UDC 661.842.532 + 668.8

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RECYCLING OF PHOSPHOGYPSUM IN COMPLEX MINERAL FERTILIZER

Background. In the production of phosphate fertilizers and phosphoric acid accumulation environmentally unsafe on the course – phosphogypsum. To date, in the territory of Ukraine is in the dumps about 30 million tons of phosphogypsum.

Objective. To get from phosphogypsum with using waste technologies complex NPCaS-fertilizer.

Methods. Processing phosphogypsum in a relatively “soft” operating conditions, without the involvement of high-temperature (1173–1753 K) processes. Conducted a research of two-stage utilization processing of typical phosphogypsum into complex fertilizer with composition 7,9 % N, 37 % P_2O_5, 35 % Ca, 1,8 % S, containing phosphorus in the form of $Ca(H_2PO_4)_2$, $CaHPO_4$ (at a ratio $P_2O_{5(\text{w-soluble})}/P_2O_{5(\text{overall})} = 94\,\%$), and the nitrogen – in the form $(NH_4)_2SO_4$. The first stage of the process is implemented decomposition of phosphogypsum at temperature (323 ± 5) K by solutions of $(NH_4)_2CO_3$ at pH > 5,1 with formed a precipitate (suspension) $CaCO_3$ in solution $(NH_4)_2SO_4$. In the second stage formed a thick slurry is processed (without filtration separation $CaCO_3$) by solutions of sub-standard phosphoric acid without external heating at the support of the pH of the medium to 6,8–6,9. The final solid fertilizer is drying of slurry in apparatus of type “fluid process” at temperature (390–423) K.

Results. The final solid fertilizer, consumer quality is tested on samples of soil for agricultural purposes.

Conclusions. On the base of phosphogypsum is received a complete fertilizer for little-stage non-waste technology in environmentally sound conditions.

Keywords: phosphogypsum; complex fertilizers; suspension; little-stage technology; substandard phosphate acid.

Introduction

Phosphogypsum ($CaSO_4 \cdot 2H_2O$ with impurities P_2O_5, F, etc.) is obtained as a large-tonnage by-product (waste) of the production of extraction phosphoric acid (EPA). Its stock at fertilizer chemical plants in Ukraine reaches tens millions tons and, for phosphogypsum stacks, large areas are discharged (hundreds of hectares in Ukraine) often being suitable for agricultural applications [1, 2]. Phosphogypsum storage in stacks is, firstly, economically unfeasible for enterprises and, secondly, doing serious damage to the environment.

The negative impact of phosphogypsum stacks on the environment consists in air pollution by toxic chemical compounds, in migration of these and other compounds into ground and surface waters with atmospheric precipitation, in wind erosion (dusting) with the phosphogypsum particles transfer for sufficiently long distance and with damage of vegetation mantle and agricultural crops [3, 4]. Thus, during phosphogypsum storage, up to 0.1 % of fluorine (phosphogypsum contains about 1,0–1,5 kg of fluorides per ton) is evolved into atmosphere, and up to 10 % of fluorine is washed out by atmosphere precipitation almost every year [3].

In addition, the phosphogypsum transportation (with moisture content up to 44 %) to the stacks and its storage in them are connected with large capital investment and operating costs (both in Ukraine and abroad, 11-12 % of the average construction costs of the EPA production facility by itself, and up to 17-18 % of the average processing costs of raw materials (phosphates) into phosphorus containing products, respectively) [5, 6].

Traditional methods of phosphogypsum utilization from its stacks are its usage in the production of alabaster binding materials and products, in roads construction, in conversion processing into sulfuric acid, cement, lime, nitrogen fertilizers, fillers for paper, paintwork, and plastic products, in agriculture (as ameliorant) etc. [6, 7]. However, only in small number of countries having responsible and diligent ecological policy (Japan, Germany, USA, etc.), phosphogypsum utilization in one or more of the aforementioned areas reaches significant degree. In the majority of countries (including Ukraine), due to the reasons of high costs, energy intensity, and multiple stages of the phosphogypsum processing, its recycling does not exceed 2–10 % from its annual accumulation [8].

It appears that the rational way of this problem solving is the phosphogypsum processing in the “soft” mode using inexpensive reagents to obtain valuable agricultural products, particularly complex mineral fertilizers. Several methods of the phosphogypsum utilization are known to use relatively simple modes. However, these methods products are either nitrogen containing fertilizers with low nutrient concentration or carbonate, sulfate, ammonium, and urea containing mixtures with low nutrient value. Moreover, these methods are only possible to realize using expensive reagents at high temperatures [9—14].

Formulation of the problem

The aim of the present work is to develop technological foundations of a new method of phosphogypsum processing into complex NPCaS-fertilizer using alkaline reagents and phosphate solutions.

Experimental

Phosphogypsum samples from PJSC "Azot" (Rivne, Ukraine) were used in studies as typical for Ukrainian fertilizers enterprises. Their chemical composition is shown in Table (based on our own analysis data).

The average mass fraction of $CaSO_4 \cdot 2H_2O$ in phosphogypsum is 98 %. Radioactivity of the sample (~19 nCi/kg*) is close to the acceptable values limit (~16 nCi/kg, 1800 Bq/kg) established by UNIDO [15, 16].

For the processing of phosphogypsum into complex fertilizer, double-stage technology is proposed according to the following chemical scheme:

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \to CaCO_3 + (NH_4)_2SO_4 + 2H_2O, \qquad (1)$$

$$CaCO_3 + 2H_3PO_4 \to Ca(H_2PO_4)_2 + CO_2 + H_2O, \qquad (2)$$

or:

$$CaCO_3 + H_3PO_4 \to CaHPO_4 + CO_2 + H_2O. \qquad (3)$$

Reaction (1) is endothermic ($-\Delta H^0_{298}$ = = 524.3 kJ/mol), and, according to the thermodynamic calculations data, its realization becomes possible and technologically feasible at temperatures above 323 K ($\Delta G^\circ_{323} = -563$ kJ/mol) in a liquid medium. Irreversibility of this reaction is caused by the fact that it is possible to create conditions in the solution under which the solubility of $CaCO_3$ will be much less than the solubility of $CaSO_4 \cdot 2H_2O$.

Evidential substantiation of acceptable conditions of $CaSO_4 \cdot 2H_2O$ conversion into $CaCO_3$ was carried out as follows.

As $CaCO_3$ is a weak acid salt, its solubility (S) greatly depends on the pH. At the same time, solubility of $CaSO_4 \cdot 2H_2O$ ($pK_{2(H_2SO_4)} = 1.9$) depends on the pH only in strongly acidic and basic solutions area. That is, for these salts with similar solubility product (SP) values, a pH value should exist for which the condition $S(CaCO_3) < S(CaSO_4 \cdot 2H_2O)$ is true resulting in the acceptability of the conversion of $CaSO_4 \cdot 2H_2O$ into $CaCO_3$.

Determination of the appropriate pH value will be justified by the calculation of dependence of the $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ solubility values on the medium acidity.

For $CaCO_3$, the following model of solubility is valid:

$$CaCO_{3(\mathrm{solid})} \leftrightarrow Ca^{2+} + CO_3^{2-};$$

$$SP_{CaCO_3} = [Ca^{2+}] \cdot [CO_3^{2-}];\ [Ca^{2+}] = S;$$

$$[CO_3^{2-}] = S \cdot f(\mathrm{pH});\ SP_{CaCO_3} = S \cdot S \cdot f(\mathrm{pH}).$$

Based on material balance for the central atom (C), appearance of function $S \cdot f(\mathrm{pH})$ is defined as: $S = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$.

Using known values of ionization constants (K_1 and K_2) for carbonate acid, the material balance equation can be transformed to the following expression:

$$S = \frac{[H^+]^2 \cdot [CO_3^{2-}]}{K_1 \cdot K_2} + \frac{[H^+] \cdot [CO_3^{2-}]}{K_2} + [CO_3^{2-}],$$

which, after transformation with respect to $[CO_3^{2-}]$, defines the appearance of function $S \cdot f(\mathrm{pH})$:

$$[CO_3^{2-}] = \frac{S \cdot K_1 \cdot K_2}{[H^+]^2 + K_1 \cdot [H^+] + K_1 \cdot K_2}.$$

Table. Chemical composition (% w/w) of phosphogypsum samples from PJSC "Azot" (Rivne, Ukraine)

CaO	SO_3	P_2O_5 total	P_2O_5 soluble in water	Fe_2O_3	Al_2O_3	MgO	F	Cl	REEs
38,4	59,7	0,62	0,05	0,15	0,36	0,003	0,13	0,01	0,41*

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* Analysis made by manufacturer.

Then, $SP = S^2 \cdot \dfrac{K_1 \cdot K_2}{[H^+]^2 + K_1 \cdot [H^+] + K_1 \cdot K_2}$ or

$S = \sqrt{\dfrac{SP_{CaCO_3} \cdot ([H^+]^2 + K_1 \cdot [H^+] + K_1 \cdot K_2)}{K_1 \cdot K_2}}$, where

$SP_{CaCO_3} = 9{,}2 \cdot 10^{-7}$.

Similarly, using the ionization constants of sulfuric acid, formula was obtained for calculating solubility looking similar to the aforementioned one ($SP_{CaSO_4 \cdot 2H_2O} = 1{,}3 \cdot 10^{-4}$).

Calculated solubility values for $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ are shown in Fig. 1.

$$2S_{DHPh} = \sqrt{\frac{SP_{DHPh}}{[Ca^{2+}]}} \times$$

$$\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot [H^+]^2},$$

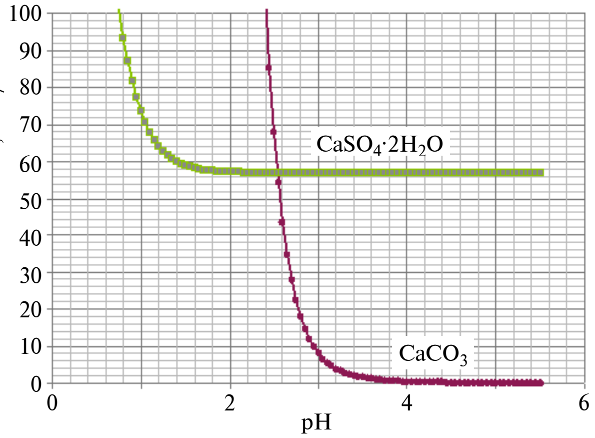

Fig. 1. The dependence of solubility of $CaCO_3$ and $CaSO_4 \cdot 2H_2O$ on pH

As it is obvious from Fig. 1, $S(CaCO_3) < S(CaSO_4 \cdot 2H_2O)$ condition is observed at pH > 5.1; i.e. conversion of $CaSO_4 \cdot 2H_2O$ into $CaCO_3$ will take place at pH values higher than 5.1.

This dependence discovered by calculations has found its complete and adequate proof in experimental studies. During partial addition of ammonia reagent ($(NH_4)_2CO_3$) into the reaction medium in the form of NH_3 and CO_2, process temperature is set at (323 ± 5) K being sufficient for the intense course of the reaction (1) up to its full completion after 50–60 min with the formation of thick slurry with Solid:Liquid ratio (S:L) ≈ ≈ 1:(1.10–1.15).

During the second phase of utilization processing of phosphogypsum, directly into the pulp obtained during the first stage, that is without technologically complicated and slow filtration separation of nascent $CaCO_3$ (in contrast to the known solutions [10, 17, 18]), solutions of substandard extraction acid (12–15 % P_2O_5), i.e. phosphate acid of second or third stage of phosphogypsum sediment washing, were added with realization of transformation reaction (2) and (3).

Reactions (2) and (3) are exothermic and apparently thermodynamically probable without the need for external heating of the reaction mixture.

Derived by the method outlined above, equations for calculation of equilibrium concentrations of $[Ca^{2+}]$ and solubility (S) of calcium phosphate in solution depending on pH in the presence of sulfate-ions and target solid phases of calcium hydro- and dihydrophosphates (HPh and DHPh) are as follows:

$$S_{HPh} = \frac{SP_{HPh}}{[Ca^{2+}]} \times$$

$$\frac{[H^+]^3 + [H^+]^2 \cdot K_1 + [H^+] \cdot K_1 \cdot K_2 + K_1 \cdot K_2 \cdot K_3}{K_1 \cdot K_2 \cdot K_3},$$

where $K_1 = 7.6 \cdot 10^{-3}$; $K_2 = 6.2 \cdot 10^{-8}$; $K_3 = 4.4 \cdot 10^{-13}$ – staged ionization constants of ortophosphate acid.

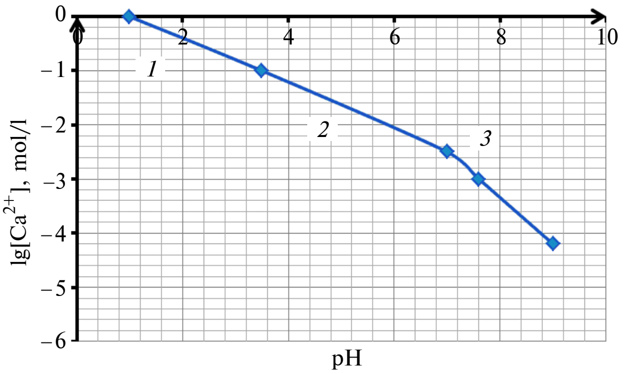

Fig. 2. Effect of the medium acidity on the equilibrium concentration of calcium ions during the phosphate-acid dissolution of calcium-containing substances: *1* – calcium dihydrophosphate; *2* – calcium hydrophosphate; *3* – calcium phosphate

Calculated dependencies of solubility of calcium phosphate on pH are shown in Fig. 2. Solutions imperfection was accounted for, as in previous cases, by correction of solubility products and ionization constants using activity coefficients.

From the Fig. 2, it is possible to conclude that, in the reaction medium, depending on its acidity is formed mono- (within the pH range of 1.1–3.7) and dibasic (within the pH range of 3.8–7.0) calcium phosphates. The solid phase of calcium phosphate $Ca_3(PO_4)_2$ being undesirable for the fertilizer destination of target product is formed mainly in an alkaline environment.

The product of the second stage of process is also quite thick suspension with S:L ≈ 1:(1.7–1.8). Moderate drying of it by waste flue gases at (390–423) K (to avoid losses of ammonia components during thermal decomposition of $(NH_4)_2SO_4$) in apparatus of the "fluidized bed" type leads to obtaining of the dry complex fertilizer with the following composition (defined chemically and by X-ray method using universal diffractometer Rugaku Ultima IV): $N:P_2O_5:Ca:S \approx 7.9:37:35:1.8$, and with the ratio $P_2O_{5(\text{soluble})}/P_2O_{5(\text{digestible})} = 94\,\%$.

The effect of the resulting fertilizer batches were tested on actual, exchange, and hydrolytic acidity of soil. It was found that the fertilizer use is recommended for alkaline and neutral Ukrainian soils or for fertilization of soil intended for growing agricultural plants requiring high soil acidity.

Conclusions

From phosphogypsum was obtained more valuable product – complex NPCa-fertilizer. Fertilizer received with a minimum of hazardous gas emissions and toxic effluents, for little-stage technology in environmentally sound conditions.

It is obtained complex fertilizer with composition 7.9 % N, 37 % P_2O_5, 35 % Ca, 1.8 % S, containing phosphorus in the form of $Ca(H_2PO_4)_2$, $CaHPO_4$ (at a ratio $P_2O_{5(\text{soluble})}/P_2O_{5(\text{digestible})} = 94\,\%$), and the nitrogen in the form $(NH_4)_2SO_4$.

Using the results of conducted theoretical and experimental studies, optimal conditions were found for two-stage utilization conversion of phosphogypsum into complex fertilizer. A further work steps will be the pilot production trial of the proposed technology and its implementation at chemical plants.

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ПЕРЕРОБКА ФОСФОГІПСУ В КОМПЛЕКСНЕ ДОБРИВО

Проблематика. При виробництві фосфоровмісних добрив та екстракційної фосфатної кислоти відбувається накопичення екологічно небезпечного відходу – фосфогіпсу. На сьогодні на території України у відвалах міститься близько 30 млн т фосфогіпсу.

Мета дослідження. Метою роботи є одержання з фосфогіпсу за безвідходною технологією комплексного NPCaS-добрива.

Методика реалізації. Переробка фосфогіпсу у відносно “м’яких” технологічних умовах, без залучення високотемпературних (1173–1753 К) процесів. Проведено дослідження двостадійної утилізаційної переробки типового фосфогіпсу в комплексне добриво складу 7,9 % N, 37 % P_2O_5, 35 % Ca, 1,8 % S з вмістом фосфору у вигляді Ca(H2PO4)2, $CaHPO_4$ (при співвідношенні $P_2O_{5(\text{водорозч.})}/P_2O_{5(\text{засв.})} = 94\ \%$), азоту – у вигляді $(NH_4)_2SO_4$. Перша стадія процесу реалізується розкладанням фосфогіпсу за температури (323 ± 5) К розчинами $(NH_4)2CO_3$ за pH > 5,1 з одержанням осаду (суспензії) $CaCO_3$ у розчині $(NH4)_2SO_4$. На другій стадії утворена густа суспензія обробляється (без фільтраційного відділення $CaCO_3$) розчинами некондиційної фосфатної кислоти без зовнішнього нагріву за витримки pH середовища у межах 6,8–6,9. Кінцева суспензія висушується в апараті типу "киплячий шар" за температури (390–423) К.

Результати дослідження. Отримано кінцеве тверде добриво, споживча якість якого перевірена на зразках ґрунтів сільськогосподарського призначення.

Висновки. На основі фосфогіпсу отримано комплексне мінеральне добриво за малостадійною безвідходною технологією в екологічно доцільних умовах.

Ключові слова: фосфогіпс; комплексне добриво; суспензія; малостадійна технологія; некондиційна фосфатна кислота.

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ПЕРЕРАБОТКА ФОСФОГИПСА В КОМПЛЕКСНОЕ УДОБРЕНИЕ

Проблематика. При производстве фосфорсодержащих удобрений и экстракционной фосфорной кислоты происходит накопление экологически небезопасного отхода – фосфогипса. На сегодняшний день на территории Украины в отвалах находится около 30 млн т фосфогипса.

Цель исследования. Целью работы является получение из фосфогипса по безотходной технологии комплексного NPCaS-удобрения.

Методика реализации. Переработка фосфогипса при относительно "мягких" технологических условиях, без привлечения высокотемпературных (1173–1753 К) процессов. Проведено исследование двухстадийной утилизационной переработки типового фосфогипса в комплексное удобрение состава 7,9 % N, 37 % P_2O_5, 35 % Ca, 1,8 % S с содержанием фосфора в виде $Ca(H_2PO_4)_2$, $CaHPO_4$ (при соотношении $P_2O_{5(\text{водораств.})}/P_2O_{5(\text{усв.})} = 94\ \%$), азота – в виде $(NH_4)_2SO_4$. Первая стадия процесса проводится разложением фосфогипса при температуре (323 ± 5) К растворами $(NH_4)_2CO_3$ при pH > 5,1 с получением осадка (суспензии) $CaCO_3$ в растворе $(NH_4)_2SO_4$. На второй стадии полученная густая суспензия обрабатывается (без фильтрационного отделения $CaCO_3$) растворами некондиционной фосфатной кислоты без наружного подогрева при поддержании pH среды 6,8–6,9. Конечная суспензия высушивается в аппарате типа "кипящий слой" при температуре (390–423) К.

Результаты исследования. Получено конечное твердое удобрение, потребительское качество которого проверено на образцах почв сельскохозяйственного назначения.

Выводы. На основе фосфогипса получено комплексное минеральное удобрение за малостадийной безотходной технологией в экологически целесообразных условиях.

Ключевые слова: фосфогипс; комплексное удобрение; суспензия; малостадийная технология; некондиционная фосфатная кислота.

Рекомендована Радою
хіміко-технологічного факультету
НТУУ "КПІ"

Надійшла до редакції
4 березня 2015 року