

# Technology for Processing Technical Calcium Carbonate Obtained from Phosphogypsum into Pure Calcium Carbonate and Rare-Earth Element Concentrate

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## Abstract

Results are presented concerning laboratory-scale studies on the thermal decomposition of technical calcium carbonate (phosphochalk) obtained *via* phosphogypsum conversion into sodium carbonate, and calcium leaching in ammonium chloride solution. It has been established that at the temperature of 900 °C, phosphochalk completely decomposes to produce CaO. As the result of leaching at a molar ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}} > 2.1$  almost all  $\text{CaO}_{\text{act}}$  passes into solution. The carbonization of  $\text{CaCl}_2$  solution obtained allows one to obtain high quality calcium carbonate. Rare-earth elements and strontium under leaching  $\text{CaO}_{\text{act}}$  are concentrated in an insoluble residue, whereas their content increases up to 4–5 and 10–11 %, respectively. Due to this fact the insoluble residue could be considered a raw material for obtaining REE compounds and strontium.

**Key words:** phosphochalk, phosphogypsum, conversion, rare-earth elements, strontium

## INTRODUCTION

Phosphochalk (technical calcium carbonate) obtained *via* conversion of phosphogypsum by means of soda solutions contains strontium and rare-earth elements (REE) [1]. Figure 1 demonstrates XRD profiles of naturally occurring M-60 calcium carbonate and phosphochalk obtained *via* soda conversion of phosphogypsum.

It is seen that the main reflexes of naturally occurring chalk and phosphochalk correspond to calcite (ASTM 5-586). The XRD pattern of phosphochalk also exhibits the reflexes of  $\text{SrSO}_4$  ( $d = 3.587, 3.314, 2.053, 1.475 \text{ \AA}$ ) (ASTM 5-593).

The testing performed has demonstrated [1] that phosphochalk could be used as a filling material in the manufacture of linoleum, as well as for obtaining cement [2]. However, the most valuable components are presented by REE and strontium, therefore first of all one should consider phosphochalk to be a raw material for obtaining REE and strontium compounds rath-

er than a commodity output. Moreover, calcium as the main component of technical calcium carbonate after phosphogypsum conversion can be converted into calcium salts.

There are almost no works available from the literature devoted to the processing of technical calcium carbonate (phosphochalk), obtained by phosphogypsum conversion into carbonates. The authors of [3] suggest using phosphochalk for obtaining ammonia-calcium saltpetre with a partial isolation of REE concentrate. However, in this case, strontium contained in phosphochalk would pass to saltpetre to be irretrievably lost. The authors of [4] have considered strontium concentrating through nitric acid treatment of technical calcium carbonate obtained *via* the conversion of phosphogypsum by ammonium carbonate. It has been established that under optimum processing conditions, the content of strontium in the residue exhibits a 9 to 11 fold increase and the concentrates enriched contain 19–25 % of

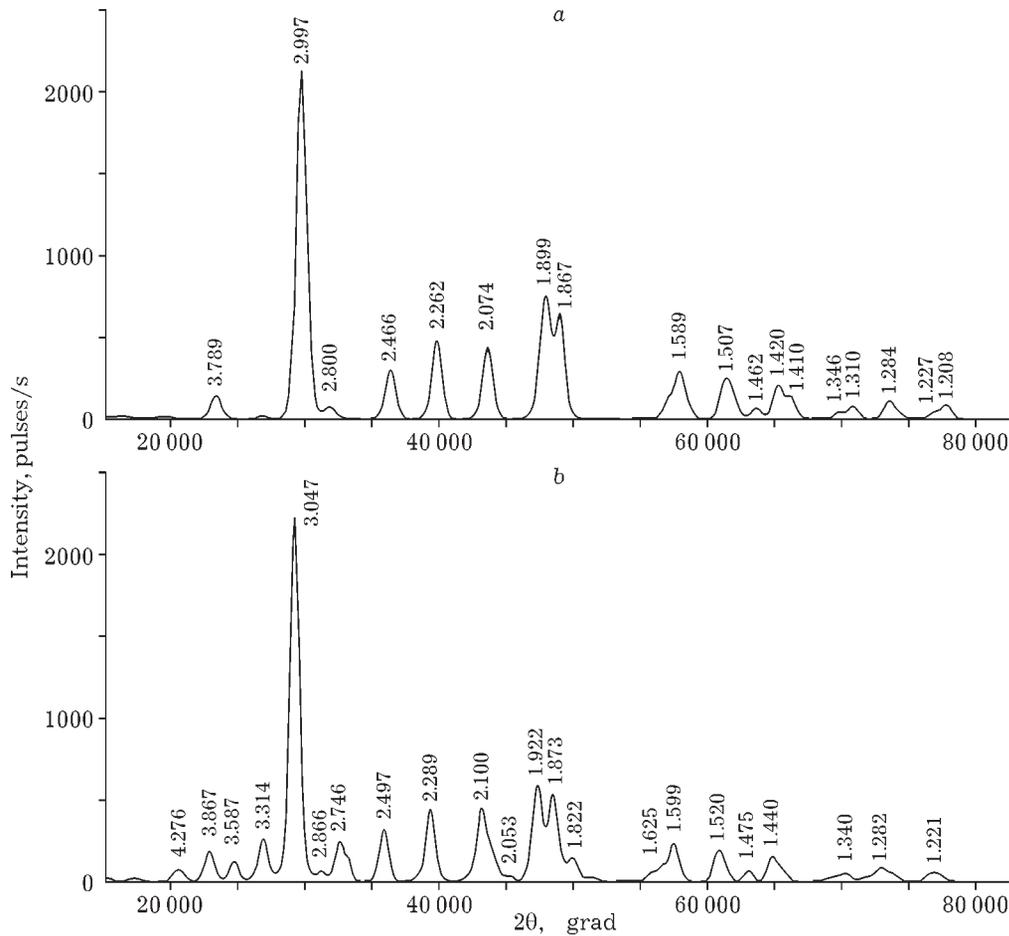


Fig. 1. XRD profiles of naturally occurring chalk M-60 (a) and phosphochalk (technical calcium carbonate) obtained from phosphogypsum (b).

strontium. However, there are no data in [3] concerning the further processing of strontium carbonate and calcium carbonate mixture for obtaining strontium salts. It is obvious that the acidic decomposition of technical calcium carbonate would complicate the extraction of REE from the solutions obtained due to high calcium content.

It is known [5] that in the chemical enrichment of ores with a high content of carbonates rocks, one employs the process of preliminary roasting in order to decompose carbonates into oxides. Calcium oxide formed in this case can be readily dissolved in ammonium chloride. It is obvious that the removal of the most part of calcium would allow concentrating the remaining components of technical calcium carbonate as well as increasing the content of REE and strontium in the insoluble residue.

The authors of [6] have proposed a method for solving this problem. It has been demon-

strated that technical calcium carbonate after the conversion of phosphogypsum by ammonium carbonate can be in a most intense manner decomposed to produce CaO at the temperature of 950 °C, however no kinetic characteristics of the decomposition process were presented in [6]. In the present work, an attempt is undertaken to make up for this deficiency. In the same work, we propose to obtain pure calcium oxide *via* the decomposition of calcium carbonate after carbonization a leaching solution. At the same time, obtaining chemically precipitated chalk (Precipitated Calcium Carbonate – PCC) whose market intensively develops nowadays is of a considerable interest. The greatest gain in the demand for PCC is observed for the manufacture of paper, plastics and general mechanical rubber goods amounting to 7–10 % one year [7].

In this communication, results are presented concerning laboratory-scale experiments on

the further processing of technical calcium carbonate obtained *via* the conversion of phosphogypsum by soda aimed at obtaining pure calcium carbonate and REE concentrate.

## EXPERIMENTAL

The studies concerning the processing of phosphochalk from phosphogypsum were carried out with the use of samples obtained by phosphogypsum conversion by soda solutions [1]. According to chemical analysis, phosphochalk exhibited the following composition, mass %: CaO 49.3, SrO 2.1,  $\text{Ln}_2\text{O}_3$  0.8,  $\text{SO}_3$  2.6,  $\Sigma(\text{Fe}_2\text{O}_3, \text{TiO}_2, \text{Al}_2\text{O}_3)$  0.7,  $\text{SiO}_2$  0.9,  $\text{F}^-$  0.4,  $\text{P}_2\text{O}_5$  total 1.4,  $\text{CO}_2$  40.6,  $\text{Na}_2\text{O}$  1.1,  $\text{H}_2\text{O}$  0.5. Chemical composition for phosphochalk, calcium oxide, solid residue, leaching solutions and pure calcium carbonate determined by means of techniques described in [8]. The XRD phase analysis of samples was performed employing DRON-4-07 diffractometer ( $\text{CuK}_\alpha$  radiation). The thermogravic curves for samples were registered using a Q1500 D derivatograph; a weighed sample portion being equal to 0.5 g, the heating rate amounting to  $10^\circ\text{C}/\text{min}$ . The kinetics of phosphochalk decomposition was studied in a series of experiments at the temperature values higher than  $800^\circ\text{C}$ , since the thermogravic analysis has

demonstrated that the decomposition of phosphochalk begins at the temperature higher than  $700^\circ\text{C}$  (Fig. 2). The decomposition of samples was performed in a SNOL 7.2/1300 muffle furnace with maintaining the temperature accurate within  $\pm 2.5^\circ\text{C}$ . Each point of the kinetic curve was registered for a separate sample. The initial mass of a sample in the experiments amounted to 10 g. At certain time intervals, residual mass of a sample was determined to accuracy within  $\pm 0.01$ . The decomposition level of phosphochalk was calculated according to the formula

$$\alpha = (P_0 - P_t) / \Delta P_\infty \times 100 \% \quad (1)$$

where  $\alpha$  is the level of decomposition into calcium oxide, %;  $P_0$  and  $P_t$  are the initial and variable (current) mass of a sample, respectively, g;  $P_\infty$  is the mass for the complete decomposition of a sample, g;  $\Delta P_\infty = P_0 - P_\infty$  is the mass loss due to the complete decomposition.

The technical calcium oxide obtained after the decomposition was processed by the solutions of ammonium chloride for leaching calcium into the solution in the form of  $\text{CaCl}_2$ . In the experiments we used technical CaO obtained resulting from the decomposition of phosphochalk at the temperature of  $950^\circ\text{C}$  during 60 min, with the following composition, mass %:  $\text{CaO}_{\text{act}}$  82.1,  $\text{CaO}_{\text{bound}}$  3.5, SrO 3.1,  $\text{SO}_3$  3.9,  $\text{Ln}_2\text{O}_3$  1.2,  $\text{SiO}_2$  1.4,  $\Sigma(\text{Fe}_2\text{O}_3, \text{TiO}_2, \text{Al}_2\text{O}_3)$  1.1,  $\text{SiO}_2$  1.4,  $\text{P}_2\text{O}_5$  total 2.2,  $\text{F}^-$  0.6,  $\text{Na}_2\text{O}$  1.6.

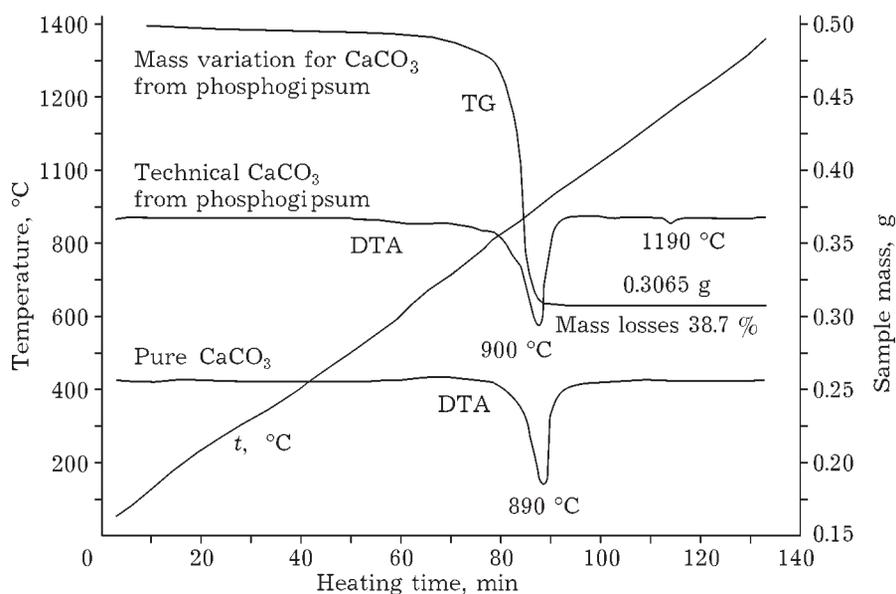
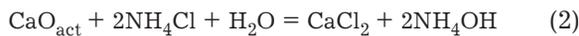


Fig. 2. Derivatographic curves of phosphochalk obtained from phosphogypsum and pure  $\text{CaCO}_3$ .

Technical calcium oxide was treated with an  $\text{NH}_4\text{Cl}$  solution at a room temperature, at a constant mass ratio  $L : S = 8$ , with various  $\text{NH}_4\text{Cl}$  concentration values in the reactor equipped with a mixer, during 20 min. Further the solid and the liquid phases were separated using a Buechner funnel. Leaching calcium into solution occurs according to the reaction



The  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}}$  molar ratio in the experiments was varied from 1.5 up to 2.5. The level of passing calcium into solution was calculated according to the formula

$$\varphi = \text{CaO}_s V_s / (\text{CaO}_{\text{act}} P_{\text{CaO}}) \quad (3)$$

where  $\varphi$  is the level of calcium passing into solution;  $\text{CaO}_s$  the content of CaO in the solution,  $\text{g}/\text{dm}^3$ ;  $\text{CaO}_{\text{act}}$  is the mass fraction of active CaO, %;  $V_s$  is the volume of filtrate,  $\text{dm}^3$ ;  $P_{\text{CaO}}$  is the mass calcium oxide for leaching, g.

The leaching solution, containing calcium chloride and ammonia was exposed to carbonization with carbonic gas (the volume fraction  $\text{CO}_2$  being equal to 38–40 %). After reaching pH 7.2–7.5 the suspension was added with a solution of ammoniac water (25 % aqueous solution of ammonia) in the amount equivalent to the residual content of  $\text{CaCl}_2$ , and then it was subjected to the further carbonization. The carbonization was carried out till the residual  $\text{CaCl}_2$  content equal to 0.5–1.2  $\text{g}/\text{dm}^3$  was reached in the solution, thereafter the solid ( $\text{CaCO}_3$ ) and liquid ( $\text{NH}_4\text{Cl}$ ) phases were separated *via* filtering through a vacuum Buechner funnel. The solid phase was dried at the temperature of 180–200 °C; then it was analyzed according to the State Standard GOST 8253–79. In the liquid phase, we determined the content of ammonium chloride, calcium,  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  employing the technique described in [8].

## RESULTS AND DISCUSSION

The thermographic analysis has demonstrated that the decomposition of phosphochalk begins at the temperature higher than 700 °C, whereas the total mass loss amounts to 38.7 % (see Fig. 2). Hence, when determining the decomposition level according to equation (1) the mass loss due to the complete decomposition of a sample amounts to  $\Delta P_\infty = 0.387P_0$ . The endot-

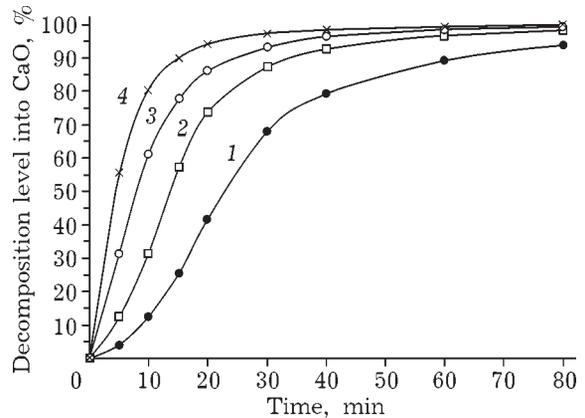


Fig. 3. Phosphochalk decomposition into  $\text{CaO}_{\text{techn}}$  at 850 (1), 950 (2), 1100 (3), 1200 °C (4).

hermic effect at 900 °C corresponds to the complete decomposition of calcium carbonate from phosphochalk. In addition, the thermographic curve of phosphochalk exhibits an endoeffect at 1190 °C, to all appearance, corresponding to the decomposition of strontium carbonate formed from strontium sulfate of phosphogypsum under conversion by soda solutions. Pure  $\text{CaCO}_3$  sample exhibits a single endoeffect at 890 °C.

Figure 3 demonstrates kinetic curves for the decomposition of the experimental samples of phosphochalk at various temperature values. One can see that an almost complete decomposition of the samples occurs at the temperature of 900–1200 °C within 60–80 min.

Kinetic curves of phosphochalk decomposition we have used to determine the constants of thermal dissociation. The processing of the decomposition kinetic curves was performed according to the Avrami–Erofeev equation [9]:

$$1 - \alpha = \exp(-k\tau^n) \quad (4)$$

Figure 4 demonstrates the anamorphoses of decomposition kinetic curves related to coordinates  $\ln(\ln(1 - \alpha)) - \ln \tau$ .

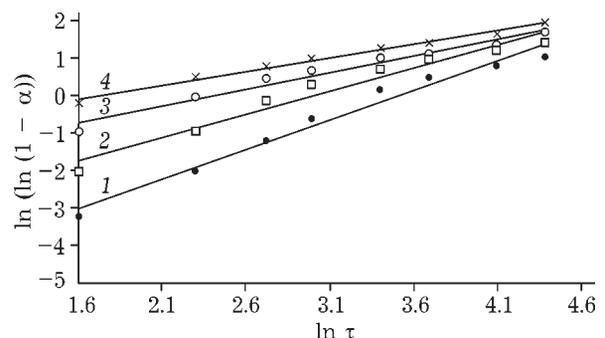


Fig. 4. Kinetic curve anamorphoses for phosphochalk decomposition at 850 (1), 950 (2), 1100 (3), 1200 °C (4).

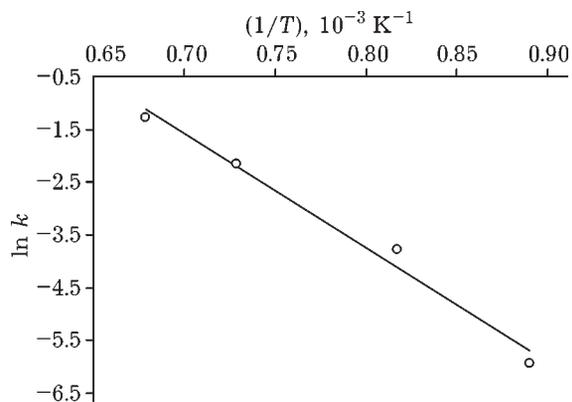


Fig. 5. Apparent rate constant for phosphochalk ( $\text{CaCO}_3_{\text{techn}}$ ) decomposition into  $\text{CaO}_{\text{techn}}$  depending on temperature related to  $\ln k - (1/T)$  coordinates.

For determining the apparent activation energy of thermal phosphochalk decomposition we performed the linearization of the obtained values for apparent rate decomposition constants related to coordinates  $\ln k - 1/T$  (Fig. 5).

The apparent activation energy amounted to  $E = (179.6 \pm 0.5)$  kJ/mol, which is close the value of apparent activation energy for the decomposition of limestone containing  $\text{CaCO}_3$  as the main component and impurities [10, 11].

Figure 6 demonstrates an influence of molar ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}}$  upon passing calcium into solution. It seen that at a ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}} = 2.1$  a complete passing of  $\text{CaO}_{\text{act}}$  into solution is attained. In the process of carbonizing  $\text{CaCl}_2$  solutions containing ammonia,  $\text{NH}_4\text{Cl}$  regeneration is observed to occur according to the reaction  $\text{CaCl}_2 + 2\text{NH}_4\text{OH} + \text{CO}_2 = \text{CaCO}_3 + 2\text{NH}_4\text{Cl} + \text{H}_2\text{O}$  (5). Due to this fact, it is possible to provide an almost complete returning  $\text{NH}_4\text{Cl}$  into the stage of leaching. Initial molar ratio  $\text{CaCl}_2 : \text{NH}_4\text{OH}$  in solutions after leaching in the experiments amounted to 1 : (1.94–1.96), which could be connected with a partial loss of ammonia un-

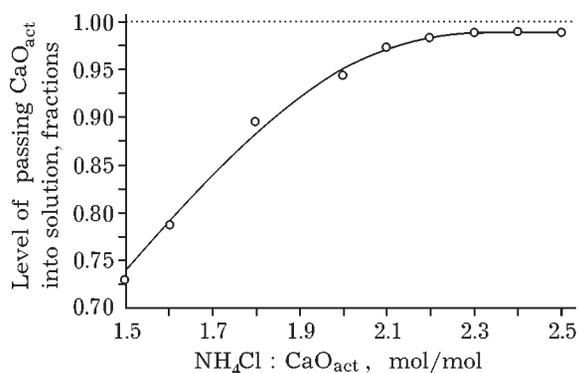


Fig. 6. Effect of molar ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}}$  on leaching calcium into solution from  $\text{CaO}_{\text{techn}}$ .  $T = 25^\circ\text{C}$ ,  $L : S = 8$ ,  $\tau_{\text{leach}} = 20$  min.

der leaching as well as solid and liquid phase separation after leaching due to ammonia volatility. The content of ammonium chloride in the liquid phase after carbonization amounted to 130–140 g/dm<sup>3</sup>. After correcting the  $\text{NH}_4\text{Cl}$  content and reaching the molar ratio  $\text{NH}_4\text{Cl} : \text{CaCl}_2 = (2.1\text{--}2.2) : 1$ , this solution could be used for leaching  $\text{CaO}_{\text{techn}}$ . The parameters of  $\text{CaCO}_3$  obtained are presented in Table 1.

Figure 7 demonstrates XRD profiles for calcium carbonate obtained *via* the leaching solution  $\text{CaCl}_2$  carbonization by the processing with  $\text{NH}_4\text{Cl}$  and the sedimentation of  $\text{CaCO}_3$  from the solution of chloride calcium by soda. It is seen that the sample of chalk obtained through the carbonization of the solution resulted from leaching technical calcium oxide from phosphogypsum by ammonium chloride is presented by calcite whose main reflexes coincide with the literature data (ASTM 5-586). The sample of calcium carbonate obtained from leaching solution *via* sedimentation by soda solutions is presented by two phases such as  $\text{CaCO}_3$  (ASTM 29-305) and calcite (ASTM 5-586). The solid residue from ammonium chloride leaching exhib-

TABLE 1

Main characteristics for calcium carbonate obtained from phosphogypsum

Parameter	State Standard GOST 8253-79, 1st grade	Calcium carbonate from phosphogypsum
Whiteness, %	≥93	≥98
$\text{CaCO}_3$ content, mass %	≥98.5	≥99.4
Alkalinity calculated for CaO, %	≤0.03	≤0.02
Mass fraction of HCl insoluble species, %	≤0.1	≤0.04

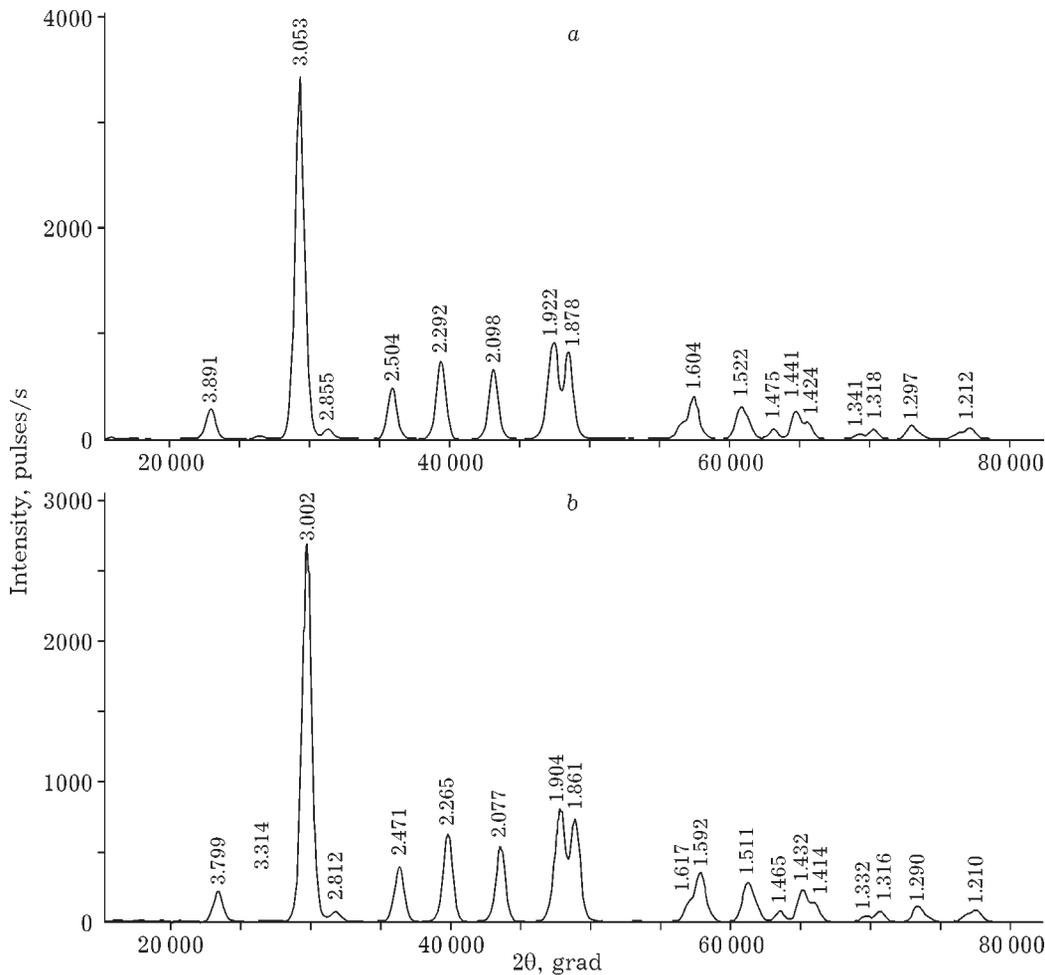


Fig. 7. XRD profiles of calcium carbonate obtained *via* carbonization of  $\text{CaO}_{\text{techn}}$  leaching solution from phosphogypsum by ammonium chloride (a) and precipitation by soda (b).

its the following composition, mass %:  $\text{CaO}_{\text{act}}$  17.8,  $\text{CaO}_{\text{bound}}$  12.3, SrO 11.3,  $\text{SO}_3$  20.3,  $\text{Ln}_2\text{O}_3$  5.1,  $\text{SiO}_2$  5.2, S ( $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ) 3.8,  $\text{SiO}_2$  5.2,  $\text{P}_2\text{O}_5$  total 7.6,  $\text{F}^-$  2.1,  $\text{Na}_2\text{O}$  5.9,  $\text{H}_2\text{O}$  6.5.

The chemical analysis of the residue has demonstrated that the processing of  $\text{CaO}_{\text{techn}}$  by ammonium chloride results in a considerable concentrating of valuable components inherent in phosphogypsum such as strontium and  $\text{Ln}_2\text{O}_3$ . Due to this fact, the solid residue from leaching could be considered to be a strontium and REE concentrate. Its further processing with the purpose of obtaining a commodity output such as strontium and REE compounds requires for the development of a technology.

## CONCLUSION

1. It has been established that the decomposition of phosphochalk (technical calcium car-

bonate), obtained by means of phosphogypsum conversion by soda solutions proceeds almost completely at the temperature of 900–950 °C during 50–60 min.

2. The apparent activation energy for the phosphochalk obtained *via* phosphogypsum conversion by soda solutions amounts to  $(179.6 \pm 0.5)$  kJ/mol.

3. The results of laboratory-scale experiments have demonstrated that ammonium chloride efficiently leaches calcium from the product of phosphochalk thermal decomposition obtained *via* soda conversion of phosphogypsum. The level of passing calcium into solution amounts to 97–98 % at a molar ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}} = (2.1\text{--}2.2) : 1$ . The solutions of calcium chloride containing ammonia could be subjected to carbonization with obtaining  $\text{CaCO}_3$ . At the same time, there is ammonium chloride regeneration occurring that can be repeatedly used for leaching calcium from  $\text{CaO}_{\text{act}}$  after cor-

recting the concentration of  $\text{NH}_4\text{Cl}$  up to a ratio  $\text{NH}_4\text{Cl} : \text{CaO}_{\text{act}} = (2.1-2.2) : 1$ .

4. Calcium carbonate obtained through the carbonization of leaching solutions meets the requirements of the State Standard GOST 8253-79, even surpassing them in some parameters.

5. In the solid residue of leaching, the content of strontium and REE increases to a considerable extent whereupon it could be considered a raw material for the extraction of these elements and obtaining a commodity output.

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