Original Article

TWO-STAGE DECOMPOSITION OF KYZYLCUM PHOSPHATE TO PRODUCE A GRANULATED SIMPLE SUPERPHOSPHATE IN AN ANHYDRITE MODE

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Abstract

It has been determined that the main phosphate mineral of Kyzylkum granular phosphate is the Francolite. Calcite, dolomite, gypsum, quartz, calcium silicate, etc. Sulfuric acid has been calculated to decompose the dried concentrate (25.75% P_2O_5) to produce a simple superphosphate (at least 17% P_2O_5). The distinctive feature of the proposed flow method before the classical (chamber) method is that the entire production cycle for processing natural phosphate is carried out in two stages. At the 1st stage, the phosphate raw material is treated with a stoichiometric consumption of concentrated sulfuric acid (at least 93%), under conditions of complete decomposition of the dried concentrate with the formation of phosphoric acid and anhydrite crystals (calcium sulfate). In this case, the reaction temperature is 130 °C. At the second stage, the formed concentrated solution of phosphoric acid in a mixture with sulphuric participates in the reaction with an additional injectable amount of dried concentrate, This is the basis for the chemical formation of monocalcium phosphate and the granulation of the superphosphate mass. In comparison with the classical scheme, the stages of storage maturation, ammonization and drying of the product are excluded from the process.

Keywords: X-rays, chemical and mineralogical compounds, sulfuric acid, decomposition, simple superphosphate.

Introduction

The global experience of many countries shows that national recovery depends largely on the level of agricultural development. The systematic application of mineral fertilizers can more than double the productivity of crops. In the context of an acute shortage of single granulated phosphorus and liquid complex fertilizers due to the limited availability of high-grade phosphate feedstock, There is a need to find effective approaches to involve the poor phosphate feedstock in the production of skilled phosphorus fertilizers. On this basis, the development of effective methods of producing single phosphorus and liquid complex fertilizers on the basis of local raw materials is an urgent task.

Research to produce simple, double and triple super-phosphate based on the use of better phosphate ores is under way worldwide, but reserves are being depleted. In this regard, special attention is paid to the development of intensive and economical ways that justify scientificTechnical solutions for developing a two-stage method for processing low-grade concentrated sulfuric acid phosphorites in an anhydrite mode to produce a granulated simple superphosphate for application under chabic and essential use.

The article studies the process of two-stage decomposition of different types of Kyzylkum phosphate by sulfuric acid in anhydritic mode depending on the norm, concentration of acid and contact time.

The distinguishing feature of the proposed method for producing a granulated simple superphosphate from low-grade phosphorites is that the process is carried out in two stages:

1) The bulk of the phosphate is degraded by concentrated sulfuric acid taken in full or in excess of the stoichiometry of the reaction to form concentrated phosphoric acid, where calcium sulfate is crystallized as anhydrite;

2) the acid reaction mass produced at the first stage, containing concentrated phosphoric acid, is treated with the second part of phosphate, where the processes of neutralization of phosphoric acid on monocalcium phosphate and the production of granulated product by rolling are combined and carried out in one apparatus.

Decomposition of a part of highly arbonized phosphate in the first stage with concentrated sulfuric acid, 92-94% H_2SO_4 concentration with a flow rate within stoichiometric norms (100-105%) and ambient temperature 110-120^{o}C in total, allows the process in anhydride mode of extraction of phosphoric acid (at concentration of P_2O_5 in liquid phase more than 40-50%), where the high rate of decomposition reaction of the raw material, which is completed in literally 15-20 min with quantitative output of P_2O_5 into liquid phase in the form of phosphoric acid.

The excess sulfuric acid is transferred to the liquid phase to form a mixture with phosphoric acid. In these conditions, until almost complete completion of the process, only the accumulation of phosphoric acid in the liquid phase is carried out, its consumption for secondary reactions to form monocalcium phosphate is eliminated. For a mixture of phosphoric acid and sulphuric acid, where H_3PO_4 concentrations of 40-50% P_2O_5 and 110-120 ^{o}C are characterized by increased chemical activity, compared with pure phosphoric acid.

The required temperature for the anhydritic mode is maintained by the heat of the reactions. According to [1, pp.139-145], the calculated thermal effect of the main reaction (1.1), depending on the concentration of sulfuric acid used in the range of 60-80% H_2SO_4, will be 379 to 530 kJ/mol fluoro. From where, extrapolating the calculated data to the point corresponding to the concentration of H_2SO_4 93%, we find the thermal effect: 564 kJ/mol. Then, the thermal effect of the reaction (1.1) per 1000 kg of Kyzylkum phosphate containing 17% P_2O_5 and 47% CaO (CaO: P_2O_5 = 2.76), excluding the heat of the side reactions involving the decomposition of impurities in sulfuric acid, is 186 500 kJ. Calculations of the thermal balance of the stage, taking into account the thermal capacity of the components of the reaction mixture of substances such as H_3PO_4 [1,082 kJ), CaSO4 0,733 kJ], and the water vapour escaping into the gas phase showed that the CO_2 and SiF_4 yields are not normalized [1,915 0,676 and 0,702, respectively]. Taking into account the loss of heat to the environment and the actual degree of decomposition of the phosphate raw material in practice, the decomposition temperature of the first stage of the process may develop to the limits of 120-180 ^{o}C.

The concentration of phosphoric acid in the mixer at the first stage of phosphate treatment depends on the ratio of phosphate: sulphuric acid and the concentration of the latter. Conventionally, in the initial mixing phase, when the reactions have not yet started, there is no water evaporation and gas release, with 93% of H_2SO_4 applied with 100-101% of stoichiometry, the water concentration in the prepared mixture will be 3.9%. The liquid phase is only a concentrated aqueous solution of sulphuric acid. After 5-7 minutes, during the time of quantitative completion of the reactions, assuming that water evaporation is intense, the minimum concentration of phosphoric acid in the liquid phase of the mixture will be 54.61 and 40.56% P_2O_5 respectively, and the maximum can reach the level Typical of 100% acid (72.4%). When applied at 101%, phosphoric acid at 40.56% P_2O_5 contains up to 2.1% of the excess sulfuric acid.

Within the limits of the acid flow rate, the $CaSO_4 : H_2O$ in the reaction mixture is 1 : 0.15, that is, enough to crystallize at the initial phase of calcium sulfate in the form of a semi-hydrate, where the theoretical $CaSO_4 : H_2O$ = 1: 0.066. The semihydrate then crystallizes instantly to anhydrite, which is promoted by both the temperature of the medium (up to 150 ^{o}C) and the concentration of phosphoric acid (more than 40% P_2O_5).

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 2{,}5H_2O = 3H_3PO_4 + 5CaSO_4 \cdot 0{,}5H_2O + HF, \qquad (1.1)$$

The use of sulfuric acid at a concentration of 92-93% of H_2SO_4 in the above-mentioned interval of its flow, due to water shortage, prevents the emergence of a movable fluid pulp. The new liquid phase accumulated at the end of the reaction (1.1) (concentrated H_3O_4) is exclusively in the occult capillary-porous framework of agglomerate crystals from anhydrite. This is why the reaction mass remains scattered.

An excess of sulphuric acid, in addition to the temperature of the medium and its concentration, is a prerequisite for the complete decomposition of phosphate, but only if the mixture is free of excess phosphate. This is confirmed by the low reaction rate of equation (1.1) and the impossibility of its complete completion, However, the traditional technology of simple super-phosphate requires an enormous amount of time - 20-30 days - to achieve a practically acceptable level of degradation of natural phosphate.

$$2Ca_5F(PO_4)_3 + 7H_2SO_4 + H_2O = Ca(H_2PO_4)_2 + 7CaSO_4 + 7H_2O + 2HF, \quad (1.2)$$

The reaction (1.2) with a noticeable speed continues the first 20-40 minutes of processing «b», where there is no mixing and the reaction mass is seized, mainly due to the crystallization of calcium sulfate. The liquid phase in the solidified reaction mass does not show its normal properties (fluidity, mobility). It is occluded in the pores of solid phase particles (calcium sulfate and undisturbed phosphate). Under these kinetic conditions, the accumulated phosphoric acid is consumed by the reaction (1.3) and the reaction product - calcium monohydrate - is crystallized. But these processes take place under conditions of diffusion braking and until their complete completion the allotted time of accumulation of the superphosphate mass in the chamber (~2.5 h). Hence the necessity of technological reprocessing «d» (superphosphate maturation).

$$Ca_5F(PO_4)_3 + 7H_3PO_4 + 5H_2O = 5Ca(H_2PO_4)_2 \cdot H_2O + HF, \quad (1.3)$$

We have proposed a two-stage scheme, where instead of reworking «a» - «d» of the classical version, only two stages are introduced: a) decomposition of a part of phosphate with concentrated sulfuric acid to form concentrated phosphoric acid and anhydritic gypsum; b) Neutralizing the acid mass produced by the remaining phosphate with simultaneous granulation.

In the «a» stage of the new variant, the process is carried out in some excess sulfuric acid in the anhydritic mode of extraction of phosphoric acid. The mode is due to the high temperature of the reaction mixture (above 120°C) and the increased concentration of phosphoric acid in it (above 40% P_2O_5). Due to the high activity of the acid, the duration of the stage «a» does not exceed 2-7 min, with it phosphorite has time to decompose completely. During this time, phosphate is fluorinated to 70% and decarbonized. The reaction product is mainly crystallized anhydrite ($CaSO_4$) and concentrated H_3PO_4 (45-50% P_2O_5).

The possibility of extracting phosphoric acid with the release of calcium sulfate in the form of a stable anhydrite in the expected temperature and acid concentration region follows from the solubility diagram in the CaO-P_2O_5-SO_3-H_2O [1, pp.139-145].

Other known works with anhydritic mode of crystallization of calcium sulfate from phosphorus acid solutions [2, p.3.] and [3; p.57-62] are devoted to optimizing the phosphate acid separation stage of anhydrite suspension by filtration or centrifugation.

Experimental method

The phosphate raw material used is phosphate flour (FM), washed dried concentrate (WDC) and washed burnt concentrate (WBC) produced at the Kyzylkum phosphate complex in accordance with SSt 2825:2014. Their compositions are given table. 1.

Concentrated sulfuric acid produced by JSC "Ammophos-Maxam" with concentrations of 70; 80; 90; 93 and 94.5% H_2SO_4 was used for their degradation.

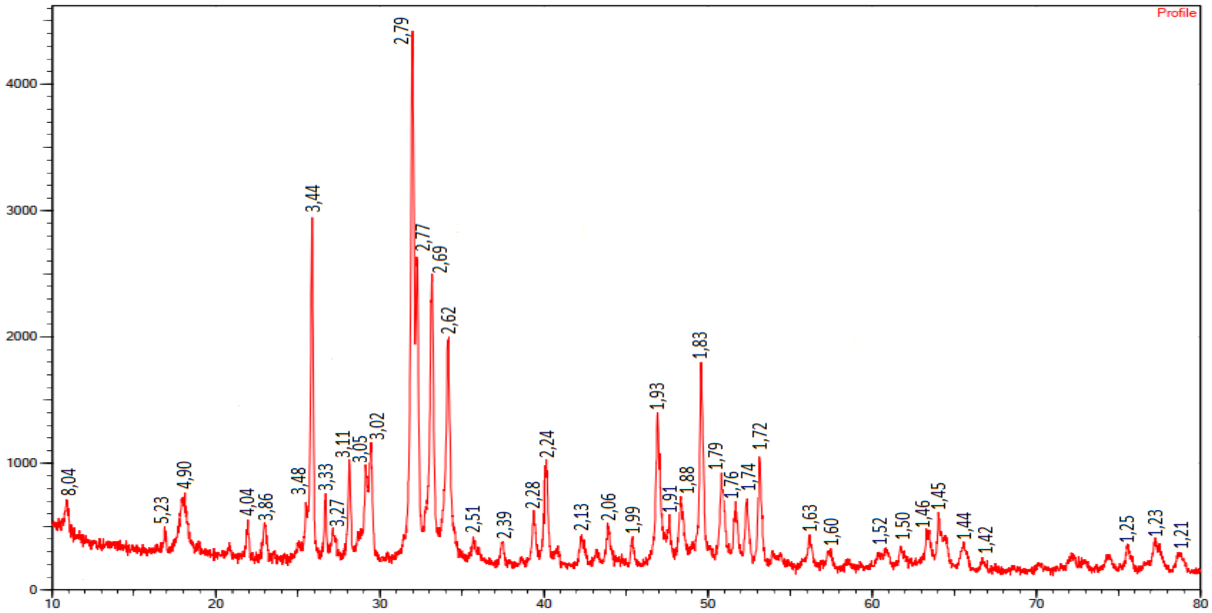
1 table: Composition of different grades of phosphate in Central Kyzylkum

phosphate raw materials	Component content, weight. %									
	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	CO_2	SiO_2	SO_3	F	i.r.
FM	17,54	47,75	1,79	0,95	0,73	16,5	1,24	4,06	1,7	4,03
WDC	25,75	52,07	0,30	1,02	0,31	10,97	1,78	1,48	2,76	1,23
WBC	25,77	52,70	1,20	1,15	0,63	3,60	2,39	2,67	2,58	4,49

To estimate the mineralogical composition of FM, WDC and WBC, their X-rays were taken on the diffractometer XRD-6100 (Shimadzu, Japan). Used CuKα-radiation (β-filter, Ni, current and voltage mode of tube 30 mA, 30 kV), constant rotational speed of detector 4 grad/min, scanning angle varied from 4 to 80o. The mineral phases were identified using the 2013 International Centre for Diffraction Data database. The WBC X-rays are shown in Figure 1.

Diffraction highs 3.44; 3.11; 2.79; 2.77; 2.69; 2.62; 2.24; 1.93; 1.83; 1.79; 1.72A° belonging to fluorocarbonapathati (Fig. 1), are available on the WBC radiograph. The remaining peaks refer to calcium oxides and hydroxides, insoluble residue and calcium silicate. This mixture is the raw material for producing EFA and ammophos.

Fig.1. Rentgenogram of washed burnt concentrate.



On the basis of the results of the chemical composition of FM, WDC and WBC, accurate data on the quantity of minerals of phosphate raw materials have been calculated. On the basis of calculations mineralogical composition of FM, WDC and WBC (Table. 2) is determined.

In the study of the process of decomposition of phosphate raw materials by a two-stage method, the first study was conducted of the decomposition kinetics of phosphate raw materials with 93% sulfuric acid at a rate of 100% of stoichiometry.

The experiments were carried out in a thermostatic reactor equipped with a bladed mixer at 122°C. The contact time of the components was 2, 5, 10, 20, 40 and 60 minutes [4; p.32-41].

2 table: Mineralogical composition of different grades of phosphate raw materials

Mineral components of phosphate raw materials	Quantity, weight. %		
	FM	WDC	WBC
$Ca_{10}P_{5,2}C_{0,8}O_{23,2}F_{1,8}OH$	47,19	69,27	69,32
$CaCO_3$	24,75	17,85	2,60
$CaMg(CO_3)_2$	8,24	1,38	1,20
$CaSO_4 \cdot 2H_2O$	6,90	3,18	4,54
SiO_2	0,26	1,24	2,39
Ca_2SiO_4	2,81	1,55	-
H_2O	-	0,92	0,96
CaF_2	0,15	0,77	0,39
Al_2O_3	0,95	1,02	1,15
Fe_2O_3	0,73	0,31	0,63
insoluble residue	4,03	1,23	4,49
$K_2O + Na_2O$ (Glauconite, chlorite)	1,5	-	-
$K_2O + Na_2O$ (glauc. and org. comp.)	-	0,1	0,1
other	2,32	<1,18	<1,50

Results and Discussion

As can be seen from Table 3, the decomposition rate of phosphate raw material (up to 90.02-92.32% (2-60 min) is increased with the extension of the decomposition time of FM by sulfuric acid. The soluble form ratio of P_2O_5 to total P_2O_5 has increased and the total acidity (sum of sulphuric and phosphoric acids) has decreased from 16.68 to 15.39%. It can be seen that when the WDC decomposes, the reaction mass temperature rises to an average of 130 C, and for the WBC to 175°C [5-8].

The content of common and free forms of P_2O_5 in WDC and WBC decomposition products was significantly higher than in FM decomposition. In addition, degradation products show an increase in the relative water form of P_2O_5 to its total form.

As can be seen, the free acidity of products at the decomposition of FM is 15.39-16.68% and 19.77-21.42% at the decomposition of WDC, while for WBC this varies between 18.51-19.98%. Increasing decomposition time from 2 to 60 minutes. The content of the general form is virtually unchanged, amounting to 13.55-14.11% for WDC and 13.52-13.91% for WBC. The water form content of P_2O_5 is 12.39-13.08% for the WDC and 12.57-13.24% for the WBC. The relative water soluble content varies between 91.44-92.70% and 92.97-95.18%, respectively.

It has been found that 20 min is sufficient for decomposition of FM, WDC and WBC. $P_2O_{5water.}$: $P_2O_{5ass.}$= 92.10% for FM and 92.24% WDC, and for WBC 93.37%. This is much faster than producing a superphosphate by chamber circuit (1.5 hours), and $K_{decom.}$ raw material is sufficient to neutralize acidity.

3 table: The coefficient of decomposition of various phosphorites with 93% sulfuric acid, depending on the duration of interaction

H_2SO_4 norm from stoichiometry, %	Temperatura, °C	Interaction time, min.	Content of P2O5 in reaction mass, weight. %		
			$P_2O_{5total.}$	$P_2O_{5water.}$	$P_2O_{5water.}$/ $P_2O_{5total.}$ · 100
FM					
100	122	2	9,42	8,48	90,02
		5	9,55	8,60	90,05
		10	9,71	8,76	90,22
		20	9,87	9,09	92,10
		40	9,89	9,13	92,31
		60	9,90	9,14	92,32
WDC					
100	130	2	13,55	12,39	91,44
		5	13,63	12,47	91,49
		10	13,71	12,57	91,68
		20	13,79	12,72	92,24
		40	13,94	12,91	92,61
		60	14,11	13,08	92,70
WBC					
100	175	2	13,52	12,57	92,97
		5	13,56	12,62	93,06
		10	13,62	12,68	93,09
		20	13,72	12,81	93,37
		40	13,82	13,07	94,57
		60	13,91	13,24	95,18

Conclusions

It can be concluded that the best option is the duration of the process of decomposition of phosphate raw materials within 20-30 minutes. Because further extension of the duration does not increase the decomposition coefficient ($K_{decom.}$) and with less time the required mass in the required quantity is not formed.

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