

## THE WAYS TO PREVENT FORMATION OF WATER - SOLUBLE FLUORINE COMPOUNDS WHEN PRODUCING PHOSPHATE FERTILIZERS

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### ABSTRACT

Natural phosphate raw materials contain up to 3.5% of fluorine. In reprocessing natural phosphate raw material 30 - 100 % of fluorine emits into the environment as toxic compounds. The acid is used for decomposing the carbon dioxides that are contained in raw materials. The way and technology of obtaining the phosphate fertilizer has been offered. This technology provides for using the carbonic acid instead of strong acids. Thus, it is possible to exclude formation of water - soluble fluorine toxic compounds and use of the acid for decomposing carbon dioxide.

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**KEY WORDS:** Phosphate raw material, fluorine toxic compounds, carbonic acid.

### INTRODUCTION

Scientific and technological progress in all fields of industry and economy put in the forefront environmental protection. Technological progress changes many technical processes, develops productive forces and new territories of the planet. At the same time, it sharply influences all spheres of the Earth - the biosphere, lithosphere, hydrosphere, atmosphere, stratosphere.

Increase of population and its welfare brings about intensification of agricultural production, which, for the last 30-35 years, has been reached due to the use of mineral fertilizers, among which phosphates have a special role, but not by expanding the arable land. This is because phosphorus and its compounds play essential role in the life of plants and animals, as well as because efficiency

of the nitrogen and potassium fertilizers drastically gets worse when phosphorus is absent or lacking in the soil (Kiperman, 1998; Kharikov and Smetana, 1999).

World production of phosphorus, calculated by  $P_2O_5$ , reached 141.3 million tons in 1996. This determined ingress to the environment of approximately 6 million tons of phosphorus in the form of water-soluble toxic compounds. It is absolutely clear that present acid processing of phosphate raw material is the source of toxic contamination of the environment.

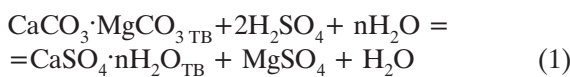
At the same time, fluorine toxic compounds enter into environment when obtaining and using phosphoric fertilizers. They are the plasmatic poisons. Maximum permissible concentration of fluorine in settlement air is  $0.1 \text{ mg m}^{-3}$ , and in the water for

industrial and/or domestic use is 1 mg l<sup>-1</sup>. It is supposed that in the presence of phosphorus, fluorine comes into the complex compound with the biocomponents (Mg, Mn, Ca, Fe etc.). As a result, the carbonic exchange is broken: suppress glycolysis and form of pyrogrape and milk acids and tissue breath is oppressed (Book for Chemist's Engineers, 3 vol., 1976). While falling water-soluble fluorine compounds together with downpour waters to ponds, water pauperization of biocomponents necessary for life takes place, the possibility of getting toxic compounds to the man's food appears.

Let's consider the reasons of water-soluble fluorine compounds forming in the phosphoric fertilizer production and the way of its elimination.

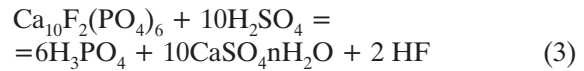
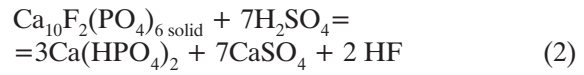
### THE FORMATION PROCESS OF THE WATER - SOLUBLE FLUORINE COMPOUNDS

Natural phosphoric ores from different deposits are differed in physical and chemical properties depending on mineralogical mixture, structure and dirt contents (Pozin, 1974). They are subdivided into two main kinds - apatite and phosphorite ores. The phosphoric substance in both kinds of raw material is minerals of apatite group with the general formula 3M<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>CaX<sub>2</sub>, where M is mainly represented by calcium which can be isomorphically substituted by strontium, rare-earth metals and other components; X is represented by fluorine, chlorine and hydroxyl group. Non-phosphate part of phosphorites contains usually nepheline (NaK)<sub>2</sub>OAl<sub>2</sub>O<sub>3</sub>2SiO<sub>2</sub>nH<sub>2</sub>O, tiff CaCO<sub>3</sub>, dolomite CaCO<sub>3</sub>MgCO<sub>3</sub>, glauconite, silicates and other impurities dirties, which complicate the natural phosphoric raw material processing (Pozin, 1974).



The most quantity of phosphoric ores is used for mineral fertilizer manufacture by transferring the natural phosphoric calcium compounds of water insoluble and soil solutions to the soluble state. The most widespread in natural ores is calcium-

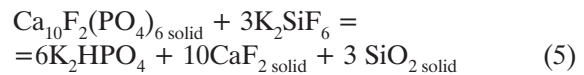
fluorineapatit Ca<sub>10</sub>F<sub>2</sub>(PO<sub>4</sub>)<sub>6</sub>, which in the chemically clear state has 3.77% of fluorine. Substantially the natural phosphate raw material is reprocessed into phosphoric fertilizers by the following main equations of chemical changes



The formed fluorohydrogen acid interacts with the phosphate raw material impurities (substantially with a silicon dioxide, sesquialteral compounds of oxides and alkaline metals) and forms water-soluble fluorine toxic compounds, which is contained in base products from 0.6 up to 2.5 % (Zaytsev, 1982).

### RESEARCH

Decomposition of the natural phosphate raw material by the silicofluoride with getting phosphate fertilizer allows almost completely excluding the yield of the toxic phosphorus compounds in the gas phase and end products. As a result of the reaction:



insoluble calcium fluoride is created that can't harm the environment (Denzanov, 1977).

Transformation of the apatite into soluble compounds (when pH is decreased) explains the possibility of the natural phosphate raw material to be decomposed by the silicofluoride. The first ionization constant of carbonic acid is K<sub>1</sub>=4.5×10<sup>-7</sup> that corresponds pH=4.6.

This implies, that decomposition phosphate raw material by a coal acid is possible at the expense of decrease pH. At that time calcium fluoride decomposition according to the reaction:

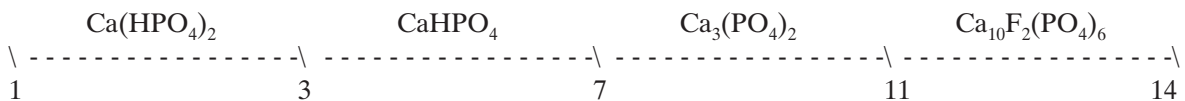
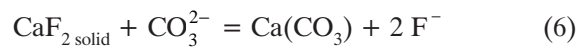


Figure 1. Diagram of existence zones of calcium phosphate at different pH.

Table 1. Phosphorite chemistry, %

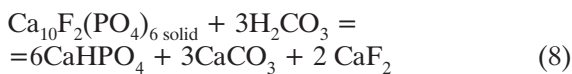
P <sub>2</sub> O <sub>5</sub> common	P <sub>2</sub> O <sub>5</sub> assimilable	CO <sub>2</sub>	F	R <sub>2</sub> O <sub>3</sub>	MgO	H <sub>2</sub> O
33.0	23.4	6.6	3.6	0.8	1.3	1.5

is unlikely as the Gibbs potential equals + 8.6 kilojoule mole<sup>-1</sup> and respectively the equilibrium constant according to the equation (7) is insignificant:

$$\ln K = -\frac{\Delta G}{RT}; \quad K=1.82 \times 10^{12}, \quad (7)$$

where  $G$  is the Gibbs potential;  $R$  is a gas constant;  $T$  is the temperature, K.

This can be carbonic acid and natural phosphate raw material decomposition should be running with formation of insoluble calcium fluoride:



Equilibrium constant of the given reaction in the standard conditions is:  $K=1.82 \times 10^{12}$ . Quite large value of the equilibrium constant of this reaction points at its possible practically complete passage. The speed of apatite decomposition by the acids with formation of new solid phases depends on difference in activities (concentrations) of hydrogenous ion in a certain amount of solution and near the surface of the phosphate seeds. The kinetic equation has the following look (Yachontova, 1988):

$$Y = KDS[a_1 - a_2]/\delta, \quad (9)$$

where  $K$  is a constant that depends on the temperature and hydrodynamic conditions;  $D$  is the diffusion coefficient;  $S$  is specific surface of the phosphate;  $a_1$ ,  $a_2$  are activities of hydrogenous ions in a certain volume of the solution and near the surface of the phosphate seeds;  $\delta$  thickness of the reaction products layer.

Comparing to sulfuric acid (ionization constant  $K=1.2 \times 10^{-2}$ ) the activity of carbonic acid hydrogenous ions is approximately 150 times lower. It means that in the same conditions the reaction speed will be lower by the same number when using carbonic acid. It is possible to increase the reaction speed (as seen from equation (9) by increasing the specific surface of the phosphate. Specific surface of the phosphoric ores of the aqueous origin is 1-2 times larger as to compare it to apatite ores of the abyssal origin. Taking this into consideration, kinetics investigation and development of the ecologically clean technology of getting phosphatic fertilizer was conducted using Algerian phosphorites which have standard milling (aperture residue not more 14%, screen aperture is 15 mm).

During decomposition of phosphate the water cut has the large significance. The experimental data of water influence on transition of phosphorus compounds in assimilable form by plants in the phosphorite processing by carbon dioxide are indicated in Table 2 and in Figure 2. In our opinion, it is explained by increase of coal acid activity with decrease of a share-connected phosphorite of water. According to the technology that we're developing for production of the phosphatic fertilizer with the carbonic gas as an acid using, high decomposition coefficient (not less 95%) of the Ukrainian and Moroccan phosphorites is reached in three hours with the power inputs of about  $5 \times 10$  kilojoules per one ton of the phosphate fertilizer [Denzanov, Molchanov, 2000].

Analysis of the water extract of the received fertilizer as to the fluorine content showed that dissolubility of the fluorine compounds in the fertilizer

Table 2. Dependence of ratio the assimilable P<sub>2</sub>O<sub>5</sub> to common from water cut in reactionary mixture

P <sub>2</sub> O <sub>5</sub> assimilable/ P <sub>2</sub> O <sub>5</sub> common	0.71	0.78	0.88	0.93	0.96	0.97	0.98	0.98
H <sub>2</sub> O, %	1.5	5	10	15	20	25	30	35

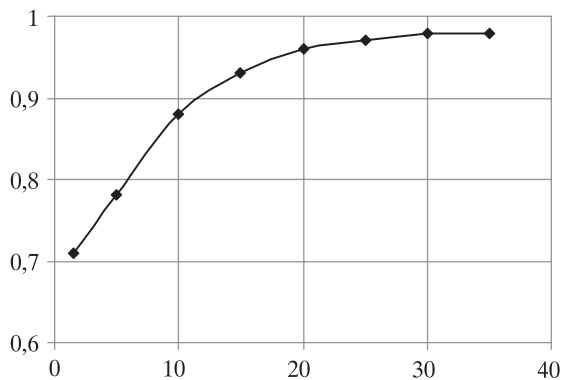


Figure 2. Dependence of ratio the  $P_2O_5$  assimilable/  
 $P_2O_5$  common from water cut

approximately equals the dissolubility of the calcium fluoride. And this means that when using this fertilizer harm to the environment is excluded.

## DISCUSSIONS

Natural phosphate as raw material contains fluorine. The fluorine toxic compounds are obtained when modern methods of processing are used. The unauthorized release of those into environment is dangerous for people's health. In order to exclude formation of fluorine toxic compounds, it is necessary to substitute the phosphate of strong acids by weak acid, such as the carbonic acid.

The use of a carbonic acid leads to a decision of one more important ecological problem. The possibility of changing the global climate because of the growth of concentration of carbonic gas  $CO_2$  in atmosphere at the expense of economic activity of man was recognized in the documents of the

World Meteorological Organization in 1976-1977 [Butiko, 1979]. For the production of 1 million kilowatt-hour of electrical energy on a thermal power station burning coal approximately 2 thousands of tons of a carbonic acid will be produced. The ingress of carbonic gas to atmosphere promotes development "greenhouse effect". One from paths of reduction of ingress  $CO_2$  to atmosphere can be a path of use of carbonic acid formed by burning of fuel, for production of mineral phosphoric fertilizers. The prevention of ingress to atmosphere of the order 45 million tons of  $CO_2$  per one year is possible by using a coal acid instead of a sulfuric acid.

## CONCLUSIONS

The present work offered the environmentally appropriate technology of opening natural phosphate raw material with production of mineral fertilizer which does not contain water - soluble fluorine compounds. It is reached by processing the water soliquid of phosphorite by the carbonic dioxide. The industrial realization of this technology in phosphate fertilizers producing can allow excluding the possibility of turning insoluble fluorine compounds from the natural raw material into soluble ones. Also this prevents formation of fluorine toxic compounds and their ingress in the environment. It is possible to get ecologically clean phosphate fertilizer and decrease the entrance of poisonous carbonic gas into the atmosphere, by means, of substitution of strong acids for carbonic gas in the technology of the phosphate fertilizer.

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