Phosphogypsum Processing into Sodium Sulphate and Technical Grade Calcium Carbonate

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Absract

Potentialities are considered for processing phoshogypsum into sodium sulphate and technical grade calcium carbonate with the use of soda. It is demonstrated that the process of phoshogypsum conversion proceeds during 20-30 min resulting in 96-98% conversion level. In order to obtain the solutions of sodium sulphate with a low content of calcium sulphate the conversion should be carried out under the conditions of 5-10% excess amount of soda with respect to sulphate ion as compared to the stoichiometric requirement. It has been established that in this case sodium sulphate corresponds to a superior quality product. The second product of phoshogypsum processing such as technical grade calcium carbonate is promising for utilizing as a filling material in the linoleum manufacture, being useful in the case of further processing as a raw material for obtaining of calcium, strontium and rare earths salts.

Key words: phoshogypsum, conversion, soda solutions, sodium sulphate, technical grade calcium carbonate

INTRODUCTION

The problems of processing the residues and refuse disposals of the chemical industry whose volumes have already reached a critical value are gaining a paramount importance all over the world. Waste products lie dormant on the cost price of industrial production resulting in a number of complicated problems.

The use of by-products of various industries allows one to solve a series of major problems such as a more complete utilizing the sources of raw materials, the development of new product manufactures as well as the improvement of regional environmental conditions. Moreover, the mining of man-caused deposits is worthwhile from the economic standpoint, too, since they are located at habitable areas. In addition, the development of man-caused deposits does not demand carrying out the expensive processes of crushing and chopping, and in the case of their complex use one can obtain a wide variety of useful products required.

Phoshogypsum represents one of such promising by-products. The volumes of phoshogypsum stored in the territories of the enterprises producing phosphate fertilizers (Belorechensk Minudobreniya Ltd., Balakovo Minudobreniya Ltd., *etc.*), constrain the growth of productive capacities and cause increasing the cost price of products because of a high payment for the use of lands for refuse disposals. Moreover, the storage of phoshogypsum results in a number of environmental problems. In this connection, solving the problem of recycling this product is of currently central importance.

There is a number of methods for the processing of phoshogypsum for today [1]:

1) conversion with the help of ammonium carbonate to yield ammonium sulphate and technical grade calcium carbonate;

2) reducing roasting up to obtaining calcium sulphide, hydrogen sulphide obtaining from calcium sulphide and further H_2S processing to yield sulphur;

3) reducing phoshogypsum with carbon oxide up to obtaining sulphur dioxide gas and its transformation into sulphuric acid;

4) obtaining sulphuric acid and cement by means of phoshogypsum roasting with clinkerforming additives.

In the course of the processes listed above the formation occurs of secondary by-products and wastes products whose scope is rather limited. At the same time phoshogypsum contains a number of valuable components such as calcium, strontium and rare-earth metal sulphates. The maximum extraction of these valuable components from phoshogypsum could allow one to reduce the volumes of mining. In this connection the development of a technology for phoshogypsum processing that allows one to extract calcium, sulphates, strontium and rare-earth metals (REM) to a maximal extent with the transformation into target products as well as to minimize the amount of waste products represents an important scientific and practical problem. The most optimal way to process phoshogypsum consists in the consecutive extraction of valuable components from the stuff with the retention of other compounds in an insoluble residue. Simultaneous concentrating these compounds in the solid residue could facilitate the extraction of these components at the following stage.

Similar approach was offered earlier in [2]. The authors carried out the conversion of phoshogypsum with the use of ammonium carbon ate and obtained ammonium sulphate, calcium oxide as well as the concentrate of rare-earth metals. A solution is known concerning the processing of phoshogypsum to produce ammonium sulphate, REM concentrate and calcium nitrate [3].

The goal of the present work consisted in the studies on the potentiality of carrying out the conversion of phoshogypsum with the use of soda solutions and with the obtaining sodium sulphate, an important chemical component for synthetic detergents (SD) as well as technical grade calcium carbon ate.

EXPERIMENTAL

The X-ray diffraction phase analysis of pure gypsum and phospogypsum samples was carried out with using a DRON-07 diffractometer (CuK_{α} radiation).

The phosphogypsum conversion by soda solutions was investigated using the samples taken from the refuse disposals of the Meleuz Mineral Fertilizers JSC (Bashkortostan), with the following chemical composition, mass %: Ca^{2+} 17.4, Sr^{2+} 0.9, Ln_2O_3 0.38, SO_4^{2-} 44.4, SiO_2 0.6, $\begin{array}{l} F^- \ 0.2, \ R_2O_3 \ 0.3, \ P_2O_5 \ (bound) \ 0.45, \ P_2O_5 \ (watersoluble) \ 0.3, \ H_2O \ (total) \ 35. \ The \ phosphogypsum \ conversion \ can \ be \ presented \ in \ the \ form \ CaSO_4 + \ Na_2CO_3 = CaCO_3 + \ Na_2SO_4 \ (1) \end{array}$

The analysis of phosphogypsum, technical grade calcium carbonate and conversion solutions for the content of calcium and strontium, sesquioxides, phosphates, fluorides and rare earth sum was carried out using the techniques described in [4, 5]. The conversion of phosphogypsum was investigated within the temperature range of 40-90 °C, the concentration of soda amounting to $240-260 \text{ g/dm}^3$. The experiments were carried out using a thermostatically controlled reactor supplied with a stirrer. The frequency of stirrer rotation amounted to 120 min^{-1} , which provided uniform suspending the solid all over the reactor volume. After completing the experiment the solid and liquid phases were separated using a vacuum dropping funnel. In order to obtain the kinetic characteristics of the conversion we determined the content of sulphate ion in the liquid and solid phases in certain time periods [4]. The mass of a phosphogypsum sample in all the experiments amounted to 50 g, the solid to the liquid ratio S/L = 1:3, the fraction size d = 0.1-0.25 mm. The initial molar ratio SO_4^{2-} : Na₂CO₃ in the experiments was varied from 1.0:1.0 up to 1.0:1.1. Each point of the kinetic curve for phosphogypsum conversion into calcium carbonate and sodium sulphate was determined using a new sample of phosphogypsum and new soda solution. The conversion level for phoshogypsum transformation into sodium sulphate was determined from the content of sulphate ion in the liquid and solid phases and calculated according to the formula

$$\alpha = (SO_4^{2-}(L)/SO_4^{2-}(S)) \times 100 \%$$
(2)

Here α is the conversion level, %; SO_4^{2-} (L) is the content of sulphate ion in the solution, g; SO_4^{2-} (S) is the content of sulphate ion in the solid phase, g.

RESULTS AND DISCUSSION

Figure 1 demonstrates X-ray diffraction profiles for pure gypsum $CaSO_4 \cdot 2H_2O$ and phosphogypsum. One can see that phosphogypsum is mainly presented by dihydrated calcium sulphate



Fig. 1. X-ray diffraction profiles for pure gypsum (a) and phosphogypsum (b).



Fig. 2. Phosphogypsum conversion by soda solution at the temperature, °C: 40 (1), 60 (2), 80 (3), 90 (4). $C_{\text{Na}_2\text{CO}_3} = 250$ g/dm³; ratio S/L = 1 : 3.

(gypsum), which is typical in the case of obtaining phosphoric acid *via* the dihydrate method.

Figure 2 displays temperature influence upon the conversion level for phoshogypsum effected soda solutions. One can see that with the increase in temperature the conversion level increases. So, at 80-90 °C conversion is completed within 20-30 min amounting to 96-98 %.

The kinetic dependences for phosphogypsum conversion could be described using equation Avrami-Erofeev equation [6]:

$$1 - \alpha = \exp\left(-k\tau^n\right) \tag{3}$$

Here α is the conversion level, expressed in fractions; τ is the conversion time, min; k is the apparent reaction rate constant, min⁻¹.

For determining the k value the equation (3) was treated with respect to $\log [-\ln (1 - \alpha)] - \log \tau$ coordinates (Fig. 3). In order to establish the temperature dependence of the reaction rate constant we linearized the equation with respect to $\ln k - 1/T$ coordinates; then we have



Fig. 3. Kinetic dependence of phosphogypsum conversion at the temperature, $^{\circ}C$: 40 (1), 60 (2), 80 (3), 90 (4).

calculated the activation energy value E = 8841.1 J/mol (Fig. 4). The data obtained indicate that the process under investigation occurs in the diffusion region [6] wherein the phosphogypsum conversion rate is determined by CaSO₄ dissolving and diffusion into the solution.

We have also investigated the influence of Na_2CO_3 : SO_4^{2-} molar ratio upon sodium sulphate quality. After carrying out the conversion of phosphogypsum the liquid was evaporated and sodium sulphate was obtained; the latter was analyzed after drying at the temperature of 160 °C using a standard technique (State Standard GOST 6318-77). Table 1 demonstrates the characteristics for the samples of sodium sul-



Fig. 4. Apparent phosphogypsum conversion rate constant (k) dependence on the temperature related to $\ln k - 1/T$ coordinates.

phate obtained at the temperature values varied within the range of 40-90 °C and various molar ratio Na₂CO₃: SO₄²⁻. One can see that with respect the basic substance all the sodium sulphate samples obtained corresponds to the requirements for a superior quality product (Na₂SO₄ content ≥99.4 %). The content of sodium chloride therein is less than 0.2 %, which is much better than the State Standard requirements, whereas the content of calcium sulphate varies over a wide range, being for many samples higher than ceiling CaSO₄ content required for SD manufacture (≤0.04 %).

It is known that $CaSO_4$ solubility in Na_2SO_4 solution depending on the temperature and con-

TABLE 1

Characteristics of sodium sulphate samples obtained at various values of conversion temperature and molar $\rm Na_2CO_3\colon SO_2^{2-}$ ratio

Ratio S/L	Conversion temperature, °C	Molar $Na_2CO_3: SO_4^{2-}$ ratio	Content in solid product, %			
			$\overline{\mathrm{Na}_{2}\mathrm{SO}_{4}}$	$CaSO_4$	NaCl	Na ₂ CO ₃
2.5	40	1.00	99.6	0.15	0.03	0.1
3.0	50	1.10	99.4	0.02	0.05	0.3
2.0	70	1.05	99.8	0.01	0.02	0.2
2.5	50	1.10	99.7	0.04	0.04	0.4
2.0	40	1.05	99.8	0.05	0.03	0.2
3.0	90	1.00	99.4	0.17	0.02	0.1
3.0	70	1.05	99.5	0.11	0.03	0.2
2.0	90	1.00	99.6	0.12	0.02	0.1
2.0	70	1.05	99.5	0.06	0.03	0.2
2.5	40	1.00	99.4	0.16	0.05	0.2
2.5	80	1.00	99.4	0.12	0.02	0.2
3.0	60	1.10	99.6	0.03	0.03	0.4
2.5	90	1.05	99.5	0.05	0.05	0.2
2.0	60	1.10	99.4	0.04	0.03	0.4
2.5	80	1.05	99.7	0.02	0.02	0.3

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Fig. 5. Soda excess effect on CaSO₄ content in sodium sulphate solution under phosphogypsum conversion process. t = 80 °C, $C_{\text{Na}_{a}\text{CO}_{a}} = 250$ g/dm³, ratio S/L = 1 : 3.

centration of the solution varies within the range of 0.19-0.22 %. Futhermore, reacting with sodium sulphate, calcium sulphate is capable to form double salts such as $Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$ and $Na_2SO_4 \cdot CaSO_4$ as metastable phases within a wide range of temperature and sodium sulphate concentration. It is known, that the stability of the metastable state of double salts depends on of soda excess [7]. In this connection we have carried out a number of experiments with various excess amounts of soda as compared to the stoichiometry with respect to sulphate ion content in phosphogypsum in order to estimate changing in the content of calcium sulphate in the solution of sodium sulphate after the conversion (Fig. 5). One can see that soda excess results in the reduction of $CaSO_4$ content in the solution of sodium sulphate under formation. At the residual concentration of soda in the solution after the conversion higher than 5 g/dm^3 the content of calcium sulphate in the solution amounts to $0.1-0.15 \text{ g/dm}^3$. It is evident that in this case after a complete evaporation of the sodium sulphate solution with the concentration of 280- 300 g/dm^3 the content of CaSO₄ in the finished product should not exceed 0.05 %. The results of the phosphogypsum conversion experiments with a 5-10 % soda excess with respect to the stoichiometry have confirmed this assumption.

A combined sample of technical grade calcium carbonate obtained in all the experiments, exhibited the following chemical composition, mass %: Ca²⁺ 35.2, Sr²⁺ 1.8, Ln₂O₃ 0.78, SO₄²⁻ 3.1, R₂O₃ 0.68, SiO₂ 0.9, CO₃²⁻ 55.7, P₂O₅ (total) 1.4, F⁻ 0.4, H₂O 0.5.

Laboratory tests carried out at the Kaustik Co. (Sterlitamak) for using the technical grade carbonate as a filling agent for linoleum obtaining indicate that the stuff meets the requirements of the standard STP 00203312-101-2002. At the same time, taking into account that all the calcium, strontium and rare-earth metals are contained in the solid phase, the technical grade calcium carbonate is first of all worthwhile for using as a chemical raw material for obtaining these components.

CONCLUSION

1. The conversion of phosphogypsum into sodium sulphate and calcium carbonate proceeds within 20-30 min resulting in 96-98 % conversion level. The conversion rate increases as the temperature increased.

2. In order to obtain predominantly sodium sulphate (the content of calcium sulphate being less than 0.05 %) the process of phosphogypsum conversion should be carried out with soda amount equal to 105-110 % of the stoichiometry with respect to sulphate ion in phosphogypsum.

3. In the case of phosphogypsum conversion with soda one could obtain a superior quality sodium sulphate meeting the requirement for sodium sulphate used in the manufacture of synthetic detergents. Another product of phosphogypsum conversion represents technical grade calcium carbonate that could be used in construction or for cement obtaining, and as a filling material in linoleum manufacture. With the further processing phospogypsym could represent a raw material for obtaining calcium, strontium and REM salts.

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