany
7	Brno University of Technology	VUT	Czech Republic
8	Mendeleev University of Chemical Technology of Russia	MUCTR	Russian Federation
9	GNII “IREA” Moscow Research Institute	IREA	Russian Federation
10	St. Petersburg State Technical University	SPSTU	Russian Federation
11	OOO Promtrak	PROMTRAK	Russian Federation
12	South Kazakhstan State University	SKSU	Kazakhstan
13	OAO Sodruzhestvo-T	SODRU	Ukraine

2. Technologies for the production of sodium hypophosphite, sodium phosphite, phosphorous acid and dibasic lead phosphite

The industrial processes utilized for the transformation of phosphate ores into commercially viable phosphorous containing products also produce substantial amounts of wastes. A major type of such waste is phosphorous sludge, which can cause significant environmental damage, while it constitutes a serious fire threat for plants producing phosphoric acid through the dry method. The high phosphorous content of the sludge, ranging approximately from 30 to 80%, makes it an ideal candidate for reprocessing and transformation into useful products such as sodium hypophosphite, sodium phosphite, phosphorous acid and dibasic lead phosphite. While routes for the chemical synthesis of these products are available in published literature, major causes that prohibit their development and wider application into full-scale production processes are the hazardous and toxic nature of some of these routes (e.g. phosphorous acid through phosphorous tri-chloride hydrolysis), the use of expensive white phosphorous as a raw material instead of the freely available phosphorous sludge and the lack of dependable kinetic data, especially in view of the utilization of phosphorous sludge as a raw material. To address these shortcomings and enable the production of important phosphorous containing products by utilization of waste phosphorous sludge, research undertaken in ECOPHOS aims at:

a) The experimental study of the reaction mechanism of known chemical synthesis routes for sodium hypophoshite, sodium phosphite, phosphorous acid and dibasic lead phosphite.

b) The development of mathematical models for the synthesis of these compounds based on the experimental observations and the derivation of reaction kinetic data using these models.

c) The validation of the developed models based on the available experimental results and their potential utilization for the determination of the processing conditions that enable maximization of the obtained product yields.

d) The development of process flowsheets that can be used for the production of these chemicals in industrial scale and the determination of the equipment types and capacities required at each stage of the developed flowsheets.

e) The further development and refinement of the proposed flowsheets using a knowledge-based approach.

f) The consideration of the environmental sustainability of the proposed production methods and flowsheets by implementation of Life Cycle Analysis and Assessment techniques.

2.1 Experimental investigations and model development for sodium hypophosphite, sodium phosphite, phosphorous acid and dibasic lead phosphite.

The chemical route that was investigated experimentally for the **synthesis of sodium hypophosphite** involves reaction of the phosphorous containing sludge with a mixture of calcium hydroxide, sodium hydroxide and water. It was assumed that 9 major reactions take place during mixing of these components and based on these reactions the main by-products developed consist of sodium phosphite, calcium phosphite, dual salt, hydrogen and phosphine. The main reaction parameters that affect the yield of sodium hypophosphite involve the P:NaOH:$Ca(OH)_2$:H_2O ratio, the reaction mixture pH, the reaction temperature and the phosphorous composition of the sludge. The performed experimental studies determined that optimum reaction conditions require a 1:0.6:0.6:20 molar ratio of the four major reactants, a pH value that should not be allowed to drop lower than 11 and a temperature in the range of 85-95^{o}C. The sludge employed as a raw material for the determination of these parameters contained 68% phosphorous and it was found that the proposed conditions should only be used for a phosphorous sludge content of over 50%. Other significant observations indicated that a pH value of less than 11 leads to intense formation of phosphates and decrease in sodium hypophosphite yield, the increase of the sodium hydroxide ratio from 0.6 to 1.2 leads to increase in by-products formation and deterioration of the product yield, while it was also reported for the first time in published literature that the double salt $NaCa(H_2PO_2)_3$ also forms as an intermediate component of the sodium hypophosphite synthesis. Based on the performed experimentations, the behavior of the participating components in the proposed reaction mechanism was represented by a comprehensive set of differential equations that was subsequently solved numerically using a finite differencing method. Appropriate mathematical manipulation of the developed set of equations allowed the efficient and robust identification of the process kinetic parameters. The calculated model predictions were then compared with the available experimental data. Using suitable statistical analysis, the proposed reaction scheme and the associated mathematical model were verified to adequately describe the synthesis of sodium hypophosphite from phosphorous containing sludge.

The chemical route that was investigated experimentally for the **synthesis of sodium phosphite** involves reaction of the phosphorous containing sludge with a mixture of sodium hydroxide and water. It was assumed that 5 major reactions take place during mixing of these components and based on this scheme the preferential NaH_2PO_2 formation with liberation of hydrogen was shown as a viable route both through the polyphosphide mechanism with phosphine formation as well as the consecutive sodium hypophosphite oxidation with formation of hydrogen. Based on the performed experiments, it is observed that the product composition and yield as well as the synthesis time (time in which stationary concentrations are achieved) strongly depends on the P:NaOH ratio in the system and on the alkali solution introduction mode and can be optimized through adjusting these parameters as well as the stirring rate. The optimum values determined for these parameters are 1:2.10-2.35:15-18 for the P:NaOH:H_2O ratio, 90-100ºC for the reaction temperature and 100-150 turn/min for the reaction stirring rate. The development of the mathematical model of the process follows a methodology and solution procedure similar to the case of sodium hypophosphite synthesis. The model structure involves the reaction rates associated with the phosphorous sludge transformation as well as the amount of reacting phosphorus based on the model of phosphorus sludge destruction. Comparison of experimental and computed model predictions shows an adequate description of the experimental process by the proposed model. Furthermore, the Lyapunov thermodynamic function is used in order to determine the sensitivity of sodium phosphite synthesis to the main process parameters, selected as the concentration and the flow rate of NaOH introduced in the process. The sodium hypophosphite concentration value, unlike sodium phosphite, is sensitive to small changes in the introduced NaOH concentration and flowrate.

The **synthesis of phosphorous acid** is investigated through the reaction of phosphorous containing sludge with elementary iodine. The modeling procedure involves utilization of obtained experimental data and the development of a set of differential equations for process representation purposes, which is integrated in time with a simple Runge-Kutta method. The evaluation of the model results shows a sufficient agreement with results obtained experimentally. Furthermore, the performed experimental investigations show that during the process, the phosphorous acid formation proceeds simultaneously with phosphorous acid thermal decomposition, so that the phosphorous acid concentration passes through the maximum. To minimize the phosphoric acid content in the final solution the synthesis duration has to be limited at the moment that corresponds to the maximum phosphorous acid content in the system. The temperature dependences for phosphorous acid formation and its decomposition rates satisfactorily obey the Arrhenius law. When the process temperature increases from 15 to 45 ^{0}C the maximum phosphorous acid concentration in the system grows, while if the temperature further increases, its value decreases due to significant thermal decomposition. Following these conclusions, the developed model is employed in order to parametrically investigate the behavior of the process under different operating conditions. The reactor temperature is selected as the manipulated variable with the aim to maximize the concentration of the phosphorous acid in the final product solution. Results show that when the process is carried out at a temperature of 40-45^{O}C the time required for the phosphorous acid synthesis process to reach a maximum phosphorous acid concentration is reduced to the order of 100-115 min. The phosphorous acid produced by this method must be further purified from phosphoric acid, in order to reach the limits specified by current industrial practice.

The **synthesis of dibasic lead phosphite** involves the reaction of lead oxide with sodium phosphite in presence of acetic acid. The performed experimental investigations of the employed reaction scheme indicated agreement of the obtained results with data available from the industrial production of the dibasic lead phosphite. In this respect, research focused on the development of a mathematical model for the production of dibasic lead phosphite, which was based on the cluster theory for supersaturated solutions. The process was represented as a system of two coupled oscillators in the form of logistic-type discrete functions. The first oscillator is responsible for the dibasic lead phosphite concentration oscillations in solution, while the second is responsible for oscillations in the number of clusters. Computations of the dibasic lead phosphite crystallization processusing the developed mathematical model yielded the dynamic time dependences for reagent concentrations, supersaturation in the system, the number of clusters and the crystal distribution density. With regards to supersaturation and average crystal size, it was observed that two mechanisms are observed in the system. The first one involves increasing supersaturation with decreasing average crystal size, while the second one involves dependence of average crystal size oscillation in average supersaturation due to competition between the nucleation mechanism and crystal growth mechanism. Furthermore, the developed model was used to determine the bifurcation parameters of the system. Based on such calculations it was shown that when the reactant sodium phosphite is introduced into the system at a rate higher that the rate in which bifurcation takes place, then oscillations of different periods of both the number of clusters in solution and dibasic lead phosphite concentration emerge. The model reveals that the density of the crystal distribution function with respect to the number of included crystallized clusters may have both unimodal and bimodal character. It is further revealed that when the reactant sodium phosphite is introduced into the system at a rate lower that the rate were bifurcation occurs, the crystal size distribution is unimodal and the maximum of the distribution function is shifted towards the right part of the reaction while it proceeds. In the opposite case, the size distribution function density can be unimodal as well as bimodal. Overall, the analysis performed on the equations employed to represent the process allowed the identification of the causes of oscillatory phenomena for both the number of clusters in the solution and the dibasic lead phosphite concentration.

2.2 Development of process flowsheets and equipment

Based on the derived reaction schemes for the synthesis of **sodium hyphosphite** and **sodium phosphite** appropriate process flowsheets were developed that can be used for the industrial production of these chemicals. The production process flowsheet of sodium hypophosphite consists of several stages. The first stage involves the preparation of the raw materials that consist of phosphoric sludge, sodium and calcium hydroxide. The raw materials are separately treated in tanks under various temperature and pressure conditions in order to reach the standards required before entering the reactors. The second stage involves two reactors that are used for the decomposition of the sludge. The raw materials are introduced to the first reactor where they remain for approximately 8 hours in a temperature of 70-95°C and under a pressure of 400-1000mmH_2O. The reaction sludge is then moved to a second reactor where it remains for a further 5 hours under a constant temperature of 90°C and atmospheric pressure. During this period the sludge is subjected to agitation for 3 hours, while it is allowed to sit for 2 hours before it is further processed. Stage three of the proposed process flowsheet involves the filtration of the reaction product in a drum vacuum filter in order to separate waste solids from the produced sodium hypophosphite containing liquor. Excess sodium hydroxide is neutralized using a 9% solution of hypophosphoric acid and the produced liquor is concentrated to 57% by use of evaporation. Further filtration is invoked by use of a crystallization stage following the evaporators. Finally, suspension centrifugation is used in order to collect remaining liquors that are recycled at the second reactor. The produced crystals are dried for several hours and led to packaging.

Sodium phosphite can be produced in a process flowsheet that employs a structure similar to the production flowsheet of sodium hypophosphite. Hence details on the employed reactor scheme are only reported. The process consists of two serial reactors. The first reactor receives the raw materials, consisting of phosphoric sludge, water and sodium hydroxide and the reaction product is lead to the second reactor where it is further treated with air. The residence time at this stage is in the order of 8 hours, while temperature and pressure are 100^oC and 400-1000 mmH_2O, respectively. The reaction product is lead to a filtration process where solids are removed and the remaining solution is treated with water in a buffer tank in order to adjust its density. This density adjustment is necessary as it allows the efficient removal of phosphates through further filtering. The final product, freed of solids and phosphates, is treated with a 30% solution of phosphorous acid in water in order to neutralize the excess sodium hydroxide, therefore allowing purer sodium phosphite to be produced at the process outlet stream. Due to the few differences observed between the process flowsheets required for the production of sodium hypophosphite and sodium phosphite an integrated flowsheet for the combined production of the two chemicals was also proposed. The two flowsheets employ the same sequence of processes, therefore by varying the operating conditions and treatment agents wherever necessary it is possible to produce the two chemicals using the same processing facilities.

To achieve improved efficiency in the industrial production of sodium hypophoshite key sections of the developed process flowsheet were investigated. It was observed that the process allows the waste of heat that can be effectively recovered and utilized within the flowsheet. Several streams of the overall flowsheet were identified as targets for consideration in the performed heat integration study. Such streams involve the following: the outlet stream of the second reactor, the evaporation outlet stream, the vapor evaporation outlet stream, the evaporator condensate stream, the dryer exhaust gas stream, the calcium dioxide heating system, the sodium oxide-calcium dioxide heating system, the phosphoric sludge heating system, the phosphoric sludge decomposition system, the second reactor heating system, the air-to-dryer stream and the inlet evaporation stream. These streams were considered in a heat exchange network diagram, where hot and cold utility requirements are targeted based on the performed heat balances. Following this investigation several potential measures of improving the heat performance of the process were identified. The use of water was proposed as a heat carrier as it was expected to reduce the observed temperature differences and to participate in the process as saturated or super-heated steam, while its easy desalination makes it safe for use in the employed equipment. Furthermore, the use of plate heat exchangers was proposed as it is expected to significantly intensify the heat transfer. Potential improvements in the concentration unit were also considered by using a stirred vessel with a plate heat exchanger as a pre-heater.

The above investigation provided the means to develop an **integrated heat exchanger network of sodium hypophosphite production**. The composite curves of the sodium hypophosphite production process were plotted and the energy saving potential was illustrated. This was followed by a detailed economic analysis of the heat exchanger network retrofit design and improvements were proposed. Cost dependences were investigated in a wide interval of energy prices. The optimal ΔT_{min} of the heat exchanger network was defined and the impact of these trends was analyzed for different prices of hot and cold utilities. By use of the obtained data a grid diagram of the integrated heat exchanger network for the sodium hypophosphite production process was developed, while a principle flowsheet of the integrated sodium hypophosphite production process was constructed and evaluated in terms of economic cost performance.

The main stages of the process flowsheet developed for the **production of phosphorous acid** consist of the oxalic acid preparation stage, phosphorous acid synthesis stage, the suspension filtration and the evaporation and crystallization of phosphorous acid and sodium oxalate. The results of the performed mass balances for the proposed flowsheet are provided, while the performed discussion focuses on the evaporation and crystallization conditions. Experimental investigations indicate that during evaporation the sodium oxalate concentration increases until reaching the equilibrium point, after which sodium oxalate crystallization starts. During the crystallization process, sodium oxalate crystallization proceeds driven by a steep temperature decrease (70^0C to 20^0C), while phosphorous acid concentration increases as sodium oxalate leaves the solution in crystal form. Two parameters hinder the optimization of the evaporation process performance, namely the phosphorous acid properties that set an upper limit on further heating of the mixture and the low level of water content in the mixture that limits the process duration. On the other hand, the crystallization process conditions allow the decrease of the admixture content in the produced phosphorous acid solution as well as the decrease of the process duration by manipulating the cooling rate and the final crystallization temperature. With regards to purification of the produced phosphorous acid a comprehensive model of a batch crystallization process was proposed that consists of rate-based heat and mass balances as well as population balances addressed using the moments of distribution method. The solution of the model equations follows an iterative procedure where initial calculations are performed for the concentrations and the degrees of supersaturation and then the population balances are solved followed by mass and heat balances. The developed model was further used for the optimization of the crystallization process, where the key optimization parameters utilized were the reactor temperature, the volume of the crystallizer and the sequence and duration of the different process stages (e.g., evaporation, cooling, cooling+evaporation).

Finally, a **dibasic lead phosphite** production flowsheet was developed. At first, the optimal crystallization conditions for dibasic lead phosphite were identified, involving an appropriate sodium phosphite introduction regime to avoid large local supersaturation zones. This is accomplished by allowing several reactant feeding points, dispersive reactant introduction and effective stirring of the reaction mixture. The developed crystal size should not exceed 20 micrometers, the reaction introduction time should be greater than 20 minutes and the lead content in the precipitate should be over 81.5%. Following this investigation, the choice of appropriate commercially available raw materials was discussed and the reactions leading to dibasic lead phosphite were provided. The main stages of the dibasic lead phosphite production process involve the preparation of sodium phosphite and sodium stearate solutions, the synthesis of dibasic lead phosphite, the production of hydrophobic dibasic lead phosphite, the suspension filtration, the drying of the product and the packaging section. Detailed mass balances, processing conditions and mechanical specifications were provided for these stages and the associated production vessels involved.

2.3 Knowledge-based flowsheet development

The knowledge derived from the performed experiments and the model simulations was implemented based on the CALS (Continuous Acquisition and Life Cycle Support) concept in the **development of comprehensive flowsheets** that allows **phosphorus sludge transformation to sodium hypophosphite, sodium phosphite, phosphorous acid and dibasic lead phosphite**. The CALS concept involves the continuous information support regarding the life cycle of a product and allows the collection of complex information regarding a product, the standardization of ways to access this information as well as its correct interpretation based on international standards. In this respect data are gathered regarding the production technology of sodium phosphite and hypophosphite that include the following categories: (1); characteristics of the executed research and experimental work (2); feasibility study of a recommended production method (3); patent cards (4); characteristics of feedstock, auxiliary materials (5); physical and chemical constants and properties of initial, intermediate and a final products (6); chemical, physicochemical bases and basic production flow sheet (7); operating technological parameters of production process (8); the mass balance of production process (9); characteristics of by-products and solid waste (10); the mathematical description of technological processes and devices (11); data for calculation, designing, a choice of the basic production equipment (12); recommendations for process automation (13); the analytical control of production process (14); methods and technological parameters of purification from chemical and industrial pollutants (15); safety data sheet including fire and explosion hazard data, fire fighting procedures, health hazard data, regulatory information (16); the list of reports and recommended literature on considered technology (17). Based on the available information knowledge-based refinement and further development of potential flowsheets for the production of the considered chemicals was implemented by combining different parts of the available information.

2.4 Sustainability of process flowsheets

The **foundational aspects of a design framework for the sustainable production of phosphorous compounds** that focuses on the **Life Cycle Assessment** (LCA) of the production process has been developed. Such an approach involves the explicit consideration of numerous factors with a direct environmental impact. LCA techniques have been considered for process development and optimization, being the ultimate goal of this research to enable the discrimination between production alternatives for the same product, and given possible combinations of process schemes, to assess which one provides the best solution from an environmental point of view. This investigation has been structured following the ISO standard for environmental management (ISO14040). Goal definition has been performed, followed by data gathering, and finally impact calculation and interpretation of results has been done. Goal definition seeks the establishment of screening criteria between production alternatives for the same product, and given possible combinations of processing schemes, assessing the one showing the best performance from an environmental point of view coupled with robust planning and scheduling and safe process operations. Data was gathered from specialized literature and other partner’s experimental results in order to compile emissions inventory and resources consumption based on the use of outlet and inlet mass flows. Transport and electricity consumption was not considered at this research stage. As a result of this investigation it has been found that environmentally friendly strategies for the production of sodium hypophosphite or phosphite should be implemented aiming at reducing the consumption of raw materials, given that the production step for both chemicals is not the largest contributor to environmental impacts. Among all raw materials required for the production of P compounds, NaOH was found to be the highest contributor for most of environmental impact categories. Otherwise, the scheduling for hypophosphite production to be coupled with LCA technique has been initiated. The generated schedules take into account available production resources, raw materials and intermediate materials, while considering time constraints imposed by the sequence of the operations. Ultimately, a mandatory comparison between continuous and batch/hybrid processes alternatives will be carried out.

3. Technologies for the production of phosphoric acid and associated products

A major part of the research efforts focused on the development of technologies that will have a strong impact on the phosphoric acid production process and the products associated with it. In this respect, the performed research aimed at:

a) The development of a comprehensive mathematical model for the representation of the dihydrate phosphoric acid production process, the determination of the process behaviour through parametric analysis and the experimental investigation of the dihydrate-hemihydrate production process.
b) The design and optimization of the phosphoric acid production flowsheet with the aim to maximize the phosphoric acid production yield and minimize the generation of waste.
c) The design and optimum operation of sub-systems and utilities employed in the phosphoric acid production process.
d) The systematic consideration of sustainability issues in the phosphoric acid production process by implementation of Life Cycle Assessment techniques.
e) The experimental investigation and development of methods to enable the production of purified phosphoric acid that improve the quality of fertilizers.

f) The experimental investigation of alternative raw materials and methods that enable the production of phosphorous containing chemicals suitable for use in fodder and food.
g) The investigation of technologies for aqua-accumulating fertilizers
h) The investigation and development of efficient phosphogypsum utilization methods.

3.1 Model development and parametric analysis for the dihydrate and the dihydrate-hemihydrate phosphoric acid production methods

The development of a comprehensive mathematical model for the production of phosphoric acid using the dihydrate wet method takes into account the two major phenomena characterizing the reaction process: (a) apatite decomposition and (b) calcium sulfate crystallization. The apatite decomposition model is developed based on heterogeneous media mechanics and consists of equations describing the polydispersity of the apatite grain size, the apatite decomposition mechanism and the sulfate film formation on apatite. The proposed apatite decomposition model reveals that the rate of growth for the sulfate film on the apatite surface depends on the size of the apatite particles. Based on irreversible process thermodynamics, it has been found that the decomposition rate of apatite depends on the formation of the sulfate film. With regards to calcium sulfate crystallization, the method of moments is employed in order to estimate the calcium sulfate dihydrate distribution function with respect to particle sizes. Two main calcium sulfate dihydrate particle characteristic lengths are identified, the crystal length and width. The proposed models are applied on the modeling of a multi-section reactor for the production of phosphoric acid. Multidimensional partial derivative equations are solved in each section of the reactor, accounting for phosphate particle balances, calcium sulphate crystal size distribution function moments and component concentration dynamics. The solution procedure employed for the set of the complex differential equations representing the process is in the form of a difference-based numerical method. The obtained model kinetic parameters for the apatite decomposition as well as the nucleation and growth rates of calcium sulfate dihydrate are validated experimentally.

The developed model is employed to investigate the effect of certain operating parameters in the optimal operation of the phosphoric acid production such as varying flowrates of sulfuric acid and apatite as well recycle phosphoric acid and slurry flowrates. Based on this investigation, it was found that the optimal sulfuric acid concentration values for dissolution and crystallization processes lie in different ranges. In order to achieve maximum P_2O_5 extraction it is rational to run the process at SO_3 concentration less than 2%. However, under such conditions, calcium sulfate crystal linear sizes are sharply decreased. At SO_3 concentration > 2.5% an avalanche-like growth of apatite grain passivation starts, leading to decrease in the extraction coefficient. Additionally, the considered "critical" sulfuric acid concentration value is not a constant but depends on the solution supersaturation degree in the reactor zone. The actual calcium sulfate concentration is determined by the ratio of substance transport intensities in the decomposition and crystallization processes. In its turn, the intensity of calcium sulfate transfer to the liquid phase depends on the load per unit of the extractor working volume, the phosphate raw material reaction activity and its passivation rate. Furthermore, the dissolution process characteristics were calculated for a wide fractional composition spectrum for raw apatite and sulfuric acid concentration range. It was found that the distribution in the sections of non-dissolved apatite particles is mainly determined by the passivating film thickness and the rate variations for the basic crystallization processes at different solution supersaturation degrees. It was further shown that running the process at maximum apatite dissolution intensity will not always be rational from the viewpoint of calcium sulfate crystal face formation conditions. From these considerations it follows that the process mode optimization problem is reduced to the maintenance of a certain proportionality between the intensity of apatite dissolution, its passivation and calcium sulfate crystallization. Further work investigated the intensity and depth of P_2O_5 extraction through use of the extractor efficiency index. It was found that part of the reactor volume is passive and accounts for nearly 25% of the total extractor working volume. The presence of passive reaction volume allows realization of technical and constructive solutions aimed at their capacity improvement. The use of raw phosphate was employed as a means of increasing the reactors load. It was found that increased supersaturation degree in the liquid phase, activates sulfate film growth and homogeneous nucleation that in its turn decreases the average statistical crystal size and P_2O_5 extraction degree. In order to retain the former process characteristics at increased loads it is necessary to provide liquid phase supersaturation degree in the reaction zone in the former range. Changing of the reactant components composition along the reactor profile is possible only through variation of the recycling rate of the slurry. Another way of decreasing the supersaturation degree in the active mass-exchange process zone is using of various additives. The presence of surfactants in the system selectively influences calcium sulfate crystal surface properties, slowing down or accelerating crystal growth rate. The ability of a certain class of surfactants to selective intensification of mass transfer from liquid phase to specific crystal face surface enables to obtain calcium sulfate precipitate with high filtering capacity at loads considerably exceeding the project ones. Finally, it was proposed that the reactant concentration profile change in the reactor to meet as closely as possible the optimal conditions for dissolution and crystallization processes can be achieved by formation of two sulfate zones in the reactor volume. In this case it was found that the apatite decomposition and calcium sulfate crystallization mainly proceed under the first sulfate zone conditions. This determines the advantages and shortcomings of the methods used for organizing the process mode in the reactor with two sulfate levels.

Following the thorough investigation of the dihydrate production method, the research focus is shifted towards the simultaneous dihydrate-hemihydrate phosphoric acid production without intermediate filtration through experimental investigation of the process flowsheet. This process scheme enables the increase of the produced phosphoric acid concentration within a plant layout similar to the one employed by the dihydrate production method, while the produced calcium sulfate hemihydrate is of low imputity content, hence allowing further utilization in various applications. The investigation is performed by decomposing the process into two stages, namely the phosphorite decomposition-calcium sulfate dihydrate crystallization stage and the calcium sulfate dihydrate recrystallization into calcium sulfate hemihydrate stage. A detailed account of the followed experimental procedure as well as the layout of the utilized laboratory flowsheet is provided for both stages. A procedure targeting the effective analysis and processing of the obtained experimental data is also presented, addressing two key experimental indicators, namely the determination of the P_2O_5 and SO_3 concentrations in the liquid phase. The experiments are performed by sampling the reaction slurry and studying physical and chemical characteristics of the crystals. The results obtained at the first stage indicate that a high phosphoric acid recycle rate and low sulfuric acid load at the first stage enhance the phosphate ore decomposition phenomena and lead to a higher P_2O_5 production rate. These results as well as the observed behavior of the crystals distribution during varying phosphoric acid recycle and sulfuric acid input regimes will allow the development of a mathematical model in future work. The performed investigation in the second stage of the process flowsheet addressed the oscillation patterns observed in P_2O_5, CaO and SO_3 concentrations. In the case of CaO and SO_3 such patterns indicate that the dihydrate recrystallization into hemihydrate occurs mainly through the liquid phase. Furthermore, investigation of SO_3 concentration under varying temperature conditions showed that for high SO_3 concentration at the hemihydrate stage the dihydrate-hemihydrate recrystalization ratio is also high due to increased hemihydrate supersaturation. Experiments also showed that low P_2O_5 slurry concentration has a positive impact on the recrystallization ratio. Finally, experimental results showed that intense mixing of the reaction slurry leads to increased hemihydrate crystallization. Following the above investigation a conceptual flowsheet representation of the dihydrate-hemihydrate process was proposed. The structure and layout of the flowsheet is described, processing conditions are identified, while design details of the employed reactors are also discussed.

3.2 Systematic design and optimization framework for phosphoric acid production processes

To enable efficient utilization of the previously discussed technological developments, a comprehensive modeling and optimization framework was proposed for the design of phosphoric acid production processes. The framework concept is based on a bi-level iterative design strategy targeting the systematic development of both inclusive process models as well as optimum process schemes. Developed designs are validated based on available industrial/experimental data and account for insights emerging from interactions and trade-offs among structural and operating flowsheet options. The functionalities of the employed generic-modular RMX units are analyzed and their rich representation potential is demonstrated. This potential is fully exploited by an effective optimization framework that is based on the use of a stochastic search algorithm in the form of Simulated Annealing. The employed design and optimization approach was applied on an industrial phosphoric acid production flowsheet. The flowsheet at hand was modeled as a two-phase-per-task process and the connectivity features provided by the RMX unit representation are used to connect the reaction and filtering units. The employed optimization framework was further implemented on four extensive case studies. The case studies addressed the synthesis of simple as well as complex phosphoric acid production schemes accounting for multiple recycle and bypass streams, varying reaction and filtering topologies as well as varying processing conditions. The results obtained from the case studies showed that targets of increased process performance can be reached through a wide-ranging investigation of the available design options. Useful insights were generated in each case regarding the predictive ability of the utilized process models as well as the implementation of the proposed design alterations in the investigated phosphoric acid production plant. Design options that can be considered for implementation in the existing process flowsheet were proposed. Such designs involved process schemes similar to the one utilized by the investigated phosphoric acid production plant but operating under different processing conditions. On the other hand, designs of amplified complexity, yet increased performance, provide the incentives to further investigate these options using more detailed and accurate process models. In such cases, comparisons against the existing phosphoric acid production process in terms of key processing indices identified the limitations of the employed process models. At the same time, novel process schemes were identified and set previously unexplored phosphoric acid production targets.

A realistic representation of the phosphoric acid production process requires consideration of the uncertainty effects stemming from fluctuation of several factors that affect optimum operation of the process such as variations of the raw material composition or the temperatures in the reactors, to name a few. However, existing stochastic optimization technology is unable to effectively address the design of extensive process flowsheets. In this respect, the performed research lead to the development of a systematic bi-level approach for process optimization under uncertainty that aims to significantly reduce the number of simulations required by the stochastic optimization algorithm of Simulated Annealing after implementation of the sampling procedure. The first level of the proposed method implements a data mining technique in the form of clustering on the samples obtained from the probability distribution of the uncertain parameter. The implementation of clustering in the obtained samples leads to the generation of distinct and coherent groups of similar points representing the uncertain parameter values. A cluster centre is then defined for each cluster based on statistical criteria and this central point approximately represents the contents of the cluster. At this stage the central point of each cluster is introduced to process simulation and an objective function value is calculated for each cluster centre. The second level of the proposed approach involves using the available cluster centre points in conjunction with their corresponding objective function values to fit a continuous model that represents the objective function value as a function of the cluster centres. At this point the objective function values of the remaining sample points are calculated based on the developed model, hence avoiding the time consuming simulations. The fitted model provides objective function value predictions that are either identical or lie within very close proximity to the values calculated through simulations. The fitting of the developed model is facilitated by the beneficial cluster-inherent statistical properties as well as from efficient sampling techniques, such as Hammersley sampling, that allow uniform multi-dimensional representation of the uncertain parameter distribution. The proposed approach enables the use of constantly large uncertain parameter samples regardless of the size of the optimization problem addressed or the stage of the performed optimization search. The number of generated clusters is decided by the utilized clustering algorithm based on statistical criteria, is maintained at low, yet sufficient, sample representation levels and presents very limited variations throughout the optimization search. The implementation of clustering and model fitting are fast and computationally insignificant compared to the numerous, time consuming simulations required.

The developed framework is further exploited to address the design of cost optimal and environmentally conscious phosphoric acid (PA) production processes under uncertainty stemming from a number of process inherent as well as external factors. The industrial operation of phosphoric acid production processes is susceptible to a number of variations from external factors that must be considered during design and optimization in order to develop process schemes that will maintain a robust performance against such variations. The developed framework was adapted to account for a number of process related or external uncertainties associated with the PA production process in response to the necessity of a pragmatic representation of the PA production industrial reality within the utilized models. The developed framework employs the stochastic Simulated Annealing optimization algorithm previously developed to incorporate different uncertainties within the design of PA process flowsheets, while economic objective functions and constraints of increased detail are utilized to provide the venues for development of optimum designs closer to the industrial reality. The results obtained from the implementation of the proposed developments into three extensive case studies demonstrated the importance of accounting for uncertainties in process design. In particular, PA process schemes of improved performance were proposed for unfavorable processing conditions such as low reactor temperatures, particles of high radius entering the reactors and increased raw material prices. Results showed that the flowsheet optimization by incorporating additional structural components in the initial simplified flowsheet lead to PA process schemes of increasing robustness and reduced susceptibility to imposed external variations.

3.3 Design of sub-systems and equipment

A major sub-system that affects the operation of a phosphoric acid production plant is the evaporation and concentration unit. In this respect, a comprehensive retrofit design study of the concentration unit utilized in the phosphoric acid production process was presented based on data available from the PFI plant. The pinch analysis method is employed to develop targets for heat and cold utilities consumption improvements in the existing process. The targeted improvements were implemented through retrofit design of the existing heat exchanger network. Overall, 13 heat exchangers are required with a total surface area of approximately 2765 m^2, while the designed heat exchanger network enables an overall 25% reduction in hot and cold utilities. Network composite curves were developed to estimate the value of the necessary investment, profit and payback period taking into account the existing heat exchangers. An approximate investment of 560 k$ is required for the creation of a new heat exchange system for the phosphoric acid production plant, with $\Delta T_{min}=5°C$. The calculated annual profit is 292 k$ and payback period is approximately 1.9 years with a credit rate of 10%. The proposed heat exchange system is realized using Alfa Laval plate type heat exchangers, while detailed design data are provided on the technical specifications of the employed heat exchangers. Furthermore, a through overview of merits and shortcomings of existing evaporation methods was presented. Such methods mainly involve bubble concentration equipment, air lift units and circulating units with external tanks. Different flowsheets were also presented that employ varying combinations of such units. Each such unit presents advantages and disadvantages based on the material used in the various equipment as well as the ways that it affects the involved fouling and heat transfer efficiency. The software developed for the simulations of the heat exchange operations previously discussed was also presented as well as the theoretical foundations used for the development of the software. Based on this study, a closed loop circulation system was additionally proposed for the phosphoric acid production concentration, to improve the operation of the employed barometric condenser. In this case the installation of an additional heat exchanger is required and tests were performed using different types of heat exchangers. It was concluded that spiral type heat exchangers are the best choice due to their ability to maintain low fouling levels.

The solid-liquid nature of the processes taking place during phosphoric acid production requires appropriate heat exchange equipment. Efficient heat exchange can be achieved using plate heat exchangers rather than the usual shell-tube heat exchangers. The geometry of the channels utilized for the transfer of heat is the most important factor affecting the performance of the heat exchanger. A combination of the existing geometries in a single plate has the advantage that the heat transfer is intensified while the heat transfer area is reduced, the available pressure drop is exploited at the maximum possible level and the non-productive losses are also reduced. Therefore, a comprehensive heat exchanging model for a plate type heat exchanger was proposed that combines different channel geometries. The use of the developed model enabled the study of heat exchanging processes taking place in various locations of the PFI plant, with regards to the type of heat exchanger, the materials that are most suitable for the particular process and fouling that is caused on the heat exchanger.

The gas cleaning system utilized in the phosphoric acid production process is based on conventional scrubbing technology that requires high energy consumption. To address this issue, an innovative equipment was tested for usage in the flowsheet; namely the o-element. High mixing of the cleaning gas with the solvent stream at relatively low pressure drops make o-element a very promising and attractive unit for efficient gas separations. Models for the o-element and a Venturi scrubber were developed and results obtained from simulations revealed a definite advantage for the o-element in terms of separation efficiency and imposed pressure drop. The o-element was designed for the specific conditions prevailing in the cleaning of the gas effluent stream from the main reactor, based on data available from the PFI plant.

3.4 Sustainable phosphoric acid production

Sustainability issues were addressed in the phosphoric acid production processes through the implementation of systematic Life Cycle Assessment techniques, based on data available for the phosphoric acid plants of PFI in Kavala and Thessaloniki. A comprehensive model of the process was developed using *Aspen Plus*® simulator. Special effort was devoted to accurately represent the highly non-ideal electrolyte behaviour of the solutions that appear in the process. The process flowsheet was derived from the information provided by the partners and both the input data and the model parameters were fine-tuned to reproduce a realistic operational scenario, plant performance and operating data. The developed model was used to assess the impact of certain variables in the study of several environmental waste treatment options. The impact assessment (IA) method applied is CML 2 baseline 2000 V2.03 with normalization and weighting data sets based for West Europe, 1995. The environmental burdens were aggregated according to the relative contributions to specific potential environmental effects. Ten impact categories were considered, namely abiotic depletion (AD), global warming potential (GWP), ozone layer depletion (OLD), human toxicity (HT), photochemical oxidation (PO), acidification potential (AP), eutrophication potential (EP) and ecotoxicity to fresh water (FWE), marine (ME) and terrestrial (TE) ecosystems. The environmental impact calculations were performed both deterministically and stochastically. In the latter case a number of uncertain variables were considered such as process uncertain parameters, trace species model parameters and parameters from process units that affect the investigated plant though the broader supply chain. The obtained results in both cases indicated that abiotic depletion and marine aquatic ecotoxicity were the most important process environmental impacts.

3.5 Purification methods in phosphoric acid production

The purification of phosphoric acid from metals by treatment with diethyl-hexyl-phosphoric acid (D_2EHPhA) and active 2-ethylhexanol (2EHX) was addressed to improve the quality of the final product obtained from the phosphoric acid production process. At the same time, an integrated phosphoric acid production-purification flow diagram accounting for optimum purification conditions was proposed. Available research on phosphoric acid purification addresses the thermodynamics of the removal of a single metal from phosphoric acid-water mixtures. The performed experiments provided correlations for the simultaneous extraction of metals such as Al, Ca, Fe, Mg, Pb and As in presence of the employed reagents. The mechanism of the interactions between the metals and D_2EHPhA during the extraction process has also been identified. The limiting phenomenon in the extraction of the metals using D_2EHPhA is the molecular diffusion of the reagent towards the aqueous phase, through a phase boundary. The reaction between the reagent and the metals is determined by a cation exchange reaction that is of first order with respect to the metal concentration. The order of the reaction with respect to the reagent concentration varies depending on the mass transfer conditions and the chemical affinity between the cation and the reagent. Furthermore, it was found that the introduction of an active donor such as the 2EHX system into the extraction process improves the efficiency of the purification. This occurs by improvement of the conditions of the reagents molecular diffusion through the phase boundary due to the increase of the dissociation degree of the D_2EHPhA reagent and also the increase of the dehydration cations of metals in the aqueous phase. Following the above investigation, models of the reaction rate of the previously described metals are developed based on experimental data. The models are then used to identify the reagent concentration spans that lead to optimum reaction rates. Special attention is given to the influence of temperature on the reaction rate. Temperature variations lead to different reaction rate effects for each one of the investigated metals. Temperature increase has a negative effect on the reaction rate for metals such as Ca and Pb, while in the case of Mg temperature increase leads to increase in the reaction rate. Overall, Fe is the limiting impurity in the rate of the purification process as it has the lowest reaction rate. In view of this, the optimum concentration and temperature conditions are identified in order to allow simultaneous extraction of all the involved metals. Further investigations showed that it is possible to increase the process performance by improving the mass transfer (i.e. increasing the mixing intension, increase the reagents dissociation) or utilize a purification cascade rather than a single extractor. Based on the above findings a process flowsheet was developed that that allows the optimum purification of phosphoric acid from the previously described metals.

The purification of phosphoric acid from fluorine and arsenic containing compounds was also investigated. The performed study identified the optimum conditions of the defluorination process of phosphorus-containing solutions with sodium carbonate, with simultaneous separation of arsenic containing compounds. It was shown that the sodium carbonate content should not be over 200% of the fluorine-ion stoichiometry, while the degree of defluorination is in the order of 50-60%. The effect of the amount of precipitant as well as of the process duration was analysed and the option of a two-stage process arrangement for the purification from arsenic containing compounds was addressed. This process scheme allows the purification degree to reach 85%, while precipitating agents such as sodium pyrolusite increase the purification to 95%. Furthermore, a process of ammonization was investigated as a means of deep purification of phosphorus-containing solutions. Through this investigation it was established that fluorine containing compounds are almost completely transferred to the solid phase at a pH level of 2.5-3.0, while this is accompanied by precipitation of sequi-oxides and magnesium.

Further research efforts addressed the purification of magniferous-phosphorous containing raw material from impurities such as magnesium, iron aluminum and fluorine. The preliminary removal of magnesium compounds in acidic environments was addressed as well as the prospect of separating insoluble impurities using the flotation enrichment process. It was established that while the phosphoric acid mass fraction increases by flotation-chemical enrichment the impurities of heavy metals almost completely remain in the concentrate. It was further determined that in the extraction process of phosphoric acid there is a degree of sedimentation in the solid phase for cadmium compounds of 56-57%.

3.6 Alternative raw materials for the production of phosphorous containing chemicals used in fertilizers, fodder and food.

The Kola-apatite concentrate is investigated as a raw material for the production of phosphoric acid. This raw material has several advantages over other phosphorous containing ores, namely it contains decreased quantities of salts such as fluorapatite, the produced phosphoric acid is of lower sulphate contents, while the produced amount of phosphogypsum is significantly reduced. On the other hand the major disadvantage identified is that the produced phosphoric acid is more dilute. The chemical structure of the concentrate is investigated and a mineralogical structure of Kola-apatite poly-dispersed is proposed consisting of coarser and finer fractions. It is shown, that the currently utilized concentrate in the form of impoverished fluorapatite is enriched in hydroxydapatite, nepheline, aegirine and forsterite. In this context, it is recommended to modify the temperature and sulphur intake modes of the wet phosphoric acid production process, and to fractionate the phosphate raw material. Finally, it is shown that the cadmium contained in the Kola-apatite concentrate currently passes through the phosphoric acid production processes and goes through to the final product.

Additionally, the use of phosphorous containing ores from the Baltic Sea is proposed as a phosphorous source for the production of phosphoric acid. The proposed method involves several stages. At first, manganese is selectively extracted through a process that involves treatment with sulphuric acid and ammonium sulphates. Appropriate processing conditions for manganese extraction involve a reaction temperature of 70^oC, a retention time of 3 hours, a pH maintained at 4-4.2 etc. The extracted manganese is used in the production of manganese carbonate, while the remaining sediment is rich in phosphorous and iron salts. A method is proposed for the extraction of phosphoric salts by further treatment with sulphuric acid. Experimental determination of the optimum operating conditions is performed, while the potential of extraction of phosphorous-ferriferous fertilizers is also discussed. Furthermore, the decomposition of Syrian phosphorus containing ores is investigated as a means of producing fertilizers. The proposed process flowsheet consists of several stages that involve processing of the ores with agents such as nitric and sulfuric acid, ammonium sulfate and potassium chloride. The reaction constant and activation energy are identified for the ore decomposition stage, while a number of process operating parameters are also identified. Furthermore, research on chemical and physical characteristics of the produced fertilizers shows that they are of acceptable quality, while it is shown that major process advantages involve the low requirements is reactants and the production of reduced amounts of waste.

To enable the production of fodder and food grade phosphorous containing salts, research efforts address the synthesis of calcined phosphates by sintering of Syrian phosphorite deposits of Knefis origin. The sintering is performed at temperatures of 900-1000°C with soda-products, received from a concentrate produced from soda ash, potash and a double salt in the form of sodium-potassium carbonate. The performed investigation aims at determining the duration of the sintering process in order to exploit approximately 93-97% of the utilized phosphatic mineral and obtain fertilizers containing 22-23% of the available

P_2O_5. The level of K_2O in the calcinated product is determined by the alkaline reagent utilized during sintering which is in the order of 22-28%. The performed research establishes that the utilization of the double salt leads to intense implementation of the process for up to 1 hour, while the required temperature is lowered to 900°C. Furthermore, the production of food grade sodium tripolyphosphate from phosphoric acid produced by the wet method is investigated. The utilized process involves at a first stage stepwise increase of the phosphoric acid pH using the soda obtained from nepheline as a neutralizing agent. It is found that initially the solution is cleared of impurities in the form os sodium hexafluorosilicate and cryolite. The following stages involve purification from calcium, iron, aluminum, cerium and titanium oxides and when the remaining solution reaches a pH of 6.7 it can be used for the production of sodium tripolyphosphate, meeting the Procter and Gamble specifications. At this point the synthesis of sodium tripolyphosphate is carried out in two stages that involve recrystallization in the hexahydrate tripolyphosphite form with dissolution of water-soluble impurities and subsequent calcination at 150 to 200°C. It is found that the obtained product quality is of low pH and contains very limited amounts of impurities.

3.7 Investigation of technologies for prolonged and aqua-accumulating fertilizers

The use of super-absorbent polymers was investigated for the production of aqua-accumulating phosphorous containing fertilizers. Super-absorbents have the ability to absorb and retain amounts of aqueous fluids equivalent to many times their own weight. A super-absorbent which is used in the form of a dry powder transforms into a gel on taking up a liquid, specifically into a hydrogel when as usual taking up water. Compounds that have the chemical characteristics of super-absorbents are usually in the form of crosslinked hydrophilic polymers, graft (co)polymers of one or more hydrophilic monomers, crosslinked ethers of cellulose or starch, crosslinked carboxy- methylcellulose, partially crosslinked polyalkylene oxide or natural products that are swellable in aqueous fluids, examples being guar derivatives, of which water-absorbing polymers based on partially neutralized acrylic acid are most widely used. Synthetic superabsorbents are obtained by polymerization of a monomer solution comprising of at least one ethylenically unsaturated acid-functional monomer, at least one crosslinker, optionally one or more ethylenically and/or allylically unsaturated monomers copolymerizable with the monomer, and optionally one or more water-soluble polymers onto which the monomers can be at least partly grafted. Among the potentially usable monomers, acrylic acid is the most preferable and ideally comprises of up to 0.025% by weight of a hydroquinone half ether, such as tocopherol. The crosslinkers are compounds having at least two polymerizable groups which can be free-radically interpolymerized into the polymer network and are usually are in the form of ethylene glycol dimethacrylate and diethylene glycol diacrylate, to name a few. Furthermore, examples of ethylenically unsaturated monomers which are copolymerizable with the monomers and can be useful are acrylamide, methacrylamide, crotonamide, dimethylaminoethyl methacrylate, and dimethylaminoethyl acrylate, to name a few. Useful water-soluble polymers include polyvinyl alcohol, polyvinylpyrrolidone, starch, starch derivatives, polyethyleneimines, polyglycols etc. The polymerization is optionally carried out in the presence of customary polymerization regulators. Suitable polymerization regulators are for example thio- compounds, such as thioglycolic acid, mercapto alcohols, for example 2-mercaptoethanol etc. Continuous gel polymerization is the economically preferred and therefore currently customary way of manufacturing superabsorbents. The process of continuous gel polymerization is carried out by first producing a monomer mixture by admixing the acrylic acid solution with the neutralizing agent, optional comonomers and/or further auxiliary materials at different times and/or locations and then transferring the mixture into the reactor or preparing the mixture as an initial charge in the reactor. The initiator system is added last to start the polymerization. The ensuing continuous process of polymerization involves a reaction to form a polymeric gel, i.e., a polymer swollen in the polymerization solvent - typically water - to form a gel, and the polymeric gel is already comminuted in the course of a stirred polymerization. The polymeric gel is subsequently dried, if necessary, and also chipped ground and sieved and is transferred for further surface treatment. Superabsorbents may have a comparatively high content of fine particles which are affixed to the surface of larger particles by means of a thermoplastic melt adhesive. The phosphorous containing salts are affixed to the super-absorbents during the neutrilization step, where they are added onto the alakaline solution used as source of hydroxide in order to release phosphate ions under the chosen processing conditions. The easiest method is adding phosphoric acid or the phosphate to an aqueous solution of the hydroxide. Adding phosphate may be advantageous where equipment could be corroded by phosphoric acid. If the equipment tolerates phosphoric acid, phosphoric acid may be advantageous due to lower cost. The amount of phosphate in the alkali hydroxide used for neutralization is generally at least 1 % by weight. In principle, the upper limit is only determined according to economic considerations. Generally, the phosphate content will be not more than 10-15% by weight.

“PolyMag” is a new type of complex fertilizer named with prolonged action. The new complex fertilizer is rich in nutritious elements for the soil and furthermore due to the biogenic elements in its structure of various degrees of solubility it possesses a prolonged release of the nutrients in the soil. Experimental tests on the performance of the new type of fertilizer in spring rapeseed cultivatios showed very positive results.

1. The obtained data on the influence of "PolyMag" on rapeseed and its economic efficiency allow to grade it as a highly effective mineral fertilizer providing not only full return on investment, but also considerable profit. Application of "PolyMag" for summer rapeseed in all ranges of doses applied in the tests has been effective. Therefore to work out an optimum dose of this fertilizer in particular conditions it is necessary to take into account the whole set of soil, agrochemical, climatic and productive and economic factors.

2. Application of "PolyMag" in doses 1÷3,5 t/hectare optimizes the nutritious conditions of well cultivated soil, increasing the content of mobile nitrogen, phosphorus, sulphur, manganese and iron – by 10÷819 % that activates growth processes of rapeseed.

3. Productivity of rapeseed green mass on well cultivated soil increases up to 67,2 t/hectares, the seeds – up to 10,1 t/hectares, crude protein and fat – up to 2,47 and 4

t/hectares accordingly. A return of 1 kg o.s. of this fertilizer is 3,8 kg per unit or 1,85 roubles per 1 rouble of costs that considerably exceeds the standard fertilizer (ammoniac saltpeter).

4. Expected economic benefit from after-effects of "PolyMag" in a field crop rotation during 5÷7 years will 1,7÷ 2,3 fold surpass its direct action on rapeseed. The net profit from single entry of a dose of 1,5 t/hectares in the current prices will be ca 30 thousand rbl.

5. Industrial tests of complex mineral fertilizer "PolyMag" in the natural and economic conditions of Tatarstan for rapeseed crops confirmed its high agronomical and economic efficiency. The increase of productivity of rapeseed under 1÷2 t/hectare doses was 1,91÷3,00 t/hectare which allowed to reach profitability of 49÷ 64 % and the net profit of 5951÷7900 rbl./hectare

6. In comparable doses "PolyMag" has surpassed standard mineral fertilizers (ammonium sulphate and azofoska (nitro-phos-pot)) by 24÷41 %. With its prolonged character of action, cumulative effect (for 5÷7 years) can double the efficiency over traditional mineral fertilizers.

7. Taking into account that 120000 hectars are occupied by summer rapeseed in Tatarstan, the application of "PolyMag" can provide the benefit worth 714 to 948 million rbl. The demand in "PolyMag" will be up to 240 thousand tons.

3.8 Methods for phosphogypsum utilization

The issue of phosphogypsum utilization was investigated as a means of mitigation of a major environmental impact associated with the production of phosphoric acid. Experimental research efforts investigated the prospect of utilizing phosphogypsum in waste water treatment plants. Laboratory experiments were performed showing that the use of phosphogypsum can increase the sedimentation speed of water impurities by 5 times. A ratio of 5gr of phosphogypsum per liter of waste water has been identified as the optimum proportion, while beyond this limit the observed sedimentation is not considerable. As a result the potential use of phosphogypsum in waste water treatment settling tanks could potentially lead to the decrease of the tanks size, due to higher sedimentation speed, thus reducing the associated costs. The existence of natural radioactivity as well as heavy metals in the phosphogypsum was also considered. In both cases detailed laboratory analysis of heavy metals composition and radioactivity levels was performed and results indicated low radioactivity levels, while it was concluded that as the phosphogypsum will remain in the tanks it is not expected to cause further pollution problems.

Experimental efforts focused on the utilization of phosphogypsum as an inert filler in fertilizer production. The main advantages of this idea involve the exploitation of all the nutrients that are otherwise lost with the phosphogypsum when it is dumped as well as the replacement of the sand currently utilized as an inert material, hence avoiding damages to the landscape. Based on the performed experiments it was soon observed that the high water content of the phosphogypsum was a major drawback because it caused frequent plant shut downs due to equipment fouling and the produced fertilizers had higher water content than required, hence deteriorating their quality. It was concluded that the use of drying is inevitable in order to use phosphogypsum as inert material. Efforts to allow physical drying were of limited success due to the very low drying rates, while the implemented use of a dryer was soon abandoned due to high operating costs.

Additional experimental efforts targeted the utilization of phosphogypsum mixed with sludge from waste water treatment plants as a means of soil conditioner in areas where soils are subject to erosion. The main focus of the experiments was maintained at the determination of the composition of the phosphogypsum and the sludge in heavy metals, such as As, Cd, Cr, Cu, Fe, Hg, Mn, Zn. The performed chemical analysis of the obtained samples showed that the concentrations of the above metals were lower than the permissible limits imposed by the organizations such as the US-EPA. At the same time, the waste water sludge samples were indicated a pH in the range of 7.7 to 9, while the phopshogypsum samples indicated a pH of approximately 3.5. However, it was observed that when the two components were mixed the concentrations of heavy metals increased at higher levels than the concentrations determined for the single materials. It was concluded that the co-disposal of phosphogypsum and sludge from waste water treatment plants is an appealing option, however further experiments should be performed in order to address the problem of the increasing concentration of metals during co-disposal.

An alternative approach for phosphogypsum utilization involves the use of phosphogypsum in its hemihydrate form as a raw material for the production of cement and sulfuric acid. Two flow diagrams representing different phosphogypsum processing methods were proposed and their merits and shortcomings were discussed. Furthermore, heat integration of the flow diagrams was proposed as a means of reducing the increased energy requirements of these processes. On the other hand, during phosphogypsum processing it is possible to retrieve rare earth elements as it is reach in such substances and there is a growing market for them. In this respect, the retrieval of rare earth elements was proposed through lixiviation and a flow diagram of the process was presented.

The option of chemical transformation of phosphogypsum into ammonium sulfate was also considered during the project. In particular, the integrated design of PA and phosphogypsum utilization processes was proposed as a means of mitigating the environmental problems associated with the PA production. The employed phosphogypsum utilization process took the form of the ammonium sulfate (AS) production process that was integrated within the PA production flowsheet to investigate the generated design synergies. To achieve this, a model for the AS production process was developed and validated based on experimental data. The obtained results highlighted ranges of optimum process performance for the integrated process as well as provided useful insights regarding the synergies generated among the two processes operating within the same plant.

4. The ECOPHOS Information System

The ECOPHOS Information System (IS) is essentially a toolbox that integrates all the research efforts of the ECOPHOS partners in the form of software applications. The toolbox provides components such as a databank of alternative process flowsheets for the production technologies developed for phosphorous containing products, mathematical models for the processes involved in the flowsheets and physico-chemical data of the involved components, to name a few. The tool is intended to help the user to model and evaluate alternative flowsheets for the production of phosphorous containing chemicals, make decisions regarding the selection of the most suitable technologies and train engineers and process operators on the new technologies. In brief, the ECOPHOS IS enables the user:

- to calculate and analyse sodium hypophosphite synthesis,
- to calculate and analyse sodium phosphite synthesis,
- to calculate and analyse dibasic lead phoshpite synthesis,
- to calculate and analyse phosphoric acid production by wet method,
- to simulate phosphoric acid production,
- to simulate sodium oxalate crystallisation ,
- to apply multipurpose production operation planner (MOPP) for phosphorous industry,
- to access to the data on the major equipment types, units and their manufacturers,
- to analyse phosphoric industry waste utilisation based on CALS technology.

4.1 Incorporated Modules

The ECOPHOS IS has a modular structure that enables future developers to build a bespoke solution to cover any client particular needs. The different software modules contained in the IS are shown in Figure 1. They consist of a set of databases incorporating information on physico-chemical properties, mathematical models and process flowsheets as well as of a set of stand alone modules developed by partners and integrated into the IS. Such modules involve the MOPP recipe module for batch production of phosphorous containing products, the phosphoric acid process simulation module, the crystallization module for purification of phosphorous acid, the crystallization module for calculations associated with the sodium hypophosphite process and the CALS-based module for quality control and knowledge based design.

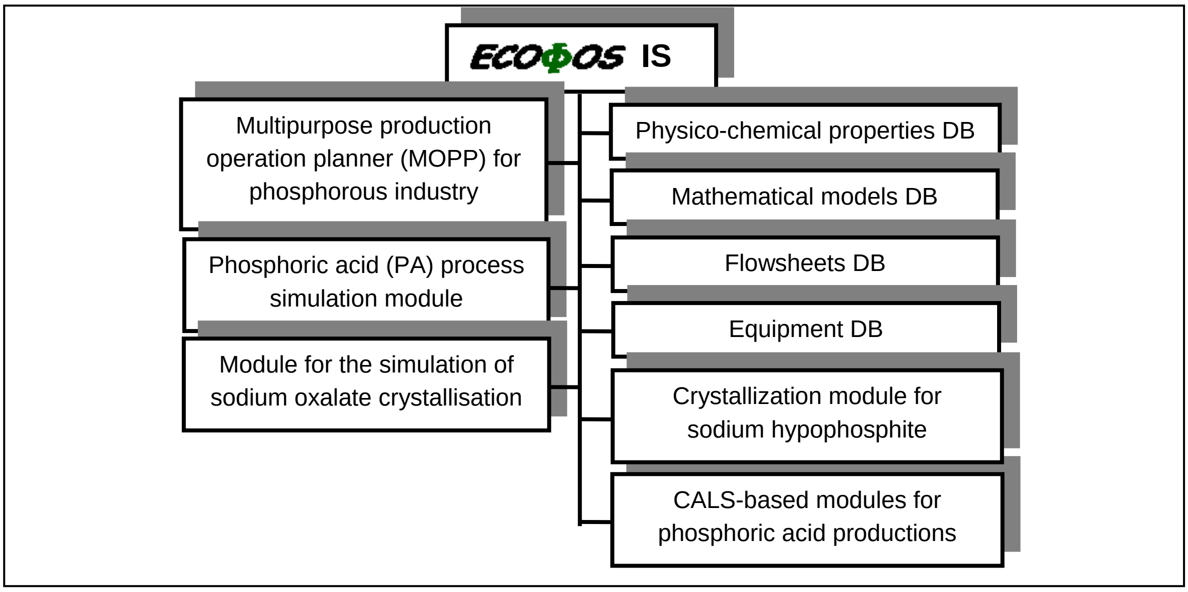
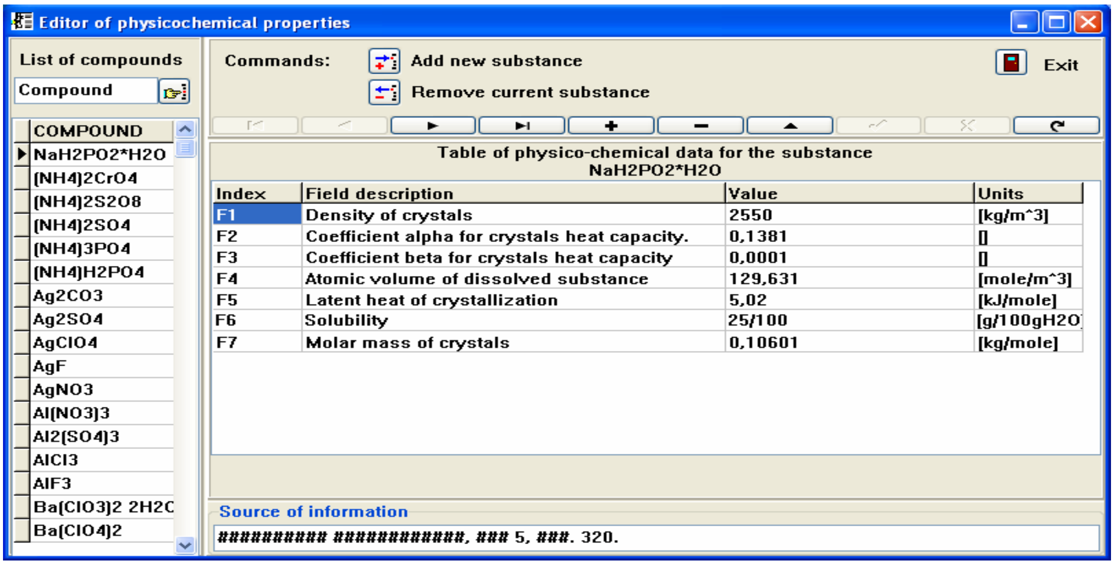


Figure 1: Components of ECOPHOS IS

The provided databases are rendered available to the user through editors that provide comprehensive information in a user-friendly manner. An example screen shot of the editor of physicochemical properties of substances is shown in Figure 2. This editor is a screen that allows to search, view, input of new and edit of already existing physicochemical characteristics of chemical substances. Typical data that can be retrieved through the editor involve densities, heat capacity coefficients, latent heat of crystallization molar mass etc. Similar editors provide information regarding the employed production process models and the process flowsheets.



COMPOUND
NaH2PO2*H2O
(NH4)2CrO4
(NH4)2S2O8
(NH4)2SO4
(NH4)3PO4
(NH4)H2PO4
Ag2CO3
Ag2SO4
AgClO4
AgF
AgNO3
Al(NO3)3
Al2(SO4)3
AlCl3
AlF3
Ba(ClO3)2 2H2C
Ba(ClO4)2

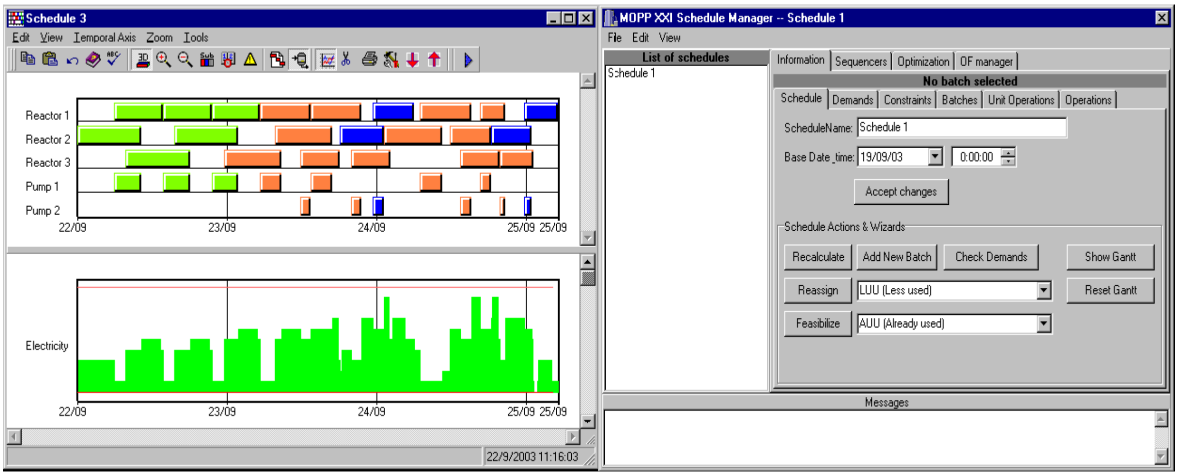
Table of physico-chemical data for the substance
NaH2PO2*H2O

Index	Field description	Value	Units
F1	Density of crystals	2550	[kg/m^3]
F2	Coefficient alpha for crystals heat capacity.	0,1381	[]
F3	Coefficient beta for crystals heat capacity	0,0001	[]
F4	Atomic volume of dissolved substance	129,631	[mole/m^3]
F5	Latent heat of crystallization	5,02	[kJ/mole]
F6	Solubility	25/100	[g/100gH2O
F7	Molar mass of crystals	0,10601	[kg/mole]

Source of information
########## ############, ### 5, ###. 320.

Figure 2: Editor of physicochemical properties

MOPP is a scheduling package developed by the CEPIMA group from the Chemical Engineering Department of the UPC. It generates a schedule taking into account available resources, raw materials and intermediate materials. It is also capable of managing and controlling changes online that can occur in a plant in real time operation. The tool is a powerful and flexible package capable of dealing with the complex scheduling cases present in industry. Its highly modular design makes it also valuable as a research tool in the field of the scheduling and planning problem as can easily be used for completely different approaches. This aspect makes it valuable for comparing different solutions of the same problem using exactly the same data model as input. Major features of the MOPP involve modular design, data model based in the ISA S88 standard from recipe to operation level of detail, embedded a standard set of sequencing and assignment algorithms, different optimization algorithms such as simulated annealing (SA), genetic algorithms (GA), ant colony (AC) and mixed stochastic enumerative search (MSES) for scheduling optimization, open framework for the development of new plug-ins, electronic Gantt chart allowing direct manipulation of the generated schedules and configuration of different objective functions (OF). Figure 3 shows two typical windows of the MOPP software.



ScheduleName: Schedule 1

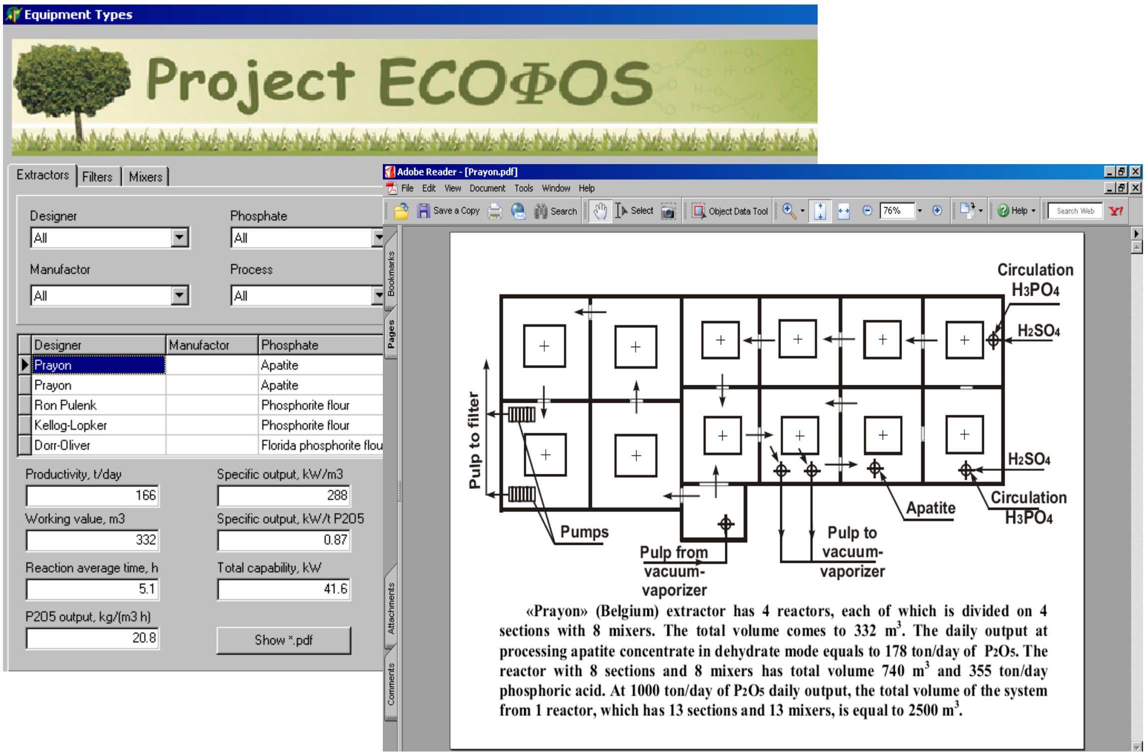
Base Date_time: 19/09/03 0:00:00

LUU (Less used)

AUU (Already used)

Figure 3: Views of the MOPP software

The equipment database module provides analytical information regarding initial treatment and supply of raw materials and reagents, extractor structures, phosphoric acid filtration, phosphoric acid concentration, evacuation and storage of phosphogypsum and utility equipment (Figure 4).



Designer: All
Phosphate: All
Manufactor: All
Process: All

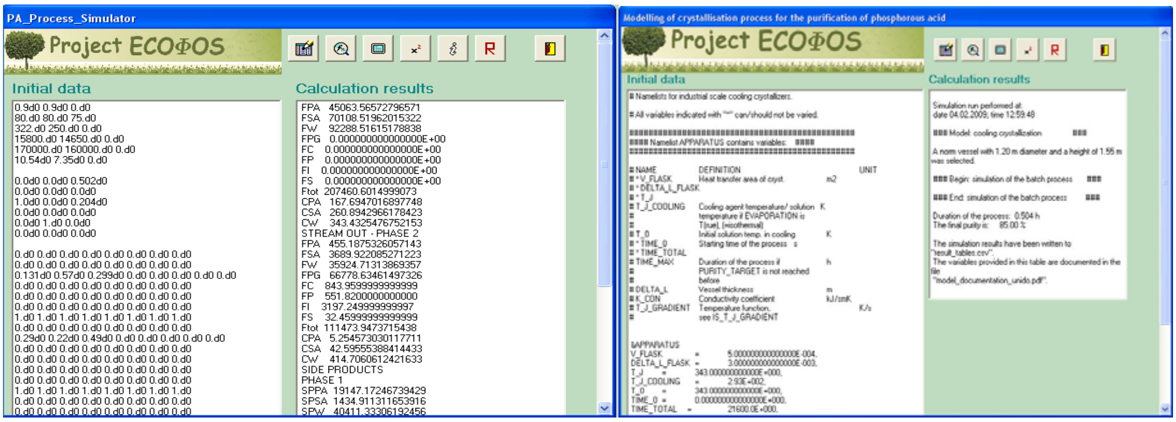
Designer	Manufactor	Phosphate
Prayon		Apatite
Prayon		Apatite
Ron Pulenk		Phosphorite flour
Kellog-Lopker		Phosphorite flour
Dorr-Oliver		Florida phosphorite flou

Productivity, t/day: 166
Specific output, kW/m3: 288
Working value, m3: 332
Specific output, kW/t P205: 0.87
Reaction average time, h: 5.1
Total capability, kW: 41.6
P205 output, kg/(m3 h): 20.8

«Prayon» (Belgium) extractor has 4 reactors, each of which is divided on 4 sections with 8 mixers. The total volume comes to 332 m^3. The daily output at processing apatite concentrate in dehydrate mode equals to 178 ton/day of P_2O_5. The reactor with 8 sections and 8 mixers has total volume 740 m^3 and 355 ton/day phosphoric acid. At 1000 ton/day of P_2O_5 daily output, the total volume of the system from 1 reactor, which has 13 sections and 13 mixers, is equal to 2500 m^3.

Figure 4: The equipment database

The developed Phosphoric Acid simulator is based on a dihydrate PA production method employed by our industrial partners that consists of two serial CTSRs followed by a filtration process. To achieve a generic representation of the connectivity among the processing components utilized in this PA production process as well as to sufficiently capture the complex multi-phase phenomena associated with PA production the simulator is based on the use of appropriate processing modules. A certain module consists of an inclusive set of equations representing mass balances for all the processes involved in a flowsheet. Several terms of the equations are linked to kinetic, thermodynamic or other phenomena taking place in the processes. By activating the appropriate terms of the equations it is possible to simulate different processes of the flowsheet through the available set of equations. These equations describe each process module in the form of compartments in different phases. Each compartment receives inlet streams within a certain phase and exchanges mass with the compartments in other phases. The mixers and splitters preceding and following the compartment-modules, respectively, act as mathematical sinks and sources of incoming and outgoing process streams, thus facilitating the interconnectivity of the modules. A view of the input and output functionalities of the software module is shown in Figure 5a.



```
0.9d0 0.9d0 0.d0
80.d0 80.d0 75.d0
322.d0 250.d0 0.d0
15800.d0 14650.d0 0.d0
170000.d0 160000.d0 0.d0
10.54d0 7.35d0 0.d0

0.0d0 0.0d0 0.502d0
0.0d0 0.0d0 0.0d0
1.0d0 0.0d0 0.204d0
0.0d0 0.0d0 0.0d0
0.0d0 1.d0 0.0d0
0.0d0 0.0d0 0.0d0

0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0
0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0
0.131d0 0.57d0 0.299d0 0.d0 0.d0 0.d0 0.d0 0.d0
0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0
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0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0
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0.29d0 0.22d0 0.49d0 0.d0 0.d0 0.d0 0.d0 0.d0
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0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0 0.d0
```

```
FPA   45063.5657279657
FSA   70108.51962015322
FW    92288.51615178838
FPG   0.000000000000000E+00
FC    0.000000000000000E+00
FP    0.000000000000000E+00
FI    0.000000000000000E+00
FS    0.000000000000000E+00
Ftot  207460.6014999073
CPA   167.6947016897748
CSA   260.8942966178423
CW    343.4325476752153
STREAM OUT - PHASE 2
FPA   455.1875326057143
FSA   3689.922085271223
FW    35924.71313869357
FPG   66778.63461497326
FC    843.9599999999999
FP    551.8200000000000
FI    3197.249999999997
FS    32.45999999999999
Ftot  111473.9473715438
CPA   5.254573030117711
CSA   42.59555388414433
CW    414.7060612421633
SIDE PRODUCTS
PHASE 1
SPPA  19147.17246739429
SPSA  1434.911311653916
SPW   40411.33306192456
```

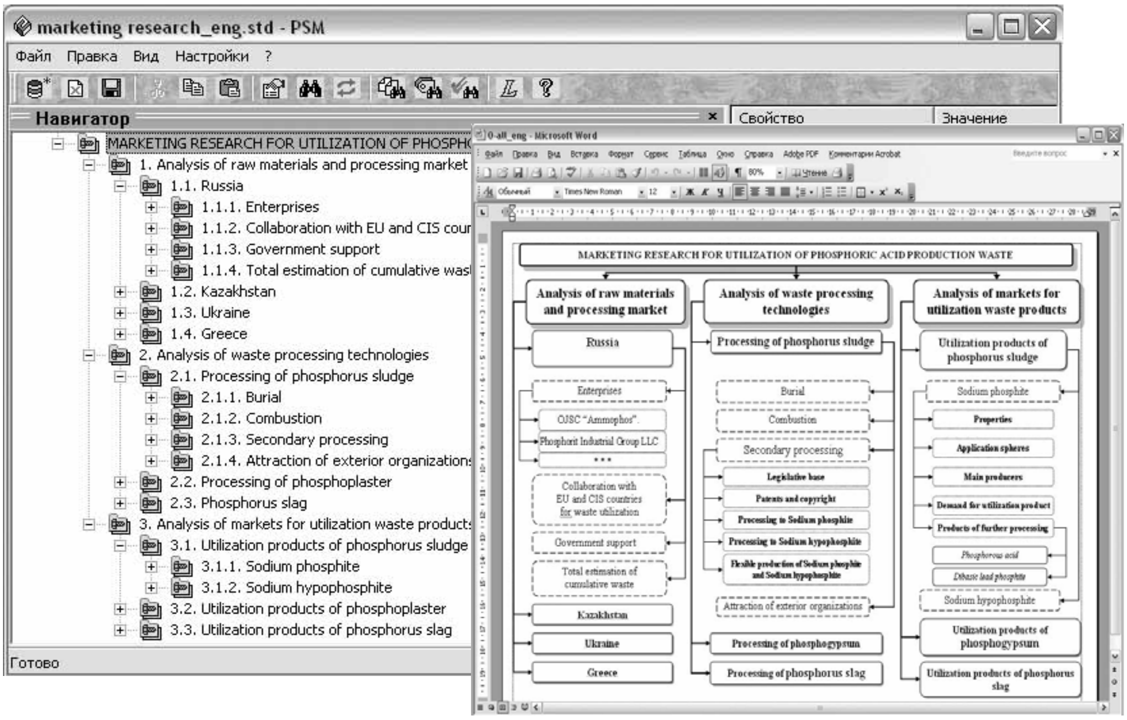
```
# Namelists for industrial scale cooling crystallizers.

# All variables indicated with "*" can/should not be varied.

##############################################
#### Namelist APPARATUS contains variables:   ####
##############################################

# NAME            DEFINITION                              UNIT
# *V_FLASK        Heat transfer area of cryst.        m2
# *DELTA_L_FLASK
# *T_J
# T_J_COOLING     Cooling agent temperature/ solution  K
#                 temperature if EVAPORATION is
#                 T[rue], (=isothermal)
# T_0             Initial solution temp. in cooling    K
# *TIME_0         Starting time of the process   s
# *TIME_TOTAL
# TIME_MAX        Duration of the process if           h
#                 PURITY_TARGET is not reached
#                 before
# DELTA_L         Vessel thickness                     m
# K_CON           Conductivity coefficient             kJ/smK
# T_J_GRADIENT    Temperature function,                      K/s
#                 see IS_T_J_GRADIENT


&APPARATUS
V_FLASK       =        5.000000000000000E-004,
DELTA_L_FLASK =        3.000000000000000E-003,
T_J      =    343.000000000000E+000,
T_J_COOLING   =        2.93E+002,
T_0      =    343.000000000000E+000,
TIME_0 =      0.000000000000000E+000,
TIME_TOTAL    =        21600.0E+000,
```

```
Simulation run performed at:
date 04.02.2009; time 12:59:48

### Model: cooling crystallization          ###

A norm vessel with 1.20 m diameter and a height of 1.55 m
was selected.

### Begin: simulation of the batch process      ###

### End: simulation of the batch process        ###

Duration of the process:  0.504 h
 The final purity is:     85.00 %

 The simulation results have been written to
"result_tables.csv".
 The variables provided in this table are documented in the
file
 "model_documentation_unido.pdf".
```

Figure 5: Input and output functionalities for the a) Phosphoric acid production process simulator and b) the sodium oxalate crystallization process simulator

The crystallization process simulator for the sodium oxalate crystallization from an aqueous solution by cooling and evaporation consists of three main steps. After all input and model parameters are read, the initial values of the concentrations and degrees of supersaturation are calculated in (1) and written to a report file. The initial solubilities and the kinetics of crystal formation result in (2). Next, the population balance can be calculated for the first time step n, and the moments of distribution are written to a report file (3). Next, the mass balance equations are solved for the second time step and concentrations and crystal mass of the this step are written to the report file (1). Further iterations can be performed. Unlike the first iteration, the heat balance is solved to calculate the temperature before the degree of supersaturation can be estimated. The simulation stops, when the process stage duration is reached. Figure 5b typical input and output reports generated from the simulator.

Finally, the CALS-based module involves the continuous information support regarding the life cycle of a product and allows the collection of complex information regarding a product, the standardization of ways to access this information as well as its correct interpretation based on international standards. A typical view of the CALS system software is shown in Figure 6.



MARKETING RESEARCH FOR UTILIZATION OF PHOSPH
- 1. Analysis of raw materials and processing market
  - 1.1. Russia
    - 1.1.1. Enterprises
    - 1.1.2. Collaboration with EU and CIS cour
    - 1.1.3. Government support
    - 1.1.4. Total estimation of cumulative was
  - 1.2. Kazakhstan
  - 1.3. Ukraine
  - 1.4. Greece
- 2. Analysis of waste processing technologies
  - 2.1. Processing of phosphorus sludge
    - 2.1.1. Burial
    - 2.1.2. Combustion
    - 2.1.3. Secondary processing
    - 2.1.4. Attraction of exterior organization
  - 2.2. Processing of phosphoplaster
  - 2.3. Phosphorus slag
- 3. Analysis of markets for utilization waste product
  - 3.1. Utilization products of phosphorus sludge
    - 3.1.1. Sodium phosphite
    - 3.1.2. Sodium hypophosphite
  - 3.2. Utilization products of phosphoplaster
  - 3.3. Utilization products of phosphorus slag

Figure 6: The CALS system

Coordinator's contact details.

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