

Processing Rare-Earth Element Concentrate Obtained from Phosphogypsum

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Abstract

It is established that the insoluble residue after leaching calcium by ammonium chloride into solution from the product of thermal decomposition of phosphochalk (technical grade calcium carbonate obtained *via* phosphogypsum conversion with soda solutions) represents a concentrate of strontium and rare-earth elements (REE) wherein the content of strontium and REE amounts up to 9–10 and 4.5–5.1 %, respectively. REE extraction into the solution with the use of various acids is considered. It has been demonstrated that in the presence of reducers the level of REE leaching into the solution amounts up to 96–97 %. The leaching solutions contain 4.2–4.6 g/dm³ REE and could be processed in order to obtain REE compounds. The insoluble residue resulting from REE leaching represents a strontium concentrate with the content of strontium sulphate ranging within 54.5–62.9 %.

Key words: rare-earth element concentrate, phosphogypsum, phosphochalk, XRD phase analysis

INTRODUCTION

In the papers [1, 2] we have demonstrated that the consecutive processing of phosphogypsum including its conversion with soda solutions, calcium leaching into solution by ammonium chloride from the product of thermal decomposition of technical-grade calcium carbonate (phosphochalk) can result in obtaining the concentrate of rare-earth elements (REE) and strontium wherein the content of REE and strontium amounts up to 4.5–5.1 and 9–10 %, respectively.

A concentrate with the composition close with respect to the content of REE was obtained by the authors of [3], who performed the conversion of phosphogypsum using ammonium carbonate. A hydrochemical method for obtaining the concentrates of REE and strontium is also known, based on leaching calcium sulphate and soluble impurities contained in phosphogypsum by aqueous electrolyte solutions and sea water, in this case an insoluble residue is formed with the following composition, %: REE 6.27, SrO 18.5 and CaO 20.6 [4]. It is obvi-

ous that such concentrates could be used as raw material for obtaining REE. In this connection the development of a method for passing REE into solution from the concentrate obtained from phosphogypsum [2], is of currently central importance as well as of scientific interest.

Figure 1 demonstrates the XRD profile of the insoluble residue resulted from ammonium leaching of calcium obtained in our work [2]. In the XRD profile there are lines corresponding to Ca(OH)₂ ($d = 4.974, 2.642, 1.930, 1.789 \text{ \AA}$), SrSO₄ ($d = 3.478, 2.807, 2.219, 1.478, 1.440 \text{ \AA}$) as well as to lanthanide phosphates ($d = 2.105, 1.329, 1.207 \text{ \AA}$).

It is known that for opening rare-earth ores and minerals depending on the composition, analysts employ hydrochloric, sulphuric, hydrofluoric acids, melting together with bisulphite or caustic soda, in some cases chlorination is used [5].

The decomposition of rare-earth minerals and ores uses to be carried out *via* the processing by means of acid or alkali solutions with high concentration under severe conditions at the temperature ranging within 200–300 °C [6].

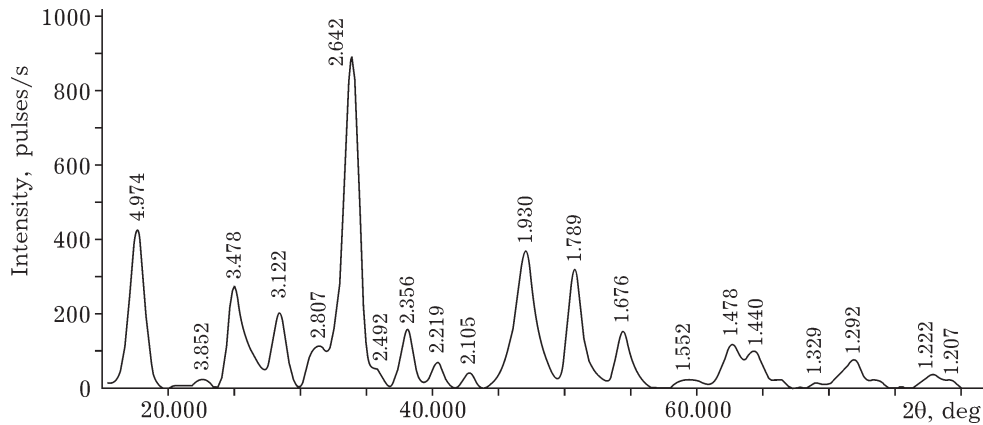


Fig. 1. XRD profile of insoluble residue after leaching calcium by NH_4Cl .

The authors of [7] have proposed to extract REE from bastnaesite using a weak HCl solution; in this case all the REE can be extracted, except for cerium. The concentrate enriched with cerium dioxide is leached by means of concentrated HCl with the use of hydrogen peroxide as a reducing agent. In order to increase the level REE passing into solution in processing phosphates of rare-earth concentrates by 40–60 % sulphuric or nitric acid solutions the authors of [8] propose to perform the treatment in the presence of hydrogen peroxide which behaves as a reducer in acidic media. No information available from the literature was found in our search concerning REE extraction from concentrates obtained basing on phosphogypsum. In the present work we have attempted to make up for the deficiency.

EXPERIMENTAL

In order to process the insoluble residue (i. r.) resulted from the ammonium leaching, obtained in our work [2], we have chosen the way of hydrochemical disclosing with the use of acid. The insoluble residue was of the following composition, mass %: $\text{CaO}_{\text{total}}$ 29.8, SrO 11.4, SO_3 20.3, Ln_2O_3 5.1, $\text{P}_2\text{O}_{5\text{total}}$ 7.6, $\Sigma(\text{Fe}_2\text{O}_3, \text{TiO}_2, \text{Al}_2\text{O}_3)$ 3.8, SiO_2 5.2, F^- 2.1, Na_2O 5.9, H_2O 6.5.

The experiments with acidic decomposition of the i. r. were carried out in the reactor under agitation with the rotational speed of a stirrer $n = 120 \text{ min}^{-1}$, at a constant mass ratio between the liquid and the solid ($L : S$) = 10. After completing the experiment the solid and liq-

uid phases were separated using a vacuum Buchner funnel, the solid phase was washed with water in the amount of ~10–15 % of the volume of the initial acid solution and dried then at the temperature of 110–120 °C to obtain constant mass. The content of calcium, total REE, phosphates and sesquioxides was determined using commonly known techniques [9]. The XRD phase analysis of samples was carried out employing DRON-4-07 diffractometer ($\text{CuK}\alpha$ radiation). As opening reagents for REE to pass into solution we tested hydrochloric, sulphuric and nitric acids.

RESULTS AND DISCUSSION

The studies on opening the concentrate aimed at REE passing into solution has demonstrated that a high REE leaching level is

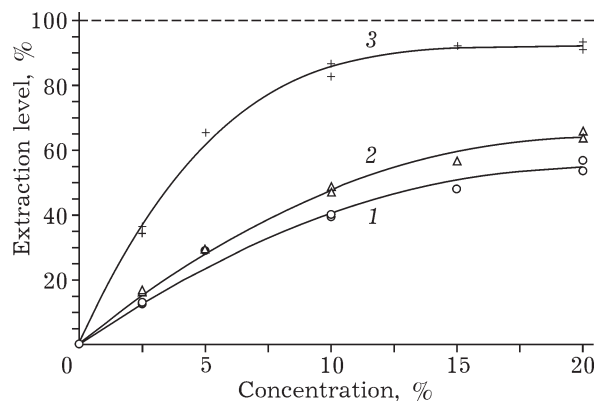


Fig. 2. Level of passing REE into solution depending on the concentration of acid ($T = 80 \text{ }^\circ\text{C}$, $L : S = 10$, $t = 60 \text{ min}$): 1–3 – nitric, sulphuric and hydrochloric acids, respectively.

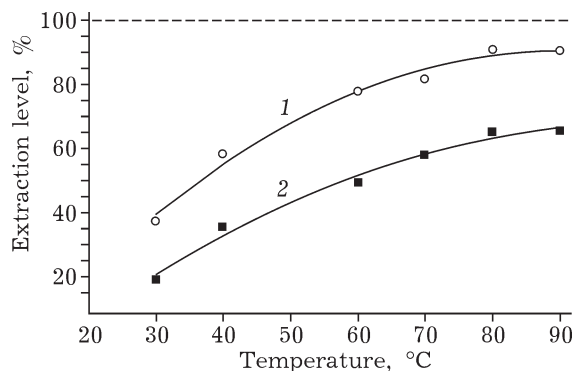


Fig. 3. Level of REE leaching from the insoluble residue depending on the temperature and the concentration of acid (L : S = 10, $t = 60$ min). C_{HCl} , %: 15 (1), 5 (2).

achieved only with the use of hydrochloric acid having the concentration of 15–20 %. Figure 2 displays the influence of the acid concentration upon REE passing into solution. As seen, the level of REE extraction into solution by sulphuric and nitric acids at the temperature of 80 °C does not exceed 60 %. Moreover with the use of HNO_3 we observed the process of the solution gelation to occur, the suspension almost could not be filtered.

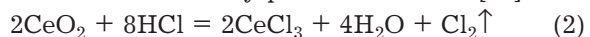
In this connection the further experiments aimed at searching the ways to leach and estimating the leaching parameters were conducted with the use of HCl. In order to determine the influence of temperature upon the leaching level we have performed experiments within the temperature range of 30–90 °C with acid concentration amounting to 5 and 15 % (Fig. 3). One can see that the temperature positively influences the REE passing into solution, but a high extraction level could be achieved only employing acid with the concentration of 15 %.

Thus, as the result of the experiments carried out (see Figs. 2, 3) we have established that a high level of REE leaching into solution can be achieved only using HCl with the concentration of 15–20 % at the temperature ranging within 80–90 °C. At a higher concentration of acid the further isolation of REE from the solution is complicated, and the profitability of the process decreases. We have posed a problem of finding a way to pass REE into solution from the concentrate with a high leaching level basing on the treatment by acids with lower concentration. It is known that among all the REE family, only cerium, samarium and

praseodymium can exhibit variable valency [6]. In a naturally occurring rare-earth raw material (such as loparite, monazite) cerium is. Being in phosphogypsum, cerium is also in a trivalent state [10], however cerium transforming into a tetravalent state is quite probable under high-temperature decomposition of phosphor-chalk (technical grade calcium carbonate) at a stage of obtaining calcium oxide before leaching by ammonium chloride [11].

With respect to the total REE of phosphogypsum the content of cerium amounts to 45.6–46.8 % depending on the method of obtaining phosphoric acid (dihydrate or semihydrate one) [10]. The observed level of REE extraction into the solution of sulphuric and nitric acids does not exceed 60 % (see Fig. 2). As the result of the analysis of total REE isolated from ir samples used in the present work we have found the content of cerium in the total REE to be equal to 45.6–46.1 %.

The experiments concerning the decomposition of i. r. by means of sulphuric and nitric acids have demonstrated 14–17.4 % of cerium to pass into solution, as calculated with respect to cerium content in the total REE. To all appearance, it could be connected with the fact that CeO_2 and cerium phosphates such as $\text{Ce}_3(\text{PO}_4)_4$ are almost insoluble in HNO_3 and H_2SO_4 [12]. Concentrated HCl represents a weak reducer with respect to Ce^{4+} , therefore cerium reduction up to a trivalent state occurs, and cerium being in this state can readily pass into solution [12]:



CeO_2 is dissolved in concentrated hydrochloric acid to result in the evolution of chlorine.

The reduction of cerium can be judged by a smell of chlorine evolving under treating the i. r. by concentrated HCl as well as by a qualitative reaction between gaseous chlorine and paper impregnated with potassium iodide and starch [9]. It is known that the solubility of Ce^{4+} compounds can be increased in the presence of a reducer [12]. Experiments we carried out concerning the leaching of the rare-earth concentrate in the presence of various reducers have demonstrated that the latter exert a positive effect on passing REE into solution.

Figure 4 demonstrates the results of the experiments concerning rare-earth elements

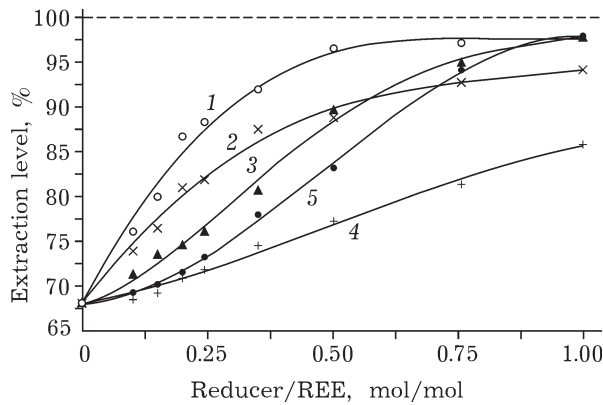


Fig. 4. Level of passing REE into solution depending on a reducer/ Σ REE ratio ($C_{\text{HCl}} = 5-6\%$, $T = 80^\circ\text{C}$, $L:S = 10$, $t = 60$ min): 1 - ascorbic acid, 2 - Na_2SO_3 , 3 - Mohr salt, 4 - H_2O_2 , 5 - FeSO_4 .

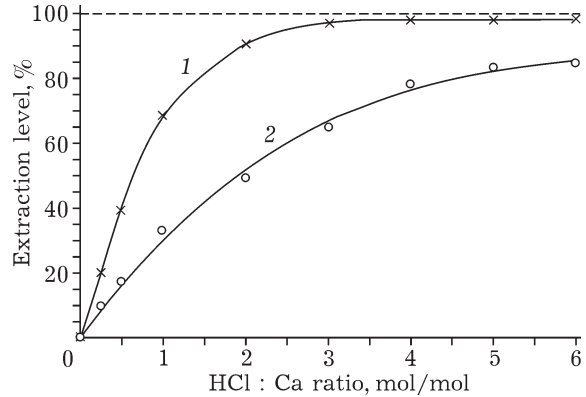
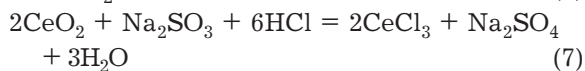
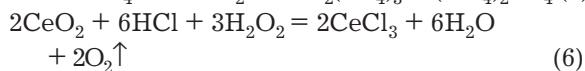
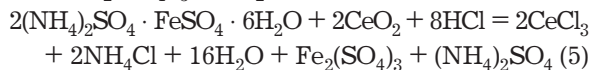
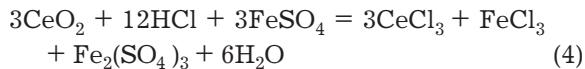
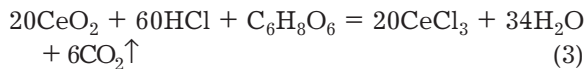


Fig. 5. Level of passing REE into solution depending on an HCl : Ca ratio ($T = 80^\circ\text{C}$, $L:S = 10$, $t = 60$ min): 1 - with the use of $\text{C}_6\text{H}_8\text{O}_6$ (molar ratio $\text{C}_6\text{H}_8\text{O}_6/\text{REE} = 0.5$), 2 - no reducer present.

extraction into solution in the presence of reducers. The process of reducing Ce^{4+} to yield Ce^{3+} may be expressed by the following reactions:



From the data obtained (see Fig. 4) it follows that the level of passing REE into solution increases to a considerable extent in the presence of the majority of reducers. A slightly positive influence of hydrogen peroxide upon REE extraction from the i. r. could be connected with the volatility of this compound as well as with the decomposition of hydrogen peroxide at a high leaching temperature; thus, to all appearance, an increased H_2O_2 consumption is required in order to achieve any reasonable efficiency. Among all the reducers under investigation the preference should be given to ascorbic acid since the oxidation of this substance occurs with gaseous carbon dioxide evolution according to reaction (3) thus the leaching solution could not be contaminated with the products of its oxidation. According to chemical analysis data, there is much calcium in the rare-earth concentrate subjected to acidic decomposition in the course of passing REE into solu-

tion. At the previous stage of the phosphogypsum processing in the high-temperature decomposition of technical grade CaCO_3 [2] calcium can enter into reactions with REE compounds as well as with impurities (Fe_2O_3 , Al_2O_3 , TiO_2) present therein to form solid solutions [11]. Moreover, in the presence of a reducer, there is a possibility for the reduction of impurity elements (Fe^{3+} , Ti^{4+} , Ce^{4+}), incorporated into the structure of solid solutions with calcium, which could result in changing and destructing the crystal structure of compounds such as $\text{Ca}_n(\Sigma\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{TiO}_2, \text{Ln}_2\text{O}_3)_m$. Basing on this assumption, a series of experiments were carried out with various molar HCl : Ca ratio values and with the use of ascorbic acid as a reducer (Fig. 5).

It is seen that in the presence of ascorbic acid an almost complete REE passing into solution (96–97%) can be achieved already at a molar ratio HCl : Ca = 3 : 1, whereas only 60–65% of total REE passes into solution at the same HCl : Ca ratio in the absence a reducer. Thus, the assumption is confirmed that the most part of cerium at the stage of thermal decomposition of technical grade calcium carbonate into calcium oxide is oxidized to yield a tetravalent state, with the formation of CeO_2 and Ce^{4+} compounds with impurity elements such as Sr, Fe, Ti those are difficult to dissolve in acids [12]. The XRD profile of the residue demonstrates the latter to consist mainly of strontium sulphate with the structure of celestine [ASTM 5-593] and silicon dioxide in various crystal forms (Fig. 6).

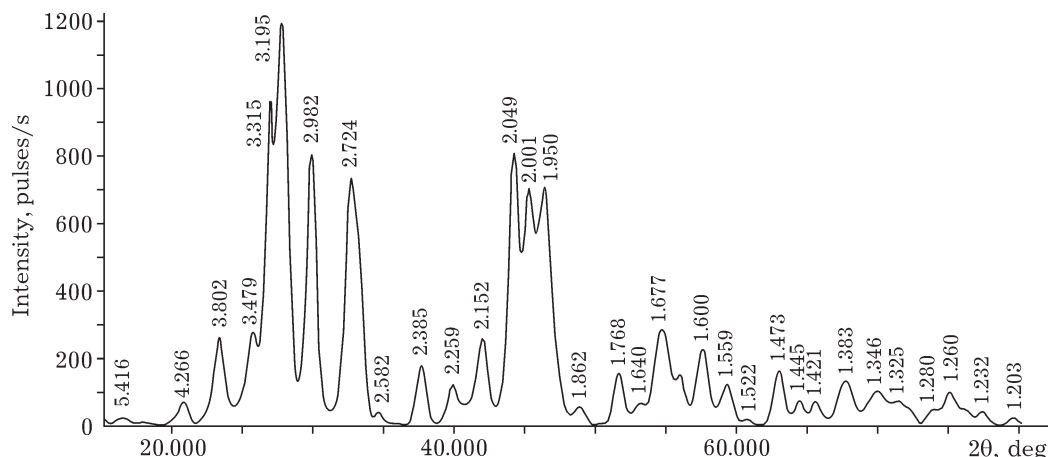


Fig. 6. XRD profile of insoluble residue after passing REE into solution with the use of HCl in the presence of ascorbic acid.

In the XRD profile for ir there are pronounced reflexes present corresponding to SrSO_4 of the celestine group ($d = 3.315, 3.195, 2.982, 2.724, 2.259, 2.049, 1.768 \text{ \AA}$), SiO_2 of various crystal forms ($d = 5.416, 1.559, 1.445, 1.346, 1.232 \text{ \AA}$), as well as the lines corresponding to CaSO_4 ($d = 4.262, 3.479, 2.152, 1.260 \text{ \AA}$). The samples of solid residues resulted from REE leaching demonstrated the following chemical composition, mass %: CaO 1.7–1.9, SrO 30.7–35.5, SO_3 26.2–28.5, Ln_2O_3 0.16–0.24, $\Sigma(\text{Fe}_2\text{O}_3, \text{TiO}_2, \text{Al}_2\text{O}_3)$ 0.2–0.4, P_2O_5 total 0.18–0.25, SiO_2 18.1–21.6, H_2O 16–20.

The solutions after leaching rare-earth elements contained, g/dm^3 : CaCl_2 54.3–56.8, Ln_2O_3 4.2–4.6, R_2O_3 2.7–3.1, P_2O_5 4.8–5.1, F^- 1.5–1.7, NaCl 9.2–9.3, HCl 14.8–15.2, SO_4^{2-} 0.1–0.14, SiO_2 0.05–0.08.

Semi-products obtained after opening the rare-earth element concentrate (solid residues and solutions) could serve as a raw material for obtaining of strontium salts and REE compounds.

Thus, the studies on opening the i. r. by various acids for passing REE into solution has demonstrated that the a high leaching level could be achieved with the use of hydrochloric acid with low concentration (5–6 %) in the presence of reducers. The use of HCl with a low concentration (5–6 %) allows obtaining REE solutions with a low residual acidity as well as the insoluble residue (strontium concentrate) with the content of strontium amounting to 26–30 %, which simplifies the further processing to yield strontium salts. Among the reducers under investigation,

ascorbic acid is the best reducing agent, since its use does not result in contamination of a leaching solution with oxidation products.

CONCLUSION

1. The experiments concerning the leaching of rare-earth elements from the REE concentrate obtained from phosphogypsum have demonstrated that a high extraction level can be achieved only using hydrochloric acid of high concentration (15–20 %).

2. In the presence of reducers the level of REE extraction into solution increases up to 96–97 % with the use of low concentration hydrochloric acid (5–6 %).

3. Leaching solutions contain 4.2–4.6 g/dm^3 of REE and could be used in order to obtain REE compounds.

4. The insoluble residue from leaching represents the concentrate of strontium presented by strontium sulphate, with the content of Sr^{2+} within the range of 26–30 %, various forms of silicon dioxide as well as impurities presented by phosphates of sesquioxides and calcium. The concentrate could serve as a raw material for obtaining strontium salts.

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