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The System Analysis of Phosphoric Industry Waste Utilization Based on CALS-Technologies

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Wastes from the phosphoric industry are one of the key environmental problems of for manufacturers all over the world. Within the framework of European Union project ECOPHOS INCO-CT-2005-013359 we an innovative strategy for phosphoric industry waste utilization has been developed. The first stage involves the analysis of main indicators of innovative development of the phosphoric industry companies. Innovative activity of 15 phosphoric industry key enterprises in 1995-2007 were selected for this task. Development was carried out within the advanced system of computer support - CALS-technologies (Continuous Acquisition and Life cycle Support).
During the development of CALS-system of waste utilization of the phosphoric industry the marketing research of the Russian market was carried. The analysis was done according to the following three top level criteria: the raw material and processing market analysis; analysis of processing technologies; and the analysis of utilization products markets.
Within the limits of CALS concept, two basic items of phosphorus industry waste (phosphorus sludge) processing were considered: with sodium phosphite and sodium hypophosphite as final products.

Keywords: utilization, phosphoric industry, phosphorus sludge, sodium phosphite, sodium hypophosphite, CALS-technologies, ISO-10303

1. Introduction - Phosphoric Industry Wastes and Utilization

Phosphoric acid is one of the major products of the phosphoric industry. The main consumer of the phosphoric acid is the production of phosphoric and combined fertilizers. Large amounts of orthophosphoric acid are consumed by the food-processing industry. The phosphoric sludge is one of the bulk wastes in production of a phosphoric acid (Bessarabov et al, 2007). The technology of phosphoric sludge processing and obtaining of two products on its basis - sodium phosphite and hypophosphite - were entered into the CALS-project.

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Both products are in great demand. Sodium phosphite is one of the scarcest phosphoric salts. It is widely used in galvanics as a reagent for synthesis of the dibasic lead phosphite – the best stabilizer of PVC-compositions, and also as a reducer in inorganic syntheses. Sodium hypophosphite is used as a reducer in industrial processes of putting nickel, cobalt and tin coatings on metals and plastics; an antioxidant preventing decolouration of alkyd resins production, etc. The deeper processing of sodium phosphite produces: dibasic lead phosphite which is an excellent thermostabilizer working at heats and phosphorous acid applied as the reducer. All of the products are in a great demand on the market.

2.Overview of CALS-System for Phosphoric Industry Wastes Utilization

Analysis of phosphoric industry waste utilization was carried out by using an advanced computer support system - CALS-technologies (Continuous Acquisition and Life cycle Support). The basis of CALS concept is the complex of uniform informational models, standardization of access ways to the information and its correct interpretation according to the international standards (ISO-10303 STEP) (Bessarabov et al 2008).

The first stage of analysis involves the analysis of main indicators of innovative development of the phosphoric industry companies. Innovative activity of 15 phosphoric industry key enterprises (Fig 1) in 1995-2007 were selected for this task.

During the development of CALS-system of waste utilization of the phosphoric industry, the marketing research of the Russian market of phosphorous-containing production manufacturers was carried out. The analysis was made according to the following three top level criteria: (i) analysis of the market of raw materials and processing; (ii) analysis of technologies of phosphoric sludge processing; (iii) analysis of the markets of products of phosphoric sludge utilization. The whole structure of research was brought to the CALS-project.

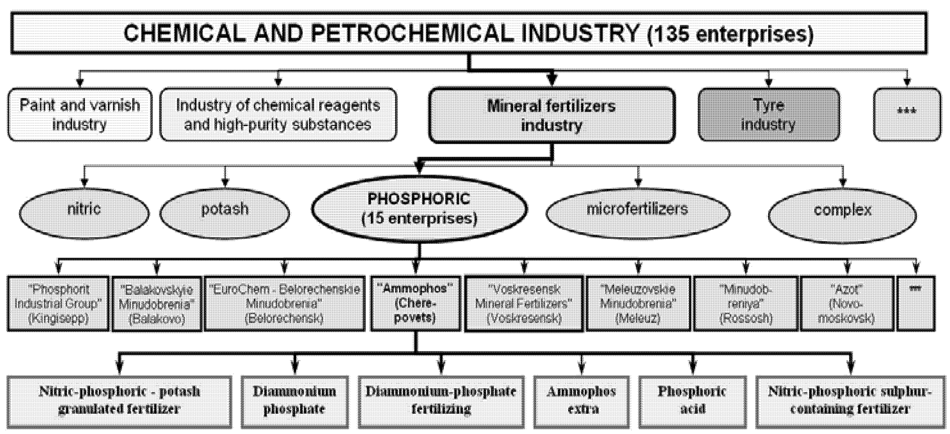

Fig. 1. The structural analysis of the phosphoric industry.

At the second stage of the CALS-project the category 'Design' was developed, in which
(i) the common data on technology are input; (ii) assignment of a target product for which production the technology was developed is done; (ii) brief data on efficiency of technology is entered; (iv) scale of experimental installations according to which the production technology was fulfilled; (v) the characteristic of the fulfilled research and development, and experimental operations is input, etc.

It was also necessary to create a category 'Production' in the CALS-project including (i) a database containing complete description of the technology of phosphoric acid waste utilization; (ii) the description, characteristics and instructions for the equipment used. Besides that, "Production" is the main source of the systematized information for manufacturers of equipment. Drawings, schemes, specifications, tables of interchangeability, the information on used materials, etc. are entered into the database.

Within the limits of CALS concept, two basic technologies of phosphorus industry waste (phosphorus sludge) processing have been considered: with sodium phosphite and sodium hypophosphite as final products. The technologies were implemented in the CALS-project. The CALS-project used a typical computer structure of initial data for design.

3. Structure of CALS-System for Production of Sodium Phosphate

On the basis of the suggested structure of the initial design data, the CALS-project for sodium phosphite production technology has been developed. The flowsheet (Fig 2) includes a preparatory stage and four basic production stages: phosphorus sludge decomposition in the reactor, filtering of a mineral part, correction of solution density, neutralization of excess of alkali in solution:

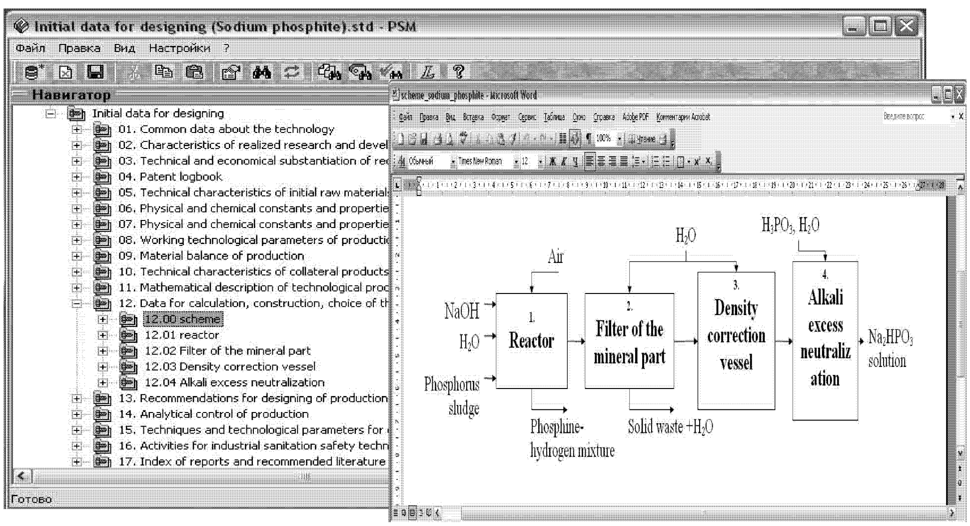

Fig. 2. An element of the CALS-project «Flow diagram of sodium phosphite production».

Preparatory stage. The phosphorus sludge is classified in a grinder by particle size optimal for interaction with sodium alkali (NaOH) and then a solution is made. In parallel alkali solution is made by diluting alkali liquor to NaOH concentration of 31 % by using water as a solvent. All stages of this process block with characteristics of the equipment as well as additional information are input in the CALS-project and are used by both developers of technology and engineering personnel.

Decomposition of phosphorus sludge in a reactor. NaOH solution is fed in reactor 1 (Fig 2), simultaneously with phosphorus sludge. The reaction is conducted at a temperature of 100°C. Upon interaction of phosphorus sludge with sodium alkali the phosphine-hydrogen mix leaves from the reactor. The obtained product solution is fed into stage 2. The corresponding process block is included in the CALS-project with all necessary characteristics of the equipment used.

Filtering of the mineral part. The solution from reactor 1 to vessel 2 is filtered. The deposit remaining on the filter is a mineral part of phosphorus sludge and it is used as a mineral fertilizer. The solution passing through filters 2 enters stage 3. Drawings of the filter, input and output parameters and other major characteristics are included in the CALS-project.

Correction of sodium phosphite solution density. The obtained sodium phosphite solution is diluted with water to a necessary concentration in process block 3. The ratio of components, temperature and characteristics of the equipment are included in the CALS-project.

Neutralization of excess of alkali. After stage 3, sodium phosphite enters a stage 4 where neutralization of excess of sodium alkali (NaOH) with phosphorous acid (H3PO3) solution is carried out.

Packing stage. Finally sodium phosphite goes to the packing stage. Types of packing and its characteristics are included in the CALS-project. The database of the CALS-project also contains the basic documents on sodium phosphite production: certificates, process regulations, characteristics of final products, performance characteristics of the equipment used, etc.

4. Structure of CALS-System for Production of Sodium Hypophosphate

Similarly to the production of sodium phosphate, the typical structure of the CALS-project has been developed for production of sodium hypophosphite. The corresponding block diagram has been developed (Fig. 3).

Preparatory stage. Phosphorus sludge with 30-50% content of phosphorus, in a liquid state, heated to the temperature 70°C, is pumped to storage tanks (receivers) with agitators.

Preparation of calcium hydroxide suspension (5) and sodium hydroxide (4) is conducted in two parallel tanks - mixers of suspension (40 м^3 volume each) heated with external pipe coil to the temperature of 50°C. Sodium hydroxide with impeller pump is pumped from intermediate storehouse to receiver tank. When the required amount of sodium hydroxide is fed, the agitator is started and feeding of calcium oxide hydrate (slaked lime) begins. The dosage of 12 tones (one batch) takes one hour. Then 12 м^3 of water is added at constant stirring and this mix is agitated in the receiver tank (6) within 8 hours.

Preparation of suspension proceeds with intense reaction and foaming. After eight-hour stirring, the mix is ready for application.

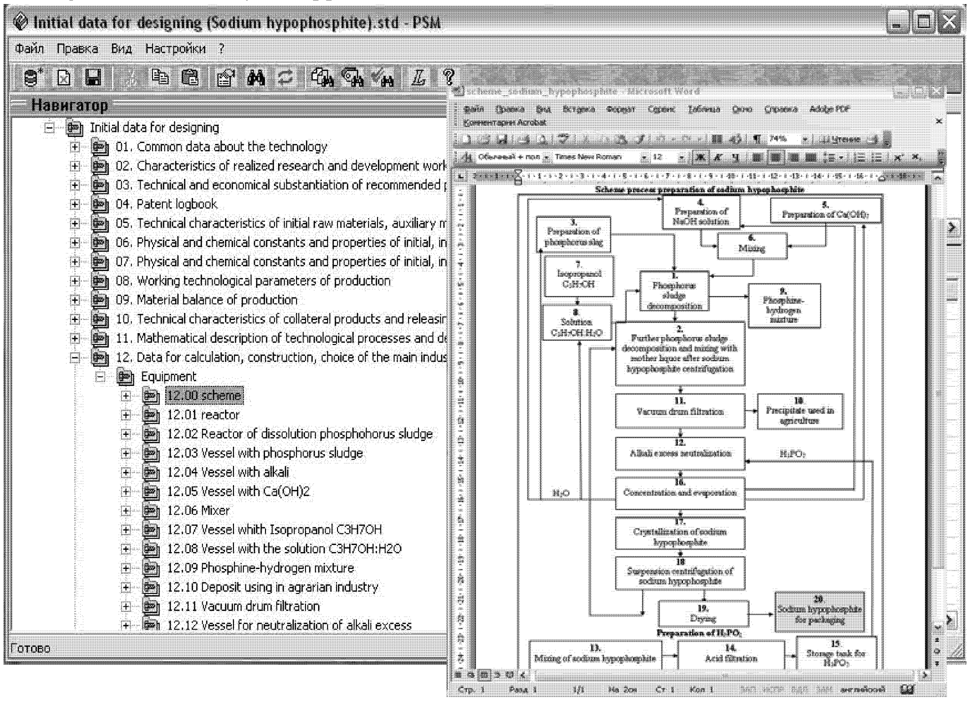

Fig. 3. An element of the CALS-project «Flow diagram of sodium hypophosphite production»).

Decomposition of phosphorus sludge in a reactor 1. The phosphorus sludge is loaded into reactor from position (3) along with the obtained solution from the mixer (6). After some time to reactor (1) the solution of isopropanol (7) is fed that is necessary for fuller extraction of phosphorus from phosphorus sludge. The reaction is conducted at a temperature of $85\text{-}90^{o}C$. Upon interaction of phosphorus sludge with sodium alkali from the reactor the phosphine-hydrogen mix leaves. The obtained product solution is directed to the next stage (2).

Further phosphorus sludge decomposition in an additional reactor (2): from the rector (1) the obtained mix is directed to reactor (2) thus mixing with a mother solution after sodium hypophosphite centrifuging. After the end of reaction, the solution from an additional reactor (2) enters vacuum filters (11).

Filtering in drum-type vacuum filters. The obtained solution from reactor 2 is filtered off in drum-type vacuum filters 11. A deposit formed at filtering is collected and used as fertilizer in agriculture. The solution passes through vacuum filters 11 enters the neutralizer 12.

Neutralization of excess of sodium alkali. After passing the drum-type vacuum filters a solution consisting of NaH2PO2 (8 %), Na2HPO3 (9 %) and CaHPO3 (25 %) enters neutralizer 12. Neutralization of sodium alkali excess is done by dilution with hypophosphorous acid which is stored in vessel 15.

Preparation of a hypophosphorous acid (H3PO2). The product solution from at stage 5 - calcium hypophosphite - with concentration of 12 % is mixed with oxalic acid. The obtained solution is filtered (14) and the hypophosphorous acid formed is stored in vessel 15 and is used as required in the neutralization stage 12.

Sodium hypophosphite concentrating. Sodium hypophosphite is concentrated (16) by evaporation for the further fine filtration which is carried out in vessel 17. The formed sodium alkali and sodium hypophosphite are directed to recycling.

Crystallization of sodium hypophosphite (17) and centrifuging of suspension (18). After crystallization 17, suspension is fed to filtration in a centrifuge. The mother solution formed is directed to recycling through an additional reactor (2). After centrifuging (18) sodium hypophosphite is dried (19) for removal of excessive moisture from the final product.

After the production cycle is finished, the product goes for packing (20).

5. Conclusions

The operation mode and constructional characteristics for each stage are included in the corresponding sections of the CALS-project. The CALS-project also contains marketing analysis results. The products considered are in great demand. Sodium phosphite is one of the most scarce salts of phosphorus. It is widely used: in electroplating, as a reagent for synthesis of dibasic lead phosphite - the best stabilizer of PVC-compositions and also as a reducer in inorganic syntheses. Sodium hypophosphite is used as a reducer at depositing nickel, cobalt and tin coatings on metals and plastic; as antioxidant preventing discoloration of alkyd resins upon their preparation etc.

The advanced innovative production development is closely connected to CALS-technologies: the use of uniform information space at all stages of the product life cycle - from design to utilization and disposal (recovery). Introduction of information CALS-technologies for productions of sodium phosphate and sodium hypophosphite enables to obtain both salts not only with high quaility characteristics, but also to provide full post-sale support including documentation in the electronic form.

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