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Technology Basis and Thermodynamic Analysis of an Acid Decomposition Process of Phosphorus Slime

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ABSTRACT

The given article contains the research results connected with the development of a technology of acid decomposition of phosphorus slime. As opposed to a known technology of manufacturing super phosphate, we have applied a double super phosphate production technology as a basis. Slime raw material is fed to both stages of acid decomposition; the first stage is sulphuric acid decomposition, and the second stage – phosphoric acid one. The basic chemistry of two step processing of phosphorus slime is described. Thermodynamic analyzes of the described reactions are given. According to the thermodynamic analysis the Law's of phosphorus slime decomposition were found. As a result the end product after phosphoric-acid decomposition contains basically $Ca(H_2PO_4)_2$, an insignificant quantity of $CaHPO_4$, water-soluble magnesium and potassium phosphates and also the insoluble residue (SiO_2). According to the thermodynamic analysis, the decomposition regularities of phosphorus slime were revealed. The ∆G0 values of sulfuric and phosphoric acids decomposition of phosphorus slime at the temperature of 600 ° C were compared.

Keywords: phosphoric slime, sulphuric and phosphoric acids, processing, super phosphate, thermodynamic analysis

INTRODUCTION

The given article contains the research results connected with the development of a technology of acid decomposition of phosphorus slime. As opposed to a known technology of manufacturing superphosphate[1-2], we have applied a double super phosphate production technology as a basis. Slime raw material is fed to both stages of acid decomposition; the first stage is sulphuric acid decomposition, and the second stage – phosphoric acid one.

The process diagram is represented in figure 1.

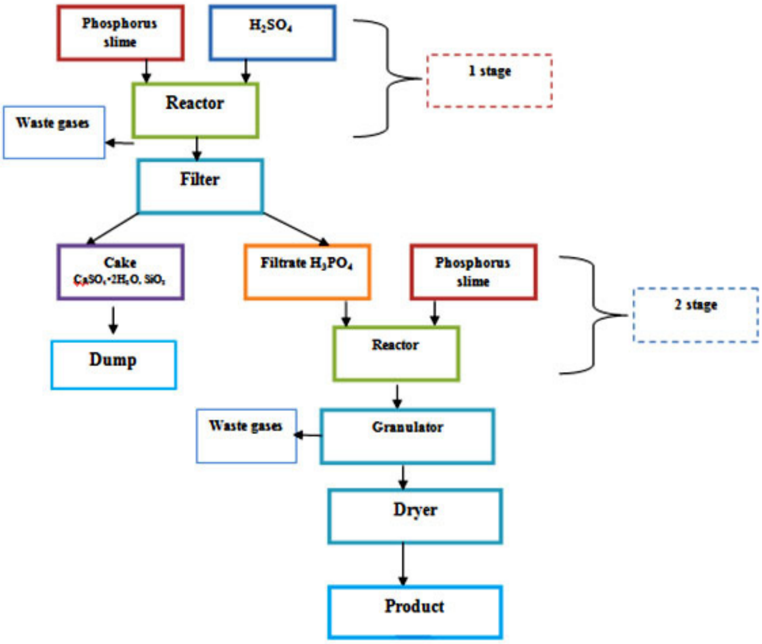


Fig. 1: A schematic diagram of acid processing of phosphorus slime into superphosphate

MATERIALS AND METHODS

Chemism of the first stage of the decomposition process (obtaining phosphoric acid) of phosphorus slime is described by known reactions:

phosphate:

$$Ca_5(PO_4)_3F + 5H_2SO_4 + 10H_2O = 3H_3PO_4 + 5CaSO_4 \cdot 2H_2O + HF \quad ...(1)$$

impurities

$$CaCO_3 + H_2SO_4 + H_2O = CaSO_4 \cdot 2H_2O + CO_2 \quad ...(2)$$

$$MgCO_3 + H_2SO_4 + H_2O = MgSO_4 + CO_2 + 2H_2O. \quad ...(3)$$

$$K_2O + H_2SO_4 = K_2SO_4 + H_2O. \quad ...(4)$$

The researches have shown, that main products of the first stage of sulphuric acid decomposition of phosphorus slime are a phosphoric acid solution with concentration of 14-17 % of P_2O_5 and a cake – the sediment containing mainly calcium sulphate and insoluble impurities (SiO_2). Thus, in the soft dihydrate regime (60 ^{0}C, formation of calcium sulphate dihydrate) a weak phosphoric acid is formed, which is fed to the second (phosphoric acid) stage of decomposition of a new portion of phosphorus slime for the purpose of obtaining a calcium-phosphate product according to the reactions:

phosphate

$$Ca_5(PO_4)_3F + 7H_3PO_4 + 5H_2O = 5Ca(H_2PO_4)_2 \cdot H_2O + HF. \quad ...(5)$$

impurities

$$CaCO_3 + 2H_3PO_4 = Ca(H_2PO_4)_2 \cdot H_2O + CO_2. \quad ...(6)$$

$$MgCO_3 + 2H_3PO_4 = Mg(H_2PO_4)_2 \cdot H_2O + CO_2. \quad ...(7)$$

$$K_2O + H_3PO_4 = K_2HPO_4 + H_2O. \quad ...(8)$$

At this stage potassium with phosphoric acid forms KH_2PO_4, which by entering in the exchange interaction with $Ca(H_2PO_4)_2$ can turn into a more acid salt – KH_2PO_4, and the phosphate anion liberated reacts with a calcium ion and forms almost insoluble $CaHPO_4$ in accordance with the reaction:

$$K_2HPO_4 + Ca(H_2PO_4)_2 = 2KH_2PO_4 + CaHPO_4. \quad ...(9)$$

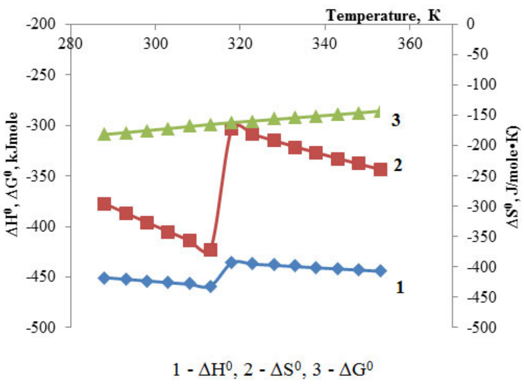
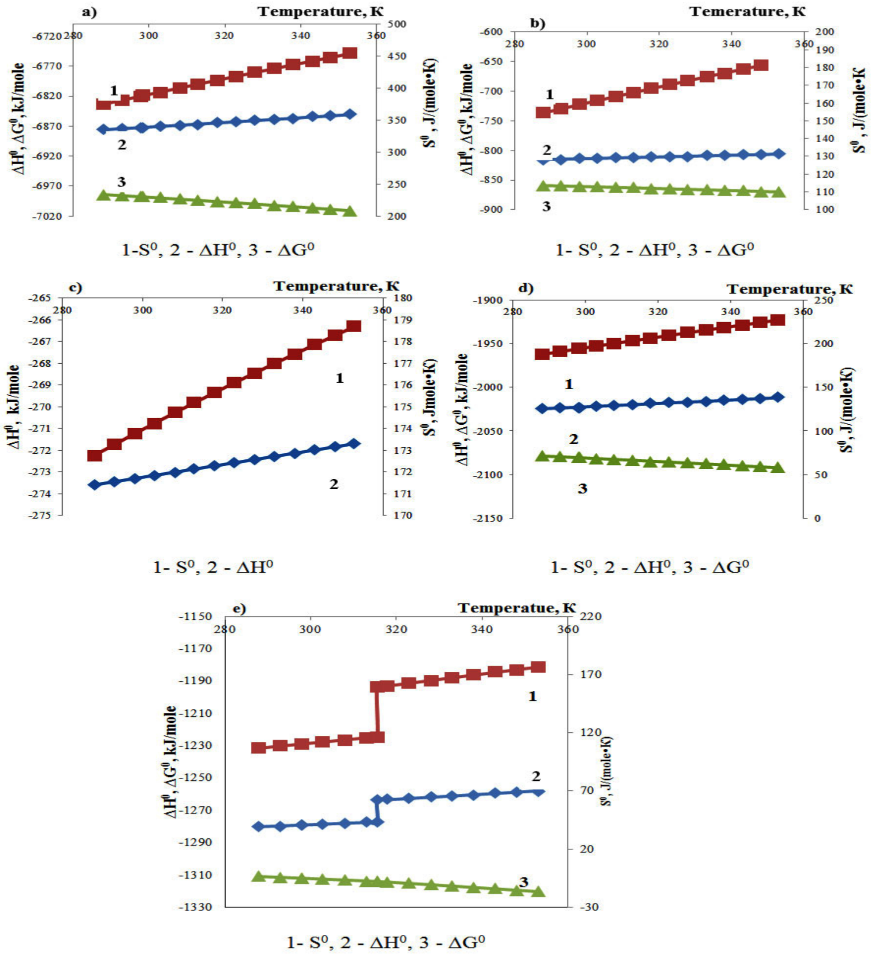


Fig. 2 : Temperature effect on thermodynamic characteristics of the sulphuric acid decomposition of phosphorus slime (reaction 1)

As a result the end product after phosphoric-acid decomposition contains basically $Ca(H_2PO_4)_2$, an insignificant quantity of $CaHPO_4$, water-soluble magnesium and potassium phosphates and also the insoluble residue (SiO_2)[3-4].

RESULTS

A thermodynamic analysis of the reactions proceeding at the acid decomposition of phosphorus slime with impurities of carbonate, acidic and alkaline compounds has been carried out with taking into account phase changes of initial components and end-products and calculation of enthalpy, entropy and Gibbs energy changes and an equilibrium constant logarithm. The calculations have been



a) – $Ca_5(PO_4)_3F$; b) – H_2SO_4; c) – HF; d) – $CaSO_4 \cdot 2H_2O$; e) – H_3PO_4.

Fig. 3: Temperature effect on thermodynamiccharacteristics of the substances in the reaction 1

fulfilled using a multifunctional software package HSC-5.1. This software program is widely applied in European universities; it has been developed by a Finnish metallurgical company Outokumpu. The program database contains information about more than 17000 substances[5].

The process thermodynamic parameters have been determined in a temperature interval of 290-353K. The calculated thermodynamic characteristics depending on temperature and foreign component composition for the guess reactions of synthesis of phosphorus- and potassium-containing mineral fertilizers are represented in figures 2-12.

Two groups of chemical reactions have been studied: the first group includes the reactions of phosphoric acid and impurities formation (reactions 1-4); the second group – formation of mono calcium phosphate and impurities (reaction 5-9).

The data (fig.2)are evidence of thermodynamic feasibility of the sulphuric acid decomposition of phosphorus slime in the investigated temperature are according to the reaction 1. The enthalpy and entropy jumps at 313K are caused by the phase changes which are taking place in the considered system.

For establishment of the jump (change) nature for dependences ΔH^0 =f(T) and ΔS^0 =f(T) we have determined temperature influence on ΔH^0 and ΔS^0 of all the reacting substances of reaction 1 according to figure3

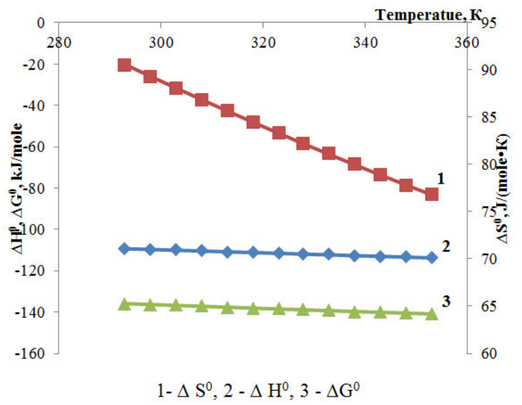


Fig. 4: Temperature effect on thermodynamic characteristics of the sulphuric acid decomposition of calcium carbonate (reaction 2)

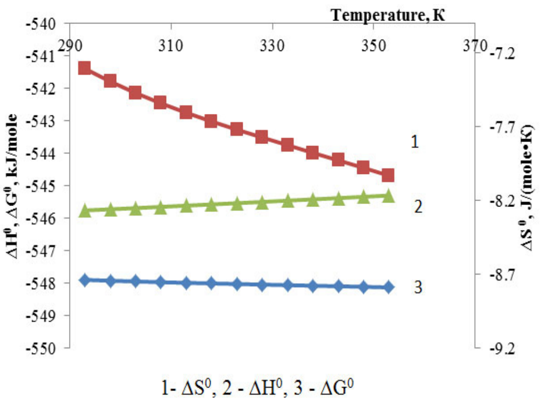


Fig. 6: Temperature effect on thermodynamic characteristics of the sulphuric acid decomposition of potassium oxide (reaction 4)

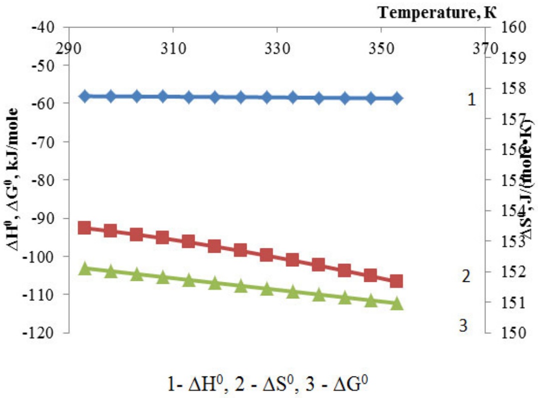


Fig. 5: Temperature effect on thermodynamic characteristics of the sulphuric acid decomposition of magnesium carbonate (reaction 3)

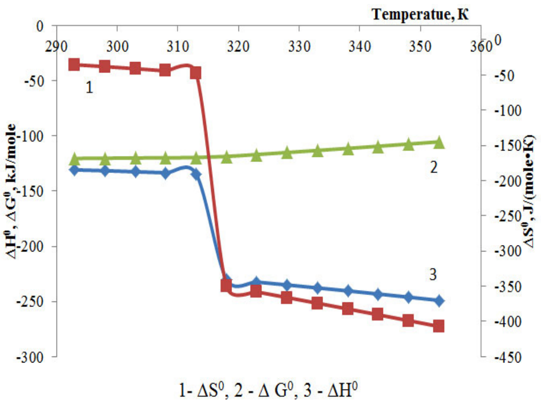


Fig. 7: Temperature influence on thermodynamic parameters of the phosphoric acid decomposition of phosphorus slime (reaction 5)

As follows from the figure 3, the observed change on the curves is connected with phosphoric acid properties. In this case there are first-type phase transitions.

The figures4 and 5 represent the thermodynamic research results of decomposition of calcium and magnesium carbonates by sulfuric acid according to the reactions 2 and 3.

Apparently the changes of thermodynamic parameters of sulphuric acid decomposition of impurity calcium and magnesium carbonates contained in the phosphorus slime have identical nature. Values of ΔG^0 in the investigated temperature range are in a negative area; it proves thermodynamic probability of the reactions 2-3.

The thermodynamic research results of potassium oxide sulphuric-acid decomposition in accordance with the reactions 4 are represented in fig.6.

As follows from this figure, Gibbs energy in the considered temperature interval has negative values, and it testifies to thermodynamic probability of the reaction 4[6].

Judging by comparison of the ΔG^0 values for the first reaction group we can say that from the thermodynamic point of view the probability of these reactions (at temperature 333K) changes in the following sequence: $K_2O > Ca_5(PO_4)_3F > CaCO_3 > MgCO_3$.

At the same time all the reactions of the given group are exothermal because of corresponding ΔH^0 have negative values.

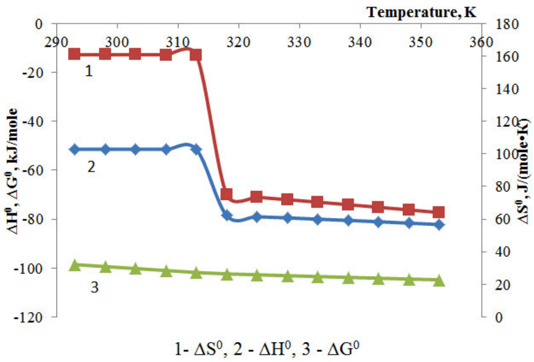


Fig. 8: Temperature influence on thermodynamic parameters of the phosphoric acid decomposition of calcium carbonate (reaction 6)

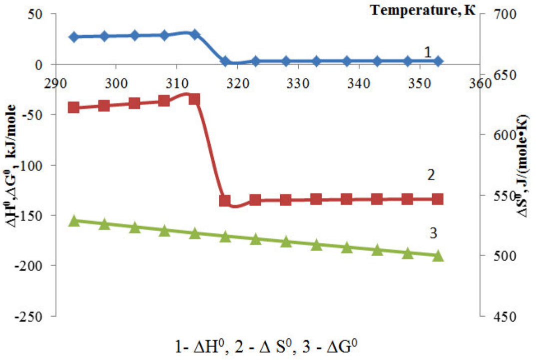


Fig. 9: Temperature effect on thermodynamic parameters of the phosphoric acid decomposition of magnesium carbonate (reaction 7)

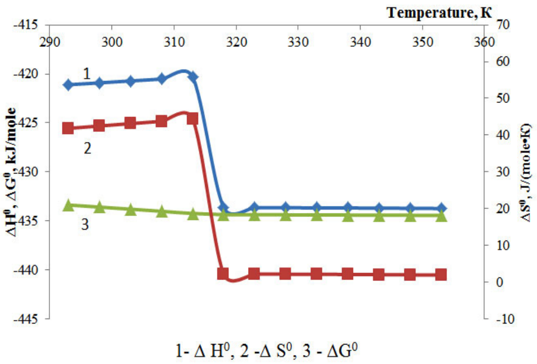


Fig. 10: Temperature effect on thermodynamic characteristics of the phosphoric acid decomposition of foreign potassium oxide

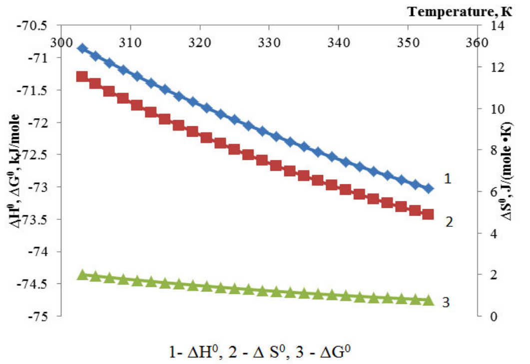


Fig. 11: Pattern of change of thermodynamic parameters of potassium and calcium phosphate interaction (reaction 9)

A dependence of thermodynamic parameters of the phosphoric acid decomposition of phosphorus slime (in accordance with the reaction 5) on temperature is represented in fig.7.

The results confirm thermodynamic probability of the reaction of phosphoric acid decomposition of the phosphate part of phosphorus slime in the investigated temperature area.

The observed jumps of enthalpy and entropy at 313K are caused by the first-type phase change, which occur in the phosphoric acid structure.

Figures 8 and 9 represent results of the thermodynamic research of calcium and magnesium carbonates decomposition by phosphoric acid (reactions 6 and 7).

As follows from the figures 8 and 9, the changes of thermodynamic parameters of processes of phosphoric acid decomposition of foreign components contained in the phosphorus slime – calcium and magnesium carbonates – have the same nature. Values of ΔG^0 for the reactions 6-7 in the investigated temperature range are in a negative area; it proves thermodynamic probability of the given reactions.

Results of the thermodynamic research of the processes proceeding according to the reactions 8 and 9 are represented in fig.10-11.

As follows from the data of the figures 10 and 11, the reactions 8 and 9 in the considered temperature conditions are realizable[7].

Proceeding from the received ΔG^0 values it is possible to conclude, that the basic substances of the second reaction group react with phosphoric acid in the following sequence: K_2O>$MgCO_3$> $Ca_5(PO_4)_3F$ >$CaCO_3$.

Thus, it has been established, that from the thermodynamic point of view the reactions 1 and 5 of acid decomposition of the phosphate part of phosphorus slime and the reactions 2, 3, 4, 6, 7, 8 and 9 describing the impurity components decomposition are probable.

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