THE POSSIBILITY OF THERMAL PHOSPHATE DECOMPOSITION IN A LOW-TEMPERATURE PLASMA JET

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The possibility of using plasma jets in the production of phosphorus-containing materials is demonstrated. A description is provided of the laboratory installation, the operational procedure, and the preliminary experimental data for the process of decomposing phosphorites in a plasma jet.

The processes occurring in phosphorus-containing materials subjected to heat treatment are of particular importance in the technology of their production. The melting of natural phosphates or the sintering of the latter with various additives results in the breakdown of the stable fluorapatite lattice – compounds insoluble in citric acid. With rapid cooling of the melt, the fluorapatite is unable to crystallize completely, and the resulting compounds based on α-$Ca_3P_2O_8$ and $Ca_4P_2O_9$ are soluble and contain from 20 to 35% P_2O_5, with the assimilated portion amounting to 90-98% of the total quantity of P_2O_5.

There has been a substantial upswing in the interest shown in the study of these processes at the present time, and this is due to the tremendous successes achieved in the field of high-temperature processes and equipment, particularly in the light of the promising application of a low-temperature plasma as the heat source for the heating of phosphorus-containing substances.

In using plasma jets, in addition to the melting process, we find significant interest in investigating the possibility and feasibility of direct dissociation of natural phosphates under high-temperature conditions to produce the phosphoric anhydride. Here we can avoid the stages of phosphate reduction with carbon, as well as the sublimation of the phosphorus, and its oxidation. The obvious advantages of such a process lie in the fact that it involves but a single stage and also in the fact that there is no need for a reducing agent, factors which must have a positive effect on improving the economics of the process.

The extremely limited data in the foreign literature on the heat treatment of tricalcium phosphate in plasma [1] to produce phosphorus, in the opinion of the authors, permit us to draw the conclusion that the industrial use of this method will make it possible to reduce capital investments and other expenditures by factors of 5-6 in the accomplishment of this process.

The Institute of Heat and Mass Transfer of the Academy of Sciences of the Belorussian SSSR, in conjunction with the Belorussian Kirov Technology Institute, has begun and is currently conducting research to determine the possibility of applying low-temperature plasma in the production technology of phosphorus-containing substances and to determine the optimal conditions for the introduction of the process of thermal phosphate decomposition.

To study the thermochemical conversions of phosphates we employed an experimental installation that is usual for plasma chemical processes, and this installation included a dc power source (a three-unit assembly with a P101 90-kW generator), a cooling system, and a system to maintain the flow of the basic finely dispersed raw material. The design of the basic unit of the installation is shown in Fig. 1.

We employed a linear plasmatron with a tungsten cathode in these experiments, the cooling being accomplished with a copper nozzle anode. With nitrogen arc stabilization the voltage was varied from 50

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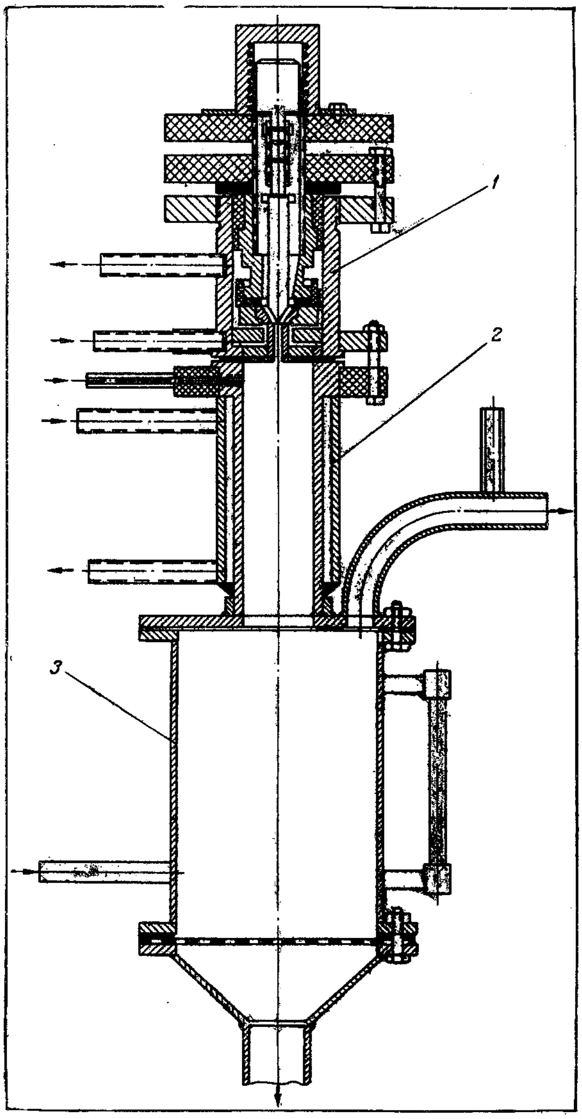


Fig. 1. Diagram of the basic unit of the experimental installation: 1) plasmatron; 2) plasmachemical reactor; 3) hardening chamber.

to 160 V, with the current ranging from 25 to 100 A. The flow rate of the nitrogen for the stabilization of the arc was 0.3-0.5 g/sec. The maximum power supplied to the plasmatron reached levels of 8 kW.

The basic phosphate raw material or the pretreated charge from the hopper was fed into a mixer from which it was carried into the reactor with a jet of the nitrogen carrier gas supplied from a tank. On mixing with the plasma jet, the original material was heated to appropriate temperatures, melted, and partially dissociated; subsequent to this, it entered the hardening chamber where the solid phase was quenched in water. The stay time for these products in the reaction zone (contact time) was 0.002-0.015 sec. The gaseous products were ejected into the atmosphere. After the hardening, we determined the composition of the thermophosphate-type solid product which had formed: P_2O_5 total, P_2O_5 citric acid-soluble, and CaO (wt.%). The P_2O_5 total and P_2O_5 citric acid-soluble were determined by a photocolorimetric method; the CaO was determined by the oxalate method. The analysis error was ±3% (relative units).

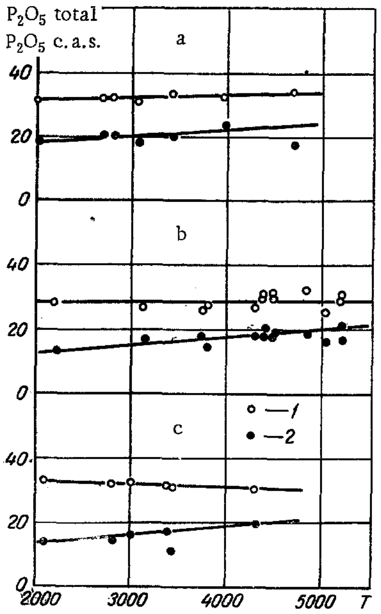
We also defined the degree of decomposition η for the basic phosphate raw material as the ratio of the difference between the quantity of raw material fed into the reactor and the thermophosphate yield to the quantity of raw material introduced.

The mass-averaged temperature of the plasma jet was determined from the heat balance of the plasmatron and varied in these experiments from 2000 to 6000°K. The temperature of the mixture formed by the plasma-forming gas and the jet of finely dispersed basic raw material was measured at the reactor inlet. We used the temperature of the mixture with the plasma-forming gas – making provision for the heat losses in the reactor – as the temperature at which the reaction was to be carried out.

For the basic raw material we used standard Kingisepp phosphate fertilizer of the following composition: P_2O_5 total = 28.75% ; P_2O_5 citric acid-soluble = 8.12% ; CaO = 41.3% ; SiO_2, approximately 5%. The fractions ranged from 0 to 160 μm and from 0 to 250 μm.

We investigated the influence exerted by the following factors on the quality of the thermophosphate yield: the contact temperature and time of the process, the hardening method, the geometric dimensions of the plasmatron nozzle and reactor – the ratio d/D (where d is the diameter of the plasmatron nozzle and D is the reactor diameter), as well as the effect of the SiO_2 additives. The selection of the geometric parameter d/D is explained by a specific feature of the process, i.e., the formation of a hardened slag lining on the reactor walls, with the thickness of this lining in certain regimes increasing substantially as the duration of the test increased. A reduction in d/D, i.e., an increase in D, did not produce the desired results, since in the light of the nonuniformity of heating the raw material there was a drop in the overall degree of conversion through the cross section of the reactor.

The results of the tests in certain of the regimes involving decomposition of the basic raw material without additives are shown in Fig. 2 (a, b, c) in the form of the percentage content of P_2O_5 total and P_2O_5



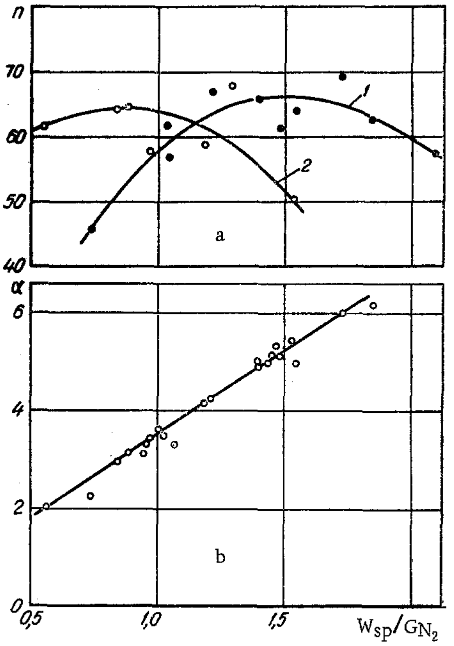


Fig. 2

Fig. 3

Fig. 2. P_2O_5 total content and P_2O_5 citric acid-soluble content, %, of the solid phase as a function of the average mass temperature T (°K) of the plasma jet for various values of d/D: a) d/D = 6/15; b) 4/15; c) 6/30; 1) P_2O_5 total; 2) P_2O_5 citric acid-soluble.

Fig. 3. Conversion ratio n, %, to citric acid-soluble form (a): 1) d/D = 4/15; 2) d/D = 6/15; and specific expenditure of energy α (kW · h /kg) (b) as a function of the specific energy of the nitrogen plasma, i.e., W_{sp}/G_{N_2} (kW · h/m^3).

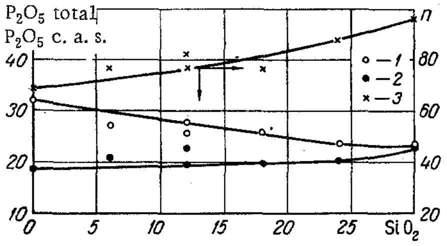


Fig. 4. P_2O_5 total and P_2O_5 citric acid-soluble yield (%) and conversion ratio n (%) as functions of the SiO_2 content (wt. %) in the charge: 1) P_2O_5 total; 2) P_2O_5 citric acid-soluble; 3) n.

citric acid-soluble as a function of the average mass temperature of the plasma jet for various values of d/D. The flow of the raw materials in each of the tests was ~9 g/min. Obviously, the increase in the P_2O_5 citric acid-soluble content with a rise in temperature, in analogy with other heat-treatment methods, should be ascribed to the disintegration of the stable fluorapatite lattice. The slight change in the P_2O_5 total content can be explained by the sublimation of several easily vaporized impurities.

For each of the values of d/D shown in Fig. 2, the duration of the process is characterized by an increase in the conversion ratio n = P_2O_5 citric acid-soluble/P_2O_5 total as the temperature rises, given an approximately equal contact time. A drop or increase in the temperature of the plasma jet leads, respectively, to a drop or increase in the efficiency of the process. From among the three considered cases the optimum d/D ratio with respect to the conversion ratio (n = 69.4) and the one which is minimum with respect to temperature is d/D = 6/15, which corresponds to the most complete filling of the reactor with the plasma jet. The effect of contact time was accounted for through the change in the ratio d/D.

One of the goals of this research was to study the effect of the hardening method. In this connection, we examined two hardening procedures: firing with a cold gas and quenching with water. The water-quenching procedure was the most efficient since, in addition to a slight increase in the ratio of conversion to the citric acid-soluble form, it made it possible to produce a useful granulated product of virtually perfect spherical shape, the granules exhibiting a diameter of 3-4 mm.

In the range of test contact temperatures and times, the degree of decomposition to the gaseous phase did not exceed 40-50%. We studied the ratio of conversion n to the citric acid-soluble form as a function of the specific energy W_{sp}/G_{N_2}. We see from the function shown in Fig. 3a that the maximum conversion ratio (~66%) for d/D = 4/15 is found at a specific energy of ~1.4-1.6 kW·h/m³. For d/D = 6/15 the specific energy drops to 0.8 kW·h/m³, with the retention – as in the first case – of the maximum attainable conversion ratio n = 66%. It is obvious that with greater intensification of the process through improved organization of the process of mixing the plasma jet with the basic finely dispersed raw material we can look forward to an even greater drop in the value of the specific energy. The specific expenditure of energy α as a function of the specific energy of the nitrogen plasma W_{sp}/G_{N_2} is shown in Fig. 3b. The minimum expenditure of electrical energy per 1 ton of the basic phosphate raw material – as determined in the experiments – amounts approximately to 3150 kW·h, while the maximum consumption is 6850 kW·h.

In the second series of experiments we investigated mixtures of Kingisepp phosphate fertilizer and silica with an SiO_2 content below that of the stoichiometric composition. The SiO_2 content in the various tests varied from 6 to 30 wt.% relative to the phosphate raw material. The average mass temperature of the plasma jet was kept as constant as possible and for d/D = 6/15 its optimum value ranged from ~3500 to 4500°K. The N_2 flow rate for arc stabilization amounted to 0.36 g/sec, while the N_2 flow rate for the phosphate feed was 0.165 g/sec. The output of the basic raw material was ~9 g/min. As in the first series of experiments, we determined the composition of the thermophosphates formed after hardening. The results for the yield of the P_2O_5 total and P_2O_5 citric acid-soluble in wt.% of the percentage SiO_2 content of the mixture are shown in Fig. 4. There we also find the change in the ratio n of conversion to the soluble form (%) of the SiO_2 content in the original mixture. The maximum conversion (n = 96.5%) at T = 4130°K was found in a mixture with a content of SiO_2 = 30%.

Thus we have experimentally established the possibility of utilizing a low-temperature plasma for the heat treatment of phosphate raw material. The need for further intensification of the process through improved mixing of the plasma jet and the finely dispersed phosphate raw material is self-evident.

LITERATURE CITED

1. Chemical Engineering News, 21, Des., No. 51, 30 (1964).