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DEVELOPMENT OF AMMOPHOS PRODUCTION TECHNOLOGY FROM ALGERIAN PHOSPHORITES

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Abstract. Technological aspects of ammophos production using Algerian phosphorites as a raw material have been investigated. The necessity of increased consumption of sulphuric acid during the Algerian phosphorites processing compared with apatite processing has been grounded. The dependence of pH solution on $\text{NH}_3:\text{H}_3\text{PO}_4$ molar ratio has been determined during neutralization of extraction phosphoric acid prepared from Algerian phosphorites. The necessity of acid solution deeper neutralization in the technology of extraction phosphoric acid production has been proved. The boundary drying temperature of ammonia pulp has been determined. The relation between ammonium nitrogen and drying time has been specified.

Keywords: ammophos, phosphorite, apatite, concentrate, acid, pulp.

1. Introduction

The industrial implementation of ammophos production consists of three main stages: neutralization of phosphoric acid by ammonia, removing moisture from the product and crystallization or granulation of dry matter containing ammonium dihydrophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) mainly. A series of theoretical aspects concerning ammophos production technology and description of industrial variants of its implementation is represented in monographs [1, 2]. In the industry the phosphoric acid is neutralized by liquid or gaseous ammonia and only sometimes – by ammonia water [3]. The final value of pH in the neutralization process ensures the complete substitution of first hydrogen ion of orthophosphoric acid for ammonium cation followed by $\text{NH}_4\text{H}_2\text{PO}_4$ formation in accordance with the reaction:



In $\text{NH}_4\text{H}_2\text{PO}_4$ the molar ratio $\text{NH}_3:\text{H}_3\text{PO}_4$ is 1:1. Literature data [3] indicate that few admixtures (K_2O , N_2O , MgO) pass into extraction phosphoric acid (EPA) obtained from Algerian phosphorite. They bound first ion of phosphoric acid into the complex of MeH_2PO_4 type, where Me is a sum of K, Na, Mg and other active cations. Using double titration method it was established that 10–15 % of EPA first ions are exchanged for active cations. Thus, the obtained salts mixture has less nitrogen. To increase the nitrogen content in the final product the presence of ammonium hydrophosphate (by partial exchange of the second hydrogen ion) together with ammonium dihydrophosphate is necessary [2]. Since EPA partially neutralized by K_2O , Na_2O and MgO contains sulphate acid and dissolved calcium sulphate, these compoundi precipitate during ammonization [4]. This exothermic process causes considerable evaporation of moisture from acids and salts crystallization. As a result, the three-phase heterogeneous system is formed [3]. Pulp rheological properties depend on its composition, temperature and components solubility [3-5]. The dependence of ammonium phosphate solubility on molar ratio $R = \text{NH}_3:\text{H}_3\text{PO}_4$ is represented in [3] at different temperatures. The dependence has maxima at $R = 0.3$ and 1.4 and minima at $R = 1.0$. A. Kononov *et al* [4] also investigated the dependence of R on pH for the acids with different amount of admixtures. For $R = 1.4-1$ the range of $\text{pH} = 3.2-5.8$ is typical. As a rule, at the industrial ammophos production and processing of EPA obtained from apatite concentrate of Kolsky deposit the acid ammonization is carried out till molar ratio $\text{NH}_3:\text{H}_3\text{PO}_4 = (1.2-1.3):1$ to obtain movable pulp [5, 6]. At the same time pH is maintained within the range of $(3.1-5.2):1$ [7]. The solubility of the $\text{NH}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ system is thoroughly scrutinized in the temperature interval of 273–348 K and the data for higher temperatures (to 448 K) are available [3, 4]. Monoammonium phosphate,

diammonium phosphate and triammonium phosphate are observed in the system. The presence of $\text{NH}_4\text{H}_2(\text{PO}_4)_2$ is also possible [4]. Expressed singular angle at the branch of monoammonium phosphate crystallization curve indicates the slight dissociation of the compound in the studied temperature interval.

Thus the aim of this work was to investigate the technological aspects of ammophos production using Algerian phosphorites as raw material.

2. Experimental

2.1. Investigation Objects

During ammophos production from EPA obtained from Algerian phosphorites the part of the second hydrogen ion of phosphoric acid exchange for ammonium cation is one of the investigation objects. The numerical value of this parameter depends on quality (properties) of the treated phosphoric acid as well as on equipment design at different stages of the technological process. Under the laboratory conditions the studies of production technology of ammophos based on EPA from Algerian phosphorites were carried out using the known methods [8]. Firstly, it allows to obtain reliable data concerning fertilizer composition while processing of phosphoric acid of the definite quality. Secondly, the grounded suggestion concerning drying temperature conditions for ammoniated pulp and physico-mechanical characteristics of ammophos granulated form are obtained. For the experiments we used the enlarged sample of EPA obtained at the model plant from the sample of Algerian phosphorite. The phosphorite composition (%) was: P_2O_5 – 28.5; CO_2 – 5.8; F – 3.7; CaO – 48.9; MgO – 1.9; Al_2O_3 – 0.20; Fe_2O_3 – 0.9.

2.2. Technological Investigations

To establish the requirements for pulp ammonization level and temperature conditions of its drying the experiments for obtaining of granulated ammophos enlarged sample have been carried out. For this purpose 5.5 dm³ of phosphoric acid were sequentially neutralized in the separate vessel by ammonia water till planned pH level was achieved. Ammonia water was introduced into the acid under intensive stirring. The final temperature of the reaction mass was 343–346 K. The density of averaged pulp at 303 K was 1235 kg/m³. The obtained pulp was loaded into a reactor by the height of 8–10 mm and then dried in drying chamber with forced circulation of heated air at 378 K for 2 h till moisture content of 4–10 %. The wet charge obtained after free water removing from dryable pulp was averaged and granulated in plate granulator with plate diameter of 600 mm. Ammophos moist granules were graded and the fraction with granules size of 2–5 mm was separated. This

fraction was placed in a pallet and again dried in the drying chamber at 368 K for 1 h till moisture content of less than 1 %. The dried product was graded and commercial fraction with the grain sizes of 1–5 mm was separated and analyzed. The technological parameters were compared with corresponding parameters of Kolsky apatites, which are usually used for ammophos production.

3. Results and Discussion

3.1. Phosphoric Acid

The acid was obtained under dihydrated regime. EPA density was 1282 kg/m³. Acid kinematic viscosity at 293 K was found to be $4.55 \cdot 10^{-6}$ m²/s and was determined using VPZH-2 viscometer with the diameter of 0.73 mm. The acid composition (mas %) was: P_2O_5 – 26.2; CaO – 0.54; MgO – 1.55; Al_2O_3 – 0.18; Fe_2O_3 – 0.22; F – 0.84; SO_3 – 2.5; Cd – 9.3 mg/kg; Pb – less than 0.5 mg/kg. (CaO + MgO): SO_3 molar ratio was 1:0.67. The lack of sulphate-anion for admixtures cations bonding indicates that the part of the phosphoric acid first ion is exchanged for magnesium [5].

Comparing the chemical composition of phosphoric acid with the initial chemical composition of phosphorite it was determined that MgO (89 %), F (25 %), Al_2O_3 (98 %), and Fe_2O_3 (85 %) were extracted by the acid. Thus, the significant amount of admixtures is removed from phosphorite by acid. Using double titration it was established that approximately 15 % of the first hydrogen ions in phosphoric acid are exchanged for cations admixtures. The mentioned peculiarity of EPA from Algerian phosphorite must be considered without any doubts during the industrial implementation of the neutralization stage. During ammophos production phosphoric acid obtained from Algerian phosphorite should be neutralized till higher value of pH compared with that from apatite concentrate of Kolsky deposit to reach the same $\text{NH}_3:\text{H}_3\text{PO}_4$ ratio in ammoniated pulp.

3.2. Ammoniated Pulp Characteristics

The results of pH estimation of ammoniated pulp are represented in Fig. 1. The initial phosphoric acid (~ 26 % P_2O_5) was neutralized by ammonia water (~ 25 % NH_3) and pH was determined with the increase of $\text{NH}_3:\text{H}_3\text{PO}_4$ ratio. By means of calculations and experiments we determined that pH level of phosphoric acid ammonization should be 4.55–4.65. Such value is necessary in order for the fertilizer produced in the laboratory to be identical to commercial ammophos (content of N is 12 % and P_2O_5 is 52 %). The molar ratio $\text{NH}_3:\text{H}_3\text{PO}_4$ should be (1.2–1.3):1. To determine the distinctions of the investigated acid ammonization the area of pH values (3.8–4.2) and corresponding $\text{NH}_3:\text{H}_3\text{PO}_4$ ratios are marked in Fig. 1. Such area is typical of the

industrial conditions for processing of phosphoric acid obtained from apatite concentrate of Kolsky deposit.

Taking into account certain losses of ammonium during drying it is necessary to prepare the ammoniated pulp with somewhat higher nitrogen content. Since the ammoniated pulp obtained from Algerian phosphorite contains the increased amount of thermally unstable $(\text{NH}_4)_2\text{HPO}_4$, the pulp should be dried under the conditions when the temperature of drying gases does not exceed 378 K and residual hygroscopic moisture of the product is 0.8–1.5 %. Under the mentioned conditions the temperature of dryable material does not exceed 363 K and nitrogen losses (transition into gas phase) for drying time (about 1 h) are at the permissible level (Fig. 2).

3.3. Technological Aspects of Ammophos Production from Algerian Phosphorite

Thus, we obtained ammophos samples of the following composition (mas %): $\text{P}_2\text{O}_{5\text{total}}$ – 52.1; $\text{P}_2\text{O}_{5\text{digestible}}$ – 51.9; $\text{P}_2\text{O}_{5\text{water-soluble}}$ – 47.9; N – 11.2; CaO – 1.1; MgO – 3.1; SO_3 – 4.95; Al_2O_3 – 0.35; Fe_2O_3 – 0.45; F_{total} – 1.55; $F_{\text{water-soluble}}$ – 0.58; $\text{H}_3\text{PO}_{4\text{free}}$ – absent; H_2O – 0.94. The content of heavy elements which are ecologically controlled (mg/kg): Cd_{total} – 17.6; $\text{Cd}_{\text{water-soluble}}$ – 4.6; Pb_{total} – 1.5; $\text{Pb}_{\text{water-soluble}}$ – < 1. The experimental results show the principal possibility to produce the fertilizer based on EPA from Algerian phosphorite. Such fertilizer meets the stan-

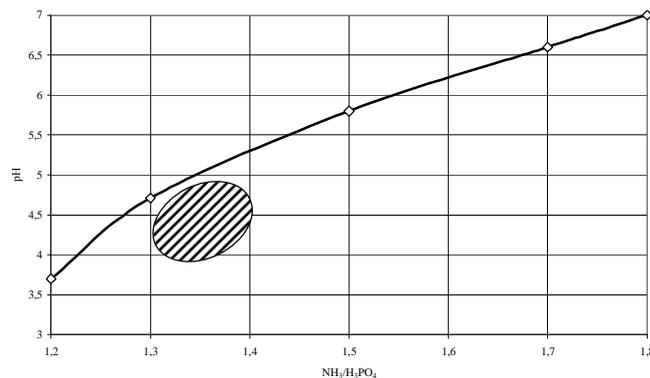
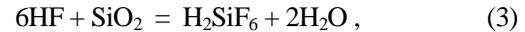
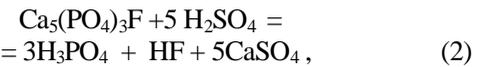


Fig. 1. Solution pH vs. $\text{NH}_3:\text{H}_3\text{PO}_4$ molar ratio at neutralization of phosphoric acid (26 % of P_2O_5) obtained from phosphorite

dard demands for ammophos by main properties. It should be noted that in the final product the iron content decreases from 3.21 to 2.97 mass parts per 100 mass parts P_2O_5 due to the partial evaporation of H_2SiF_6 [9, 10] formed while phosphorite sulphoacid decomposition and $(\text{NH}_4)_2\text{SiF}_6$ decomposition [11] in accordance with the following reactions:



Therefore while developing industrial recommendations for implementation of ammophos production technology it is necessary to take into account that used drying gases directed at gas-cleaning unit will be polluted not only by ammonia but by fluorine-containing compounds as well. The peculiarities of processing of phosphoric acid obtained from Algerian phosphorite which were observed under laboratory conditions were taken into account during the development of ammophos production regulations under the industrial conditions. We took into consideration both deeper ammonization of pulp and the problem of drying gases purification in the absorption system. At JSC “Krymskyi titan” we investigated the existing absorption system operated under ammonia increased content and gave recommendations concerning the possibility of the same system exploitation while using new raw material – Algerian phosphorite.

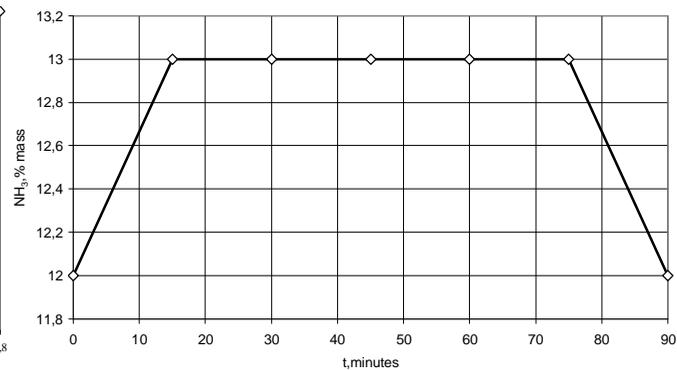


Fig. 2. Ammonium nitrogen losses vs. drying time

Table

Consumption of raw material for the production of ammophos from Algerian phosphorite (per 1 t 100 % P_2O_5)

Raw materials	Unit	Ammophos from Algerian phosphorite (laboratory studies)	Ammophos from Kolsky apatite (data from JSC “Krymskyi titan”, December 1998)
Phosphate raw material:			
- 100 % P_2O_5	t	1.187	1.165
- real ore	t	4.05	2.98
in particular at EPA preparation stage, 100 % P_2O_5	t	1.12	1.099
Sulphate acid for EPA preparation, 100 % H_2SO_4	t	3.38	2.83
Ammonia, 100 % NH_3	t	0.290	0.283

On the basis of experimental results we calculated consumption of raw material for the production of ammophos type fertilizer (Table).

The difference between consumption of raw materials for the processing of phosphoric acid produced from different types of phosphate raw material has objective explanation. The increased sulphate acid consumption while processing of Algerian phosphorite compared with that of apatite concentrate from Kolsky deposit is explained by the presence of carbonate minerals in the phosphorites.

The reason of increased ammonia consumption was specified by us while commercial tests. Slight increase of phosphoric acid consumption is connected with the presence of raw material admixtures (magnesium, ferrum and aluminum) in EPA composition. During EPA ammonization these admixtures lead to the retrogradation of part of P_2O_5 digestible form. The laboratory results were confirmed during commercial tests.

On the basis of the above-mentioned one can see that there are no special technological difficulties for ammophos production from Algerian phosphorite. The magnesium, ferrum and aluminum admixtures are present in amounts which have no essential effect on physical characteristics of ammophos pulp [12]. The pulp is movable and causes no complications while its preparation and drying. The ammophos charge does not complicate granulation and granules are not deformed while drying.

4. Conclusions

The technological aspects of ammophos production based on Algerian phosphorites were investigated. The necessity of EPA dihydrated regime and H_2SO_4 increased consumption (by 19.43 %) while Algerian phosphorites processing compared with apatite concentrate were grounded. The necessity of phosphoric acid ammonization till pH = 4.55–4.56 to obtain the fertilizer identical to commercial ammophos (content of N = 12 % and P_2O_5 = 52 %) was demonstrated. The molar ratio $NH_3:H_3PO_4$ must be (1.2–1.3):1. The ammophos production based on EPA (approximately 26 % of P_2O_5) from Algerian phosphorites is accompanied by 15 % displacement of first hydrogen ions from phosphoric acid by admixtures cations of the initial phosphate raw material. The peculiarity of EPA obtaining from Algerian phosphorite is the necessity of acid deeper neutralization (till pH = 4.5–4.56), which differs from the same process on the basis of Russian apatite concentrate. The boundary drying temperature of ammoniated pulp was grounded to be 378 K, which is connected with the increased amount of thermally unstable $(NH_4)_2HPO_4$ in the obtained pulp. On

the basis of experimental results the regularities of fluorine eliminating were established. In particular, F: P_2O_5 ratio, fluorine supply, as well as excess of NH_3 in the drying gases lead to the adjustment of cleaning system operation compared with the regime for EPA production on the basis of Kolsky apatite concentrates.

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РОЗРОБЛЕННЯ ТЕХНОЛОГІЇ ОДЕРЖАННЯ АМОФОСУ ІЗ АЛЖИРСЬКИХ ФОСФОРИТІВ

Анотація. Досліджено технологічні аспекти виробництва амофосу за умови використання як сировини алжирських фосфоритів. Обґрунтована необхідність підвищених витрат сульфатної кислоти при переробленні алжирських фосфоритів у порівнянні із технологією перероблення апатитового концентрату. Встановлено залежність рН розчину від молярного співвідношення $NH_3:H_3PO_4$ при нейтралізації екстракційної фосфатної кислоти, виготовленої із алжирських фосфоритів. Доведено потребу більш глибокої нейтралізації кислотного розчину у технології отримання екстракційної фосфатної кислоти із алжирського фосфориту. Обґрунтовано граничну температуру сушіння амонізованої пульпи. Встановлені залежність втрати амонійного азоту від часу сушіння.

Ключові слова: амофос, фосфорит, апатит, концентрат, кислота, пульпа.