Study of cerium and neodymium leaching from Kazakhstan phosphogypsum

Abstract. The processes of extraction of cerium and neodymium from Kazakhstan phosphogypsum, a large-tonnage waste of mineral fertilizer production of “Kazphosphate” LLP, have been studied. The influence of the nature of the leaching agent, temperature and duration of the process on the efficiency of cerium, neodymium leaching using the methods of X-ray fluorescence, X-ray phase and energy dispersive elemental analysis was studied. It has been found that the use of hydrogen peroxide as an oxidizer in the leaching of rare earth metals intensifies the process of recovery from phosphogypsum by 20% for cerium and by 28% for neodymium. Optimal parameters of cerium and neodymium leaching under atmospheric and autoclave conditions have been found. In atmospheric conditions, recovery of cerium and neodymium were 70.3% and 92.0%, in autoclave conditions 72.9% and 87.5%, respectively. The obtained results allow us to hope for the processing possibility of these wastes with the aim of rare-earth metals and other valuable products recovery.

Key words: phosphogypsum, leaching, microwave sample preparation, hydrogen peroxide, rare-earth metals, cerium, neodymium.

Introduction

It is well known that the concept of “integrated use of mineral raw materials” is not implemented at existing enterprises for a number of reasons, the main of which is the need to redo multiple technological processes, which ultimately leads to additional costs. The rate of extraction and processing of natural raw materials grows annually, and the volume of man-made waste increases accordingly. The accumulation of such waste in nature leads to environmental pollution. For example, the waste dumps of the Caspian Mining and Chemical Combine and phosphogypsum (PG) dumps of “Kazphosphate” LLP contain toxic compounds. The content of valuable components in these wastes is sufficient for their industrial development. One of the perspective sources for separation of rare-earth metals (REMs) is phosphogypsum, mentioned above. Processing of 1 ton of Karatau phosphorites produces 4.27-6.43 tons of PG, which is stored in the dumps of “Kazphosphate” LLP. It is known that more than 30 mln. tons of PG have been accumulated on the territory of the enterprise [1].

One of the problems of processing PG is the complexity of the composition, which includes the residues of mineral acids, insoluble salts and moisture. It is worth noting that the composition includes yttrium, light (lanthanum), medium (samarium) and heavy (terbium) groups of REMs, the total content of which is 0.4-0.6% wt. [2].

In recent years, there has been a growing consumption for rare earth products, driven by increased demand in a number of industries. [3-5]. Production of REM is one of the priority tasks of the rare-earth industry in Kazakhstan today [6, 7]. In this connection, the development of new, highly effective technologies for obtaining REMs from both natural and anthropogenic raw materials is important. Complex processing of PG in order to isolate REM and other components will initiate the development of rare-earth industry in the country, and will help to improve the environmental situation of the region as a whole. Waste recycling is one of the principles of low-waste and non-waste technology, which is a significant factor in the level of development of the country.

As a result of preliminary studies, it has been established that in the initial PG of “Kazphosphate” the following REM elements prevail: cerium, neodymium, yttrium and lanthanum [8]. Cerium and
neodymium are widely used in production of catalysts for magnets, in metallurgy, etc., respectively, are the most attractive elements of lanthanum series contained in PG.

The aim of this work is to determine optimal conditions of cerium and neodymium leaching from Kazakhstan PG.

In [9] processes of REM leaching from PG were studied. REMs leaching was carried out from 10%-sulphuric acid solutions, at a temperature of 60°C and 120 minutes. The leaching was carried out in two stages. As a result of leaching the total REMs recovery was 86%. The following results were obtained: cerium content was 103.13 and 105.78 ppm for neodymium in the first leaching stage; 50.85 and 50.71 ppm, respectively, in the second stage.

In [10, 11] the effect of temperature, duration of leaching processes on REM extraction from PG was also studied. The authors achieved the maximum REMs extraction at time – 120 minutes and temperature – 50°C. The leaching was carried out in the presence of 5% sulphuric acid. The total REM extraction rate was 43%, REMs content in the leaching solution was 124 ppm.

The authors of works [12-14] conducted studies as S:L ratio, temperature, process time and acid concentration were studied. It was found that hydrochloric (R(Ce)=65%, R(Nd)=75%) and nitric acids (R(Ce)=62%, R(Nd)=75%) extract REM better than sulphuric acid (R(Ce)=22%, R(Nd)=32%) under normal conditions. At S:L ratio = 1:8, temperature 80°C, 20 min for 1.5 M sulphuric acid the recovery of cerium and neodymium is not more than 10 ppm. For 3.0 M hydrochloric acid not more than 15 ppm at the same parameters. The authors of [15] leached REM from PG by organic acids (malonic and citric acid). The maximum REM extraction (42% in total) was with citric acid with concentration of 1.0 M, at temperature 90 °C, S: L = 2:1, time – 15 minutes.

In [16] the authors studied the leaching with 0.5 M sulphuric acid and 3 M nitric acid from aged PG. The leaching was carried out between 2 and 8 hours at a ratio of S: L = 1:20. The most effective extraction was observed with nitric acid (t=8 h), cerium 67% (24 ppm), neodymium 90% (43.2ppm).

In [17, 18] it was found that catalytic decomposition of hydrogen peroxide contributes to barbotage of the system, which can improve the efficiency of REM extraction. It is also worth noting that in an acidic environment hydrogen peroxide oxidizes cerium to the state Ce⁴⁺, which has a positive effect on its further selective extraction from the leaching solution [19].

As it is seen from literature review, the proposed methods do not allow to extract completely rare-earth metals from PG. That is why it is necessary to develop effective methods for their maximum extraction.

Materials and methods

The object of the study is waste PG from the “Mineral Fertilizer Plant” enterprise Kazphosphate LLP. PG was crushed on a planetary mono-mill “Pulverisette 6”, “Fritsch” (Germany) and classified to a fraction of 0.056 mm.

Study of elemental and phase composition of PG was carried out on X-ray fluorescent wave dispersive combined spectrometer Axios (“PANalytical”, the Netherlands) and energy dispersive analyzer. Study of PG surface morphology before and after leaching was carried out by EDAX on a scanning electron microscope Quanta 200i 3D (FEI Company, USA) at the National Nanotechnology Open Lab, Al-Farabi Kazakh National University.

The first stage of cerium, neodymium extraction from PG is acidic leaching. It was carried out in closed (autoclave) and open (atmospheric) modes by different mixtures of acids (HCl, HNO₃, H₂SO₄). All reagents used were classified as chemically pure (CP). The ratio S:L was kept constant at 1:40. Cerium and neodymium concentrations were analysed by ICP-MS method (Agilent 7500Series spectrometer). Leaching under atmospheric conditions was carried out at T=110 °C, τ=60 min. Autoclave dissociation of REM from PG was carried out in teflon vessels in microwave sample preparation system (Speed wave four “Berghof”, Germany). Leaching process conditions: T=180 °C, τ=7.5 min, P=60 bar, v=2500 Hz.

Results and discussion

The content of the target components in the initial PG sample was determined by quantitative chemical and XRF analyses and given in tables 1,2.

According to the XRF analysis (Figure 1, Table 3) the investigated PG is a phosphohydrate; the content of the main phase – bassanite is 73.3% wt. It is known from literature [20], that recovery of REM from semi-aqueous gypsum technologically requires less energy and water resources than processing of dihydrous gypsum.

Fluorite is found in PG composition – a consequence of incomplete decomposition of initial phosphorite. Quartz occurs together with phosphorite, after decomposition of which it remains in PG. Sodium hexafluorosilicate is a product of PG decomposition.
Table 1 – Results of XRF analysis

| Element | O  | F  | Na | Mg | Al | Si | P  | S  | K  | Ca |
|---------|----|----|----|----|----|----|----|----|----|----|
| C, % wt.| 42.00 | 7.90 | 3.26 | 0.41 | 0.61 | 7.23 | 1.10 | 12.02 | 0.56 | 20.42 |

| Element | Ti | Cr | Mn | Fe | Ni | Zn | Sr | Y | Pb |
|---------|----|----|----|----|----|----|----|---|----|
| C, % wt.| 0.07 | 0.03 | 0.06 | 0.63 | 0.01 | 0.02 | 0.07 | 0.01 | 0.02 |

Table 2 – Results of quantitative chemical analysis of main REM in phosphogypsum

| Element | Y  | La | Ce  | Nd  |
|---------|----|----|-----|-----|
| C, % wt.| 0.0216 | 0.0201 | 0.0204 | 0.0123 |

Table 3 – Results of X-ray phase analysis

| Name of phase       | Formula            | Content, % wt. |
|---------------------|--------------------|----------------|
| Bassanite           | CaSO$_4\times0.5$H$_2$O | 73.3           |
| Quartz              | SiO$_2$            | 16.3           |
| Calcium pyrophosphate | Ca$_3$P$_2$O$_7$   | 2.7            |
| Sodium hexafluorosilicate | Na$_2$SiF$_6$  | 2.6            |
| Fluorapatite        | Ca$_5$(PO$_4$)$_3$F | 2.2            |
| Potassium magnesium phosphate | KMgPO$_4$ | 1.6            |
| Calcium Kutonarite  | Ca(Mn,Ca)(CO$_3$)$_2$ | 1.3            |

Figure 1 – Diffractogram of composition of initial PG
The migration of major elements during leaching was estimated by energy dispersive elemental analysis of PG before and after leaching (Figure 2, 3).

The absence of REMs on PG surface before leaching indicates the isomorphic replacement of calcium by cerium and other REMs in the PG structure [21-23]. The peak corresponding to cerium indicates the formation of insoluble cerium compounds during its leaching (Figure 3). The decrease of calcium content in the sample after leaching indicates the migration of calcium ions from PG into the solution. A scheme of isomorphic replacement of calcium by REMs is shown below:

\[ \text{REM}^{3+} + \text{Na}^+ + 2\text{CaSO}_4 = \text{REMNa}({\text{SO}}_4)_2 + 2\text{Ca}^{2+} \]

Nitric acid leaching of PG. A 56% nitric acid solution and a 30% hydrogen peroxide solution were used to extract cerium and neodymium from PG. The highest recovery of REM in solution after leaching was observed at a ratio of $\text{HNO}_3:\text{H}_2\text{O}_2 = 3:1$ (Figure 4).

Nitric acid is not thermally stable and therefore cerium and neodymium leaching in autoclave mode is worse than in open mode [24], this is one of the reasons why technologies involving nitric acid stripping of REM are much less common than sulphuric acid technologies. The results of cerium and neodymium leaching are presented in Tables 4, 5.

Decomposition of PG by a mixture of nitric and hydrochloric acids. Cerium and neodymium leaching with a mixture of nitric and hydrochloric acids is worse than with free nitric acid (Tables 6, 7). This is explained by the fact that the solubility of $\text{CaSO}_4$ in hydrochloric acid is lower than in nitric acid [25].

Decomposition of PG by sulphuric acid. When PG is decomposed by sulphuric acid solution, the solubility of calcium sulphate is increased, causing cerium leaching from PG. The leaching process may proceed until equilibrium is reached; then further dissolution of gypsum is stopped due to saturation of solution with sulphate ions. Effective REMs extraction was observed using 10% sulphuric acid (Table 8).

The addition of a 30% hydrogen peroxide solution (Table 9) to sulphuric acid solution increases the leaching efficiency of cerium by 20%, of neodymium by 28% under autoclave conditions; by 19% for cerium, 11% for neodymium under open conditions, respectively.
Figure 3 – EDAX analysis of PG sample after leaching

Figure 4 – Histogram of REMs concentration dependence on volume ratio of nitric acid and hydrogen peroxide

Table 4 – Results of cerium and neodymium leaching with nitric acid

|                  | Autoclave leaching | Atmospheric leaching |
|------------------|--------------------|----------------------|
|                  | C(HNO₃), %         |                     |
|                  | 15                 | 56                   | 15                  | 56                  |
| Ce               | 75.2±8.1           | 67.9±8.7             | 76.0±3.6            | 119.7±18.8          |
| Nd               | 57.3±4.4           | 62.5±6.5             | 47.1±2.3            | 43.1±3.9            |
Table 5 – Results of cerium and neodymium leaching with nitric acid and hydrogen peroxide

| \(\text{CMe}^{++}\), ppm | Autoclave leaching | Atmospheric leaching |
|-------------------------|-------------------|---------------------|
|                         | \(\text{C}(\text{HNO}_3)\), % | \(\text{C}(\text{HNO}_3)\), % |
| Ce                      | 15                | 15                  | 56                | 56                |
|                         | 83.1±9.1          | 115.0±21.9          | 143.3±26.3        |
| Nd                      | 77.5±6.9          | 68.2±5.7            | 113.2±19.2        |

Table 6 – Results of cerium and neodymium leaching with a mixture of nitric and hydrochloric acids (“aqua regia”)

| \(\text{CMe}^{++}\), ppm | Autoclave leaching | Atmospheric leaching |
|-------------------------|-------------------|---------------------|
| Ce                      | 55.9±1.2          | 53.0±4.1            |
| Nd                      | 51.6±0.9          | 33.5±1.2            |

Table 7 – Results of cerium and neodymium leaching with a mixture of nitric and hydrochloric acids (aqua regia) and hydrogen peroxide

| \(\text{CMe}^{++}\), ppm | Autoclave leaching | Atmospheric leaching |
|-------------------------|-------------------|---------------------|
| Ce                      | 65.1±5.2          | 75.3±6.9            |
| Nd                      | 57.4±3.3          | 56.9±8.3            |

Table 8 – Results of cerium and neodymium leaching with sulphuric acid

| \(\text{CMe}^{++}\), ppm | Autoclave leaching | Atmospheric leaching |
|-------------------------|-------------------|---------------------|
|                         | \(\text{C}(\text{H}_2\text{SO}_4)\), % | \(\text{C}(\text{H}_2\text{SO}_4)\), % |
| Ce                      | 5                 | 10                  | 20                 | 5                 | 10                  | 20                 |
|                         | 79.0±3.3          | 147.8±27.7          | 115.5±16.3         | 35.4±5.0          | 58.1±9.6            | 16.8±3.3            |
| Nd                      | 81.3±5.2          | 99.4±11.3           | 77.2±1.5           | 25.7±0.6          | 38.6±1.3            | 1.5±0.2             |

Table 9 – Results of cerium and neodymium leaching with sulphuric acid with addition of hydrogen peroxide

| \(\text{CMe}^{++}\), ppm | Autoclave leaching | Atmospheric leaching |
|-------------------------|-------------------|---------------------|
|                         | \(\text{C}(\text{H}_2\text{SO}_4)\), % | \(\text{C}(\text{H}_2\text{SO}_4)\), % |
| Ce                      | 5                 | 10                  | 20                 | 5                 | 10                  | 20                 |
|                         | 32.5±6.9          | 148.8±19.6          | 144.2±12.5         | 33.0±4.3          | 71.3±6.2            | 41.0±2.6            |
| Nd                      | 29.1±4.2          | 107.6±15.9          | 107.6±9.8          | 17.6±2.9          | 43.5±9.3            | 18.9±2.6            |

The results of investigation of temperature and process duration influence on efficiency of cerium and neodymium sulphuric acid leaching from PG are given in tables 10, 11. The leaching was carried out at conditions \(S: L = 1:40\), \(T = 100^\circ\text{C}\), with mixture of \(\text{H}_2\text{SO}_4\) (10%) + \(\text{H}_2\text{O}_2\) (30%) (table 10). Autoclave leaching of Ce, Nd was carried out at \(S: L = 1:40\), \(t=15\) min, with mixture of \(\text{H}_2\text{SO}_4\) (10%) + \(\text{H}_2\text{O}_2\) (30%).
Table 10 – Study of autoclave leaching time influence on recovery of cerium and neodymium from PG

| $C_{Me}$ ppm | Leaching time, min |
|--------------|--------------------|
|              | 7.5                | 15                  | 30                  |
| Ce           | 84.6±4.3           | 148.8±10.6          | 133.0±10.5          |
| Nd           | 29.7±4.7           | 107.6±8.3           | 97.7±5.7            |

Table 11 – Study of temperature influence on recovery of cerium and neodymium from PG under autoclave conditions

| $C_{Me}$ ppm | Temperature, °C |
|--------------|-----------------|
|              | 160             | 180                | 200                |
| Ce           | 135.7±10.0      | 148.8±15.0         | 130.1±10.2         |
| Nd           | 96.4±9.3        | 107.6±9.8          | 94.5±8.9           |

**Conclusion**

According to the XRF of PG sample from Kazphosphate LLP, the main compound is the mineral bassanite, which content is 73.3% wt. Cerium and neodymium, together with other REM are in isomorphic form in the crystal structure of bassanite. The total content of cerium and neodymium in the initial raw material was 3.27×10^{-2} % wt.

The optimum conditions of Ce, Nd stripping in atmospheric and autoclave conditions have been determined. The maximum recovery of neodymium (C(Nd)= 113.2±19.2 ppm, recovery rate – 92.03%) in simple conditions is achieved when using 15%-HNO$_3$ + H$_2$O$_2$, S:L = 1:40, t = 60 min, T = 80-100 °C. For cerium: 56%-HNO$_3$ + H$_2$O$_2$, S: L = 1:40, t = 60 min, T = 80-100 °C, (C(Ce) – 143.3±26.3 ppm, recoveries – 70.25%). At autoclave stripping of PG the maximum values for neodymium and cerium (C(Nd)=107.6±9.8 ppm, recovery – 87.48 %; C(Ce) = 148.8±15.0 ppm, recovery – 72.94 %), were achieved at the following conditions: 10%-H$_2$SO$_4$ + H$_2$O$_2$, S:L = 1:40, t = 15 min, T = 180 °C, P = 60 atm, ν = 2 500 Hz.

**Funding**

This work was supported financially by the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan, Project No. AP08957404.

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Int. j. biol. chem. (Online)