ISSN 1392 – 1231. CHEMINĖ TECHNOLOGIJA. 2013. Nr. 2 (64)

Producing calcium nitrate and rare-earth element concentrates by phosphogypsum conversion

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crossref http://dx.doi.org/10.5755/j01.ct.64.2.6024

Received 3 December 2013; Accepted 30 December 2013

Experimental researches of the dissolution of calcium carbonate obtained as a result of phosphogypsum conversion by ammonium or sodium carbonate and nitric acid with obtaining a concentrate of rare-earth elements and other liquid products have been performed. The structure of phosphochalk and the outlet half-product is presented. The substantiation of recycling expediency of phosphogypsum waste – phosphoric acid and phosphoric fertilizers has been carried out.

Keywords: phosphogypsum, ammonium & sodium carbonate, calcium nitrate, a concentrate of rare-earth elements

Introduction

The recycling of phosphogypsum (PG) – a large-scale phosphoric waste of mineral fertilizers manufactured from apatite and phosphorite – remains till now, taking into account the increasing requirements of ecologists, an unresolved problem [1–3]. Being a mix of many valuable chemical substances, PG still accumulates on open areas, and its limited recycling is carried out generally by addition into building materials [4, 5]. The structure of PG phosphoric raw materials formed after processing from the known deposits, which are used or can be used by the enterprises of Ukraine, is shown in Table 1 [5]. One can see from Table 1 that PG consists mainly of calcium sulphate and is expedient for applying as a secondary raw material for the industrial production of sulphur and calcium compounds. Besides, it is known that apatite and phosphorite ores contain rare elements (RE) [6].

Table 1. Phosphogypsum composition of different sources

Chemical compound upon recalculation into solid, %	Deposit of phosphor-containing raw materials		
	The Kola	Karatau (mark P)	Syrian Knafis
CaO	39–40	32.5	38–39
SO_3	56–57	46.5	52–54
P_2O_5 (gen.)	1.0–1.2	1.6	1.0–1.2
P_2O_5 (w.s.)	0.5–0.6	0.6	0.4–0.5
R_2O_3	0.5–0.6	0.5	0.2
Fe_2O_3	-	0.2	-
F	0.3–0.4	0.3	1.1–1.3
The insoluble rest	0.7–0.8	17.0	2.0

R – Rare earth elements

Rare-earth elements and compounds on their basis have unique properties that make them irreplaceable in many branches of industry. They are used as catalysts in chemical technology, it oil refining, neutralizers in cars, in the manufacture of alloys for batteries, ceramics and magnets, and also exhaust in the processing of optical materials, radio- and quantum electronics, the nuclear technics, etc. [7]. Calcium saltpetre is in demand not only as a mineral fertilizer, but also as an industrial salt used in the manufacture of explosives, in building, municipal service, etc. Its manufacture from natural raw materials (limestone, lime) is rather expensive [8]. Decreasing expenses on saltpetre manufacture through the use of calcium contained in PG is rather urgent.

The thermal decomposition of PG with calcium and sulphur oxides in today's conditions is energetically unprofitable. The efforts of researchers are directed to studying and working out the PG processing reactants ways with outlet of some the products having a stable or extending commodity market – ammonium or sodium sulphate, phosphochalk (technical calcium carbonate), RE concentrate, etc. [9, 10].

Research objective – to study the complex processing of phosphoric acid and phosphoric fertilizers production wastes by means of calcium carbonate dissolution with nitric acid of the residue at PG conversion with ammonium or sodium carbonate for obtaining RE concentrate and high-quality saltpetre.

Materials and methods

The PG (Kola apatite wastes) conversion was carried out by water soluble ammonium or sodium carbonates.

The basic processes of calcium carbonate interaction with carbonates proceed according to the reactions:

$$CaSO_4{\cdot}2H_2O + (NH_4)_2CO_3 = CaCO_3\downarrow + (NH_4)_2SO_4 + 2H_2O; \quad (1)$$

$$CaSO_4{\cdot}2H_2O + Na_2CO_3 = CaCO_3\downarrow + Na_2SO_4 + 2H_2O. \quad (2)$$

PG conversion with ammonium carbonate.

250 g (20 % of moisture) of a PG sample was crushed to a homogeneous state, a 30 % solution of ammonium carbonate (450 ml) was prepared and poured into a glass reactor (V = 1 dm^3) built in the thermostat. The thermostat was filled the distilled water whose temperature was regulated with a contact thermometer and supervised controlled with a control glass thermometer. The ammonium carbonate solution was heated to 50 °C. Into the reactor with the solution the crushed phosphogypsum was gradually dosed out and mechanically mixed for 10–15 minutes. The rate of the mixer was 120 rev./min. The conversion process lasted 2 hours, and then the suspension was filtered under vacuum. The obtained phosphochalk was dried up and weighed, its volume and the density of the formed ammonium sulphate solution were measured.

PG conversion by sodium carbonate was performed similarly, only the temperature of the 30 % sodium carbonate solution was maintained at 70 °C and a conversion was run within 1 hour.

The content of ammonium, sodium, calcium carbonates, calcium nitrate, ammonium and sodium sulphates in the solutions determined by the known methods of chemical analysis.

To the expanded analysis of a chemical compound of the obtained substances we applied a technique with the use of the MAX-GV spectroscan, a vacuum X-ray fluorescent crystal-diffraction scanning spectrometer which enables to determine with a high sensitivity different elements from ^{11}Na to ^{92}U in a wide range of concentration – from the lowest limit to 100 %.

For the purpose of extraction the RE concentrate received calcium carbonate whose structure is scanned and resulted in Table 2 treated by HNO_3 – a solution of the technical not concentrated nitric acid (“Chemical battalion”, Dneprodzerzhinsk, Ukraine).

Table 2. Composition of the phosphochalk obtained after PG conversion by ammonium and sodium carbonates in parallel experiments 1, and 2

Component	Reagents			
	$(NH_4)_2CO_3$		Na_2CO_3	
	The content of elements recalculated to oxides, %			
	1	2	1	2
Al_2O_3	1.218	1.197	0.394	0.386
P_2O_5	0.992	1.050	0.884	0.836
$CaSO_4$	4.446	4.016	25.379	29.004
K_2O	0.021	0.030	0.024	0.023
$CaCO_3$	85.206	85.378	67.692	64.430
TiO_2	0.319	0.296	0.258	0.242
Cr_2O_3	0.043	0.031	0.027	0.030
MnO_2	0.032	0.031	0.033	0.026
Fe_2O_3	0.375	0.317	0.261	0.250
NiO	0.023	0.023	0.019	0.020
ZnO	0.029	0.030	0.027	0.026
$SrSO_4$	5.462	5.675	4.072	3.833
Y_2O_3	0.087	0.090	0.055	0.050
La_2O_3	0.355	0.375	0.225	0.218
CeO_2	0.565	0.604	0.363	0.350
Pr_6O_{11}	0.218	0.227	0.042	0.042
Nd_2O_3	0.193	0.203	0.133	0.123
Sm_2O_3	0.087	0.092	0.022	0.021
Gd_2O_3	0.080	0.084	0.023	0.023
Dy_2O_3	0.052	0.052	0.005	0.006
Er_2O_3	0.043	0.041	0.004	0.004
PbO	0.096	0.105	0.053	0.052
Eu_2O_3	0.052	0.054	0.005	0.005

Results and discussion

Complex phosphogypsum processing assumes the use of all conversion products. Differently from the solution of ammonium sulphate (nitric fertilizer) or sodium sulphate (the medical preparation, a component of washing-up liquids), phosphochalk does not correspond to the quality requirements to raw materials for manufacturing chemical products. It contains the basic insoluble impurity which has passed into it from phosphogypsum. By results of spectroscopic research of conversion products content (Table 2), the solid phase contains 65–86 % of calcium carbonate with a crystal lattice polluted with strontium impurity (basically in the sulphur-oxide compound form), lanthanum, cerium, iron, aluminium, titanium, zinc, and others.

The phosphogypsum conversion degree by ammonium carbonate is a little higher than by sodium carbonate; however, the phosphochalk structure in both cases essentially does not differ. Hence, the use of sodium carbonate would allow to lower the expenses on reagents.

The way of calcium carbonate processing is investigated by employing nitric acid solutions with the subsequent separating of a deposit in the form of a concentrate of rare elements from the calcium nitrate solution.

The calcium carbonate structure allows selective RE extraction by its dissolution in nitric acid at acidity in the range pH 5.1–7.1

Calcium carbonate dissolution by nitric acid was carried out in the reactor with a mixer, volume 1 dm^3.

A phosphochalk sample of 200 g (moisture 20 %) before charging it into the reactor has been conditioned by 10–15 % calcium nitrate solution in the ratio H : L = 1 : 1–2. In a glass with the pulp, at a constant mixing, nitric acid was dosed out from a burette, and at each 10 ml the solution pH was measured. The neutralisation lasted 10–15 minutes until the solution pH reached 5.1–7.1. The obtained suspension was filtered on a vacuum installation to separate the solid from the liquid. The volume and density of the obtained calcium nitrate solution were measured.

The deposit that remained on a funnel was washed out with hot (50 °C) water in the ratio H : L = 1 : 2, dried in a drying stove at a temperature of 105–110 °C to a constant weight, and portions of 10 g were selected to study the content of the RE concentrate with a scanning spectrometer "Spectroscanner MAX-GV".

During the experimental studies, from each trial on the average 15–20 g of the RE concentrate were obtained; their structure is presented in Table 3.

Table 3. The composition of RE concentrate of the conversion phosphochalk obtained after its dissolution with nitric acid

Component	The content of elements recalculated into oxides, % of weight	
	1	2
SiO_2	1.060	0.930
P_2O_5	3.987	4.594
K_2O	0.125	0.128
$CaSO_4$	61.403	60.629
TiO_2	1.963	2.011
MnO_2	0.117	0.119
Fe_2O_3	1.882	2.036
NiO	0.037	-
CuO	0.262	0.279
$SrSO_4$	22.507	21.524
La_2O_3	1.633	1.829
CeO_2	2.528	2.945
Nd_2O_3	0.680	0.901
Sm_2O_3	0.316	0.377
Dy_2O_3	0.133	0.140
Gd_2O_3	0.339	0.398
Pr_2O_3	0.928	1.066
Er_2O_3	0.102	0.094

From Table 3 it is obvious that the basic part of the deposit is not converted calcium sulphate and a considerable part of strontium sulphate. The RE content is at a level sufficient for its industrial allocation. The processing of the conversion calcium carbonate by nitric acid allows obtaining a calcium nitrate solution (Table 4) and the RE concentrate which contains up to 6.63 % of the rare earths and to 15 % of strontium in the form of strontium sulphate – celestine. All rare-earth elements from phosphochalk in the interval pH = 5.1–7.1 are practically not washed away and remain in the firm phase whose volume decreases 12 times.

From Table 4 data it follows that the quality of a calcium nitrate solution of 45 % conversion calcium carbonate obtained after dissolution with nitric acid in experimental conditions corresponds to the quality requirements imposed to industrial solutions.

Table 4. Comparison of calcium nitrate solution quality indicators of upon calcium carbonate dissolution with a 45 % nitric acid in experimental and industrial conditions ("Chemical Battalion", Dneprodzerzhinsk)

Index name	Data of the analysis in industrial conditions	Data of the analysis of experimental solutions					
		Experiment number					
		1	2	3	4	5	6
External appearance	The solution is colourless, light yellow or light grey	The solution is colourless, light yellow or light grey					
The mass fraction of calcium nitrate $Ca(NO_3)_2$ is no less than (%)	40.0	39.48	43.23	40.09	39.09	39.43	36.98
Activity of hydrogen ions of a calcium saltpetre solution dissolved in the ratio 1: 2, pH	5–8	5–7	5–7	5–7	5–7	5–7	5–7

On the basis of the results of the studies, a basic technological scheme of a complex chemical phosphogypsum processing with obtaining calcium nitrate, a concentrate of rare-earths elements, calcium carbonate and ammonium or sodium sulphates has been proposed (Fig. 1).

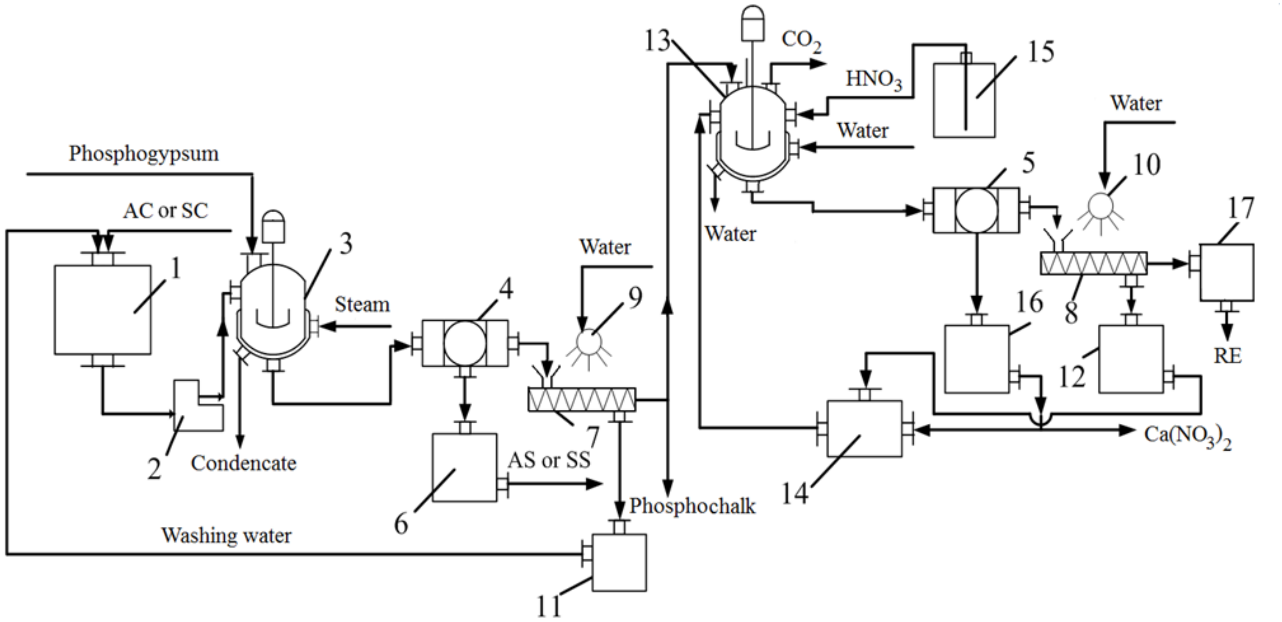

Fig. 1. The basic technological scheme of complex phosphogypsum chemical processing: 1 – capacity for the preparation of ammonium carbonate AC or sodium carbonate SC solution, 2 – the dosing pump, 3 – conversion reactor, 4, 5 – filters, 6 – collector of ammonium sulphate AS or sodium sulphate SS, 7, 8 – worm feeders, 9, 10 – sprays, 11, 12 – washing water collectors, 13 – capacity for carbonate calcium pulp dilution, 14 – capacity for the preparation of a 10–20 % calcium nitrate solution, 15 – capacity of 45–57 % nitric acid, 16 – 40 % calcium nitrate solution collector, 17 – RE concentrate collector.

The ammonium or sodium carbonate solution, prepared in the tank 1, is fed by the dosing pump 2 to the reactor 3 together with the crushed phosphogypsum. The obtained suspension is divided on the filter 4 into a sulphate ammonium or sodium solution which are collected in the collection 6, and the washed out phosphochalk which by the feeder 7 is fed into the collector 13 (washing waters are collected in the collector 11 and are used for preparing ammonium or sodium carbonate solutions). Part of phosphochalk at this stage can be considered as an end-product. In the capacity 13, the phosphochalk is pulped with 10–20 % calcium nitrate solution delivered from capacity 14. Then, to the capacity 13, 45–57 % nitric acid is delivered from the capacity 15. The obtained suspension is divided in the filter 5 into a calcium nitrate solution and a RE concentrate deposit which after washing is collected in the collector 17. The filtrate, a 40 % calcium nitrate solution, arrives into the collector 16. Part of this solution is used for the preparation of a 10–20 % calcium nitrate solution for calcium carbonate dilution. The washing water from the feeder 8 returns through the capacities 12 and 14 into the cycle (for calcium carbonate dilution).

The above technology allows overworking phosphogypsum practically without wastes with obtaining chemical products having a considerable market demand.

Conclusions

1. The possibility of working out a complex technology of phosphogypsum processing with obtaining fertilizers, industrial salts and RE concentrate is shown.
2. The spectral analysis determines the phosphochalk structure after PG conversion by ammonium or sodium carbonate and RE concentrate. It is shown that the RE content in a concentrate reaches more than 6.6 %.
3. The quality of the calcium nitrate solution obtained from phosphochalk is comparable with the quality of the industrial solution, and RE in the solution is practically absent.
4. The technological parameters of complex chemical phosphogypsum processing with obtaining calcium nitrate, a concentrate of rare-earth elements, calcium carbonate and ammonium or sodium sulphates are investigated.
5. The basic technological scheme of a complex chemical processing of phosphogypsum is proposed.

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S. V. Vlasjan, N. D. Voloshin, A. B. Shestozub

KALCIO NITRATO IR RETŲJŲ ELEMENTŲ KONCENTRATO GAVIMAS IŠ FOSFOGIPSO

Santrauka

Šiame darbe ištirtos galimybės kompleksiškai perdirbti fosforo rūgšties ir fosforo trąšų gamybos atliekas – fosfogipsą. Nustatyta, kad perdirbant šias atliekas gali būti vykdoma fosfogipso konversija amonio arba natrio karbonatu. Ištirta konversijos produktų cheminė sudėtis ir nustatyta, kad kietojoje fazėje yra 65–86 % kalcio karbonato ir retųjų metalų (stroncio, lantano, cerio, titano, cinko ir kt.). Kietąją fazę paveikus azoto rūgštimi gaunamas retųjų metalų koncentratas ir aukštos kokybės kalcio nitratas. Pasiūlyta fosfogipso perdirbimo principinė technologinė schema.