

EDN: CDKVTL

УДК 54.05

Optimization of Technological Parameters for Obtaining a Concentrated Aqueous Solution of Salts Containing Rare earth Elements Extracted from Phosphogypsum

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Received 08.09.2023, received in revised form 16.04.2024, accepted 26.04.2024

Abstract. Experimental results of the influence of technological parameters of phosphogypsum cascade leaching and evaporation of the solution obtained after the leaching on the rare earth elements (REE) content in it are presented. It was found that REE concentration in the solution grows almost linearly with increasing number of cascades [1]. Evaporation of REE – containing [2] solution down to 23 % of the initial volume leads to precipitation in which REE is about 0.5–0.6 % which coincides with the content of REE in the initial gypsum. This leads to purification of the solution from non – REE. At evaporation of the solution above 77 % an increased content of REE reaching 10–12 % was found in the precipitation. Thus, cascade leaching followed by solution evaporation is a cost-effective technological process. It allows obtaining a solution containing from several tens to few hundreds grams REE per liters with low content of Ca, P, S, Sr and other undesirable elements, which can be used for precipitation of REE carbonates or hydroxides [3].

Keywords: rare earth elements, phosphogypsum cascade leaching, evaporation of REE-containing solution.

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Acknowledgments. The work was realized under support of the State Assignment for the creation of new laboratories in 2021, including under the guidance of young promising researchers of the national project “Science and Universities”, research title is “Development of scientific and technological foundations for the creation of an integrated technology for processing gypsum-containing waste from various industrial enterprises”, FZWG-2024–0001. This work was supported by the Engineering Center LLC. We also thanks administrative support of the BSO LLC (Belgorod), and Foundation for Assistance to Small Innovative Enterprises in Science and Technology (Foundation for the Promotion of Innovation) for their very kind support.

Citation: Nikulin I. S., Nikulicheva T. B., Kolesnikov D. A., Zakhvalinkiy V. S., Vyugin A. O., Anosov N. V., Alfimova N. I. Optimization of technological parameters for obtaining a concentrated aqueous solution of salts containing rare earth elements extracted from phosphogypsum. J. Sib. Fed. Univ. Chem., 2024, 17(2), 177–185. EDN: CDKVTL



Оптимизация технологических параметров получения концентрированного водного раствора солей, содержащих редкоземельные элементы, извлекаемые из фосфогипса

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Аннотация. Представлены экспериментальные результаты влияния технологических параметров каскадного выщелачивания фосфогипса и выпаривания полученного после выщелачивания раствора на содержание в нем редкоземельных элементов (РЗЭ). Установлено, что концентрация РЗЭ в растворе растет практически линейно с увеличением числа каскадов [1]. Выпаривание РЗЭ-содержащего [2] раствора до 23 % от первоначального объема приводит к выпадению осадка, в котором РЗЭ составляет около 0,5–0,6 %, что совпадает с содержанием РЗЭ в исходном гипсе. Это приводит к очистке раствора от РЗЭ. При выпаривании раствора свыше 77 % в осадке обнаруживается повышенное содержание РЗЭ, достигающее 10–12 %. Таким образом, каскадное выщелачивание с последующим выпариванием раствора является экономически эффективным

технологическим процессом. Он позволяет получить раствор с содержанием от нескольких десятков до нескольких сотен граммов РЗЭ на литр при низком содержании Са, Р, S, Sr и других нежелательных элементов, который может быть использован для осаждения карбонатов или гидроксидов РЗЭ [3].

Ключевые слова: редкоземельные элементы, каскадное выщелачивание фосфогипса, выпаривание РЗЭ-содержащего раствора.

Благодарности. Исследование выполнено в рамках государственного задания на создание в 2021 г. новых лабораторий, в том числе под руководством молодых перспективных специалистов национального проекта «Наука и университеты», по научной теме «Разработка и развитие научно-технологических основ создания комплексной технологии переработки гипсосодержащих отходов различных промышленных предприятий и поиск новых способов применения продуктов переработки», (FZWG-2024–0001). Работа выполнена с использованием оборудования ЦВТ на базе БГТУ им. В. Г. Шухова (г. Белгород).

Цитирование: Никулин И. С., Никуличева Т. Б., Колесников Д. А., Захвалинский В. С., Вьюгин А. О., Аносов Н. В., Алфимова Н. И. Оптимизация технологических параметров получения концентрированного водного раствора солей, содержащих редкоземельные элементы, извлекаемые из фосфогипса. Журн. Сиб. федер. ун-та. Химия, 2024, 17(2). С. 177–185. EDN: CDKVTL

1. Introduction

REE is extracted on an industrial scale from rocks containing them. Most of the deposits are complex i.e. REE is extracted together with extraction of Ti, U, Ta, Th and other elements. Monazite, bastnaesite, apatite, loparite and euxenite are the most widespread minerals to extract REE [4]. These minerals differ in composition, and REE salts content in them varies from 20 to 60 %, but these minerals should be preliminary enriched by separation from waste rock. One of interesting and possibly perspective methods of REE concentrate production is treatment of phosphogypsum, a large-tonnage waste of phosphoric acid production. The content of REE in such gypsum is from 0.1 % up to 0.6 %, but phosphogypsum does not need to be extracted from rocks and besides it is already in the form of dispersed powder. REEs can be extracted from phosphogypsum by treating it with water solution of nitric acid [5]. The heavy-element-depleted phosphogypsum can be used for the production of fertilizers [6] and construction materials that will improve the economic efficiency of recycling this material [7].

The purpose of the research was to obtain concentrated REE – containing solutions with low impurity content, which is convenient to work with when precipitating REE hydroxides or carbonates. From the economic point of view, an acceptable concentration for REE precipitation from solution is a concentration of the order of several tens of grams of REE or more per liter of solution [8].

2. Experimental

A cascade treatment of phosphogypsum (at least 4 cascades), followed by evaporation of the solution to the required concentration was carried out to extract REE from phosphogypsum. It was necessary to find out whether repeated treatment of gypsum with the same solution is economically feasible to assess the effectiveness of extraction, i.e:

– Whether the increase in REE concentration is approximately a linear function of the number of treatment cascades – How the solution containing REEs would evaporate, i.e., whether the REEs would remain in solution at high concentrations or precipitate out.

This information will allow to determine what types of treatment will be acceptable and can be applied in semiindustrial and industrial technology of REE concentrate production from phosphogypsum [9].

A 2 molar solution of nitric acid in the volume of 2 liters was prepared to carry out the cascade. Phosphogypsum in an amount of 10 kg was sieved on laboratory sieves with a minimum mesh of 160 microns.

Thermal treatment of gypsum in nitric acid solution was carried out at a temperature of 103–105 °C under ° continuous stirring (rotation speed was about 100 rpm). The ratio of solid (gypsum) to liquid (2 molar solution of HNO₃) was S / L = 1: 1.8.

Time of heating the reactor contents to the boiling point of solution was about 30–40 minutes. Holding time at boiling point was 10 minutes. After cooling the reactor contents to 45–50 °C the nitric acid solution was filtered from the gypsum.

The treated gypsum was washed with distilled water in 2 steps. In the first step, it was rinsed with approximately 650 ml of water. This amount roughly corresponds to the volume of acid solution that remains in the treated gypsum after filtration, with the addition of 10–15 % for better washing. The rinse water is returned to the filtrate for use in the next experiment. The second time, the treated gypsum was washed with more water to completely wash away the acid residue. This was necessary to analyze the elemental composition of the dry residue.

The obtained solution, namely the filtrate, together with the washing water from the first wash was used to treat the next portion of gypsum. It should be noted that the acidity of the washing solution did not undergo significant changes compared to the original solution, which allowed using it in the next experiment. Moreover, the amount of acid taken to prepare the solution was excessive to treat the above amount of gypsum. The procedure was repeated similar to the first process. Thus, 10 kg of gypsum were treated with an initial amount of 2 liters of 2 molar nitric acid solution. The difference is in the last fourth process. At the end of this process, the amount of washing water was increased from 650 ml to 900 ml because the REE concentration in the solution was already very high and the washing was done with more water to avoid loss of REE.

The obtained solution (let's call it solution IV) was used for evaporation experiments. Evaporation of the solution was carried out in stages, because in the process of evaporation a precipitate fell out, which was filtered out. Samples of the filtrate and precipitate were taken for composition analysis. After sampling, the filtrate continued to be evaporated. For clarity, the IV solution was first evaporated at 50 %, then the filtered evaporated solution was further evaporated at 40 %, then at 25 %, 15 %, 15 %, 15 %, 15 %, 15 %, and lastly at 20 %. Accordingly, we obtained the corresponding points on the graphs (see in the conclusions) of the final evaporation: 50 %, 70 %, 77.5 %, 80.9 %, 83.7 %, 86.2 %, 89 %. The evaporation system for increasing the REE concentration is shown in Figure 1.

Experiments on distillation of nitric acid from solution were carried out in parallel with evaporation of solution containing REE. It was found that in 2 molar solutions of nitric acid easily dissolved REE salts more than a hundred grams per liter of solution.

Naturally, the need for distillation of excess acid arose because, on the one hand, the cost of acid is a significant part of the total cost of obtaining REE concentrate from gypsum. The distilled acid could

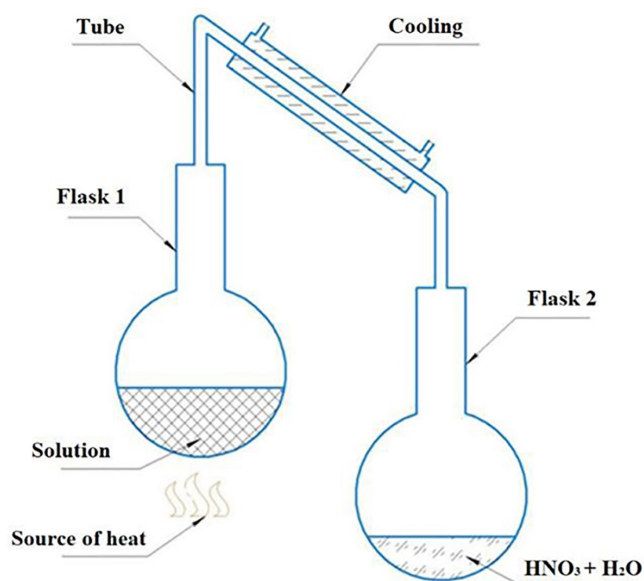


Fig. 1. The evaporation system for increasing the REE concentration

be reused to extract REE from gypsum. Secondly, the less acid in solution, the less alkali is required for precipitation of REE hydroxides. It has been observed that at temperatures below boiling point, water is preferentially distilled off, and at solution boiling point, water with acid is distilled off. At overheating (when the bottom is much hotter than the solution) predominantly nitric acid is distilled. The distillation process can thus be regulated. It has been found that up to 40–45 % of the nitric acid can be recovered in the distillation process.

1.1. Analysis

The composition of the samples from liquid phases were analyzed by ICP (PerkinElmer AVIO 220 Max). Argon of 99.996 % purity was used as an inert gas. Its flow rate was set to 16 l / min. The plasma temperature was set at 10000K. The analysis of each sample was repeated at least three times.

2. Results and discussions

It was found that the increase of REE concentration in the solution is almost linear, which allows the experiment to conduct repeated cascade treatment of gypsum with acid (Fig. 2)

Four times treatment in the same solution of 10 kg of gypsum, we obtained about 3 liters of filtrate. The composition of the filtrate was determined using a PerkinElmer Avio 220 Max optical spectrometer with inductively coupled plasma. The composition of the filtrate after 4 – fold treatment of gypsum at $S / L = 1: 1.8$ is shown in Fig. 3.

As can be seen from the figures, as a result of 4 – cascade treatment of gypsum can be obtained a solution containing a total of about 8.5 g [10] of REE per liter of solution. The volume of the solution obtained after 4 – cascade treatment of gypsum was a little more than 3 l. This is 1.5 times more than the original volume of acid in which the first portion of gypsum was treated, because we added small amounts of water at each washing step, mixing the washing water with the filtrate.

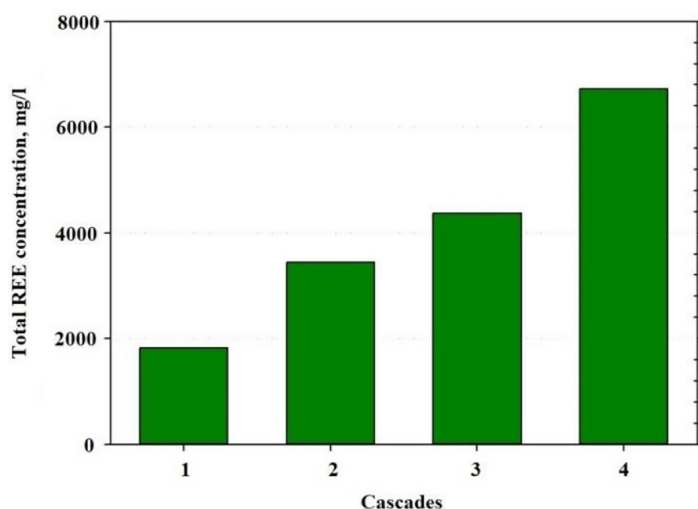


Fig. 2. Diagram of REE content in leachate after cascade treatment of gypsum in 2 molar HNO_3 solutions

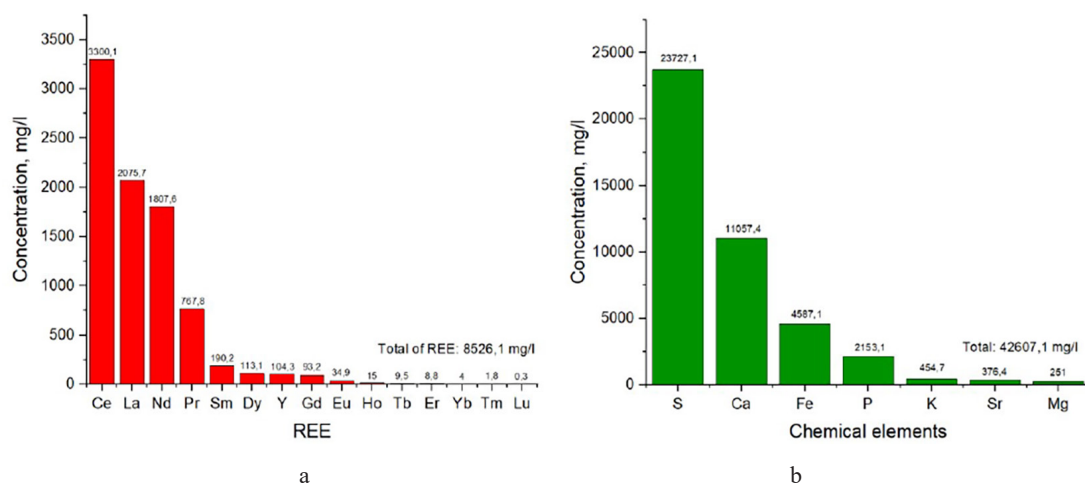


Fig. 3. Composition of the leachate after 4 cascades of gypsum treatment (there were 2 liters of 2 molar nitric acid, 10 kg of gypsum were treated): a) REE content in solution. b) Content of chemical elements in solution

Fig. 4a, b, c shows plots of dependence of REE and other elements content on the degree of final solution evaporation for filtrate and sediment [11]. These graphs refer to the samples which passed the evaporation process.

As can be seen from the graph in Figure 4 a, at evaporation to 70 % we obtain a concentration of total REE about 20 g / l, which is already sufficient for cost-effective precipitation of REE hydroxides. When evaporated to 90 %, the concentration reaches a value of 43 g / L. From Figure 4 b it can be concluded that the relative content of different REEs in the solution does not change with increasing degree of solution evaporation, i.e. the ratio between REEs remains the same as in the initial solution IV.

It has been found that the REE concentration in the precipitate increases with the degree of evaporation of the IV solution (Fig. 4c). However, the growth rate is significantly inferior to the growth

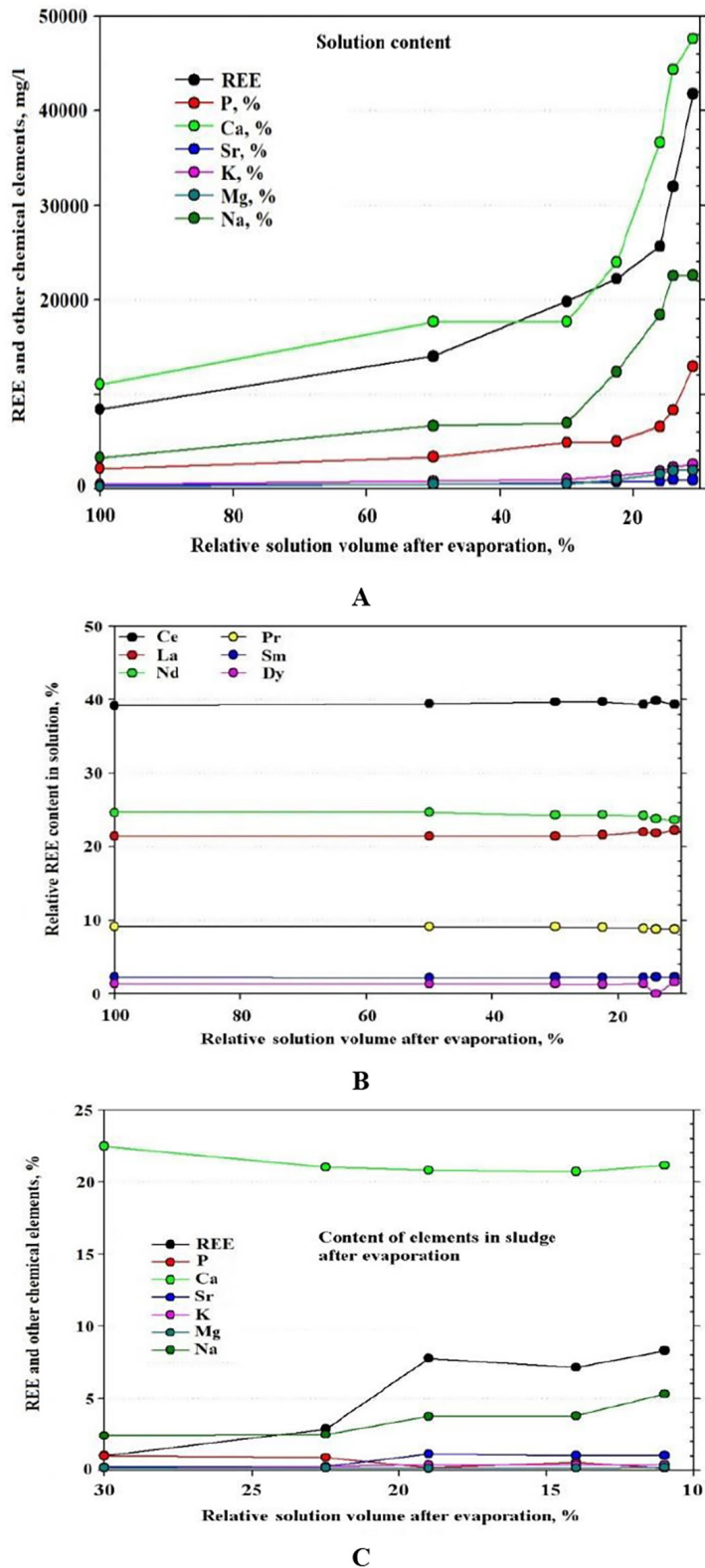


Fig. 4. Dependence of element content on the degree of solution evaporation: A) Total REE and other chemical elements in solution. B) Relative REE content in the solution. C) Content of elements in sludge after evaporation

rate of REE concentration in the evaporated solution. This allows the evaporation method to be used to enrich the REE solution. Since the precipitate contains more REE than gypsum, it can be reused for REE extraction with a new batch of gypsum powder.

3. Conclusion

To summarize, we can say the following: cascade leaching followed by solution evaporation is a cost-effective technological process. Multistage evaporation of the solution leads not only to an increase in the concentration of REE, but also to a relative reduction in the content of undesirable impurities precipitated in the process of evaporation. This also makes it possible to obtain a solution containing REE salts in an amount of several tens to several hundreds of grams per liter. Such a solution is already economically convenient for precipitation of rareearth carbonates or hydroxides.

Declarations

Ethical Approval: Not applicable.

Competing of interests: The authors declare no conflict of interest.

Authors' contributions: Ivan S. Nikulin: Conceptualization, Writing – original draft, Writing – review & editing, Tatiana B. Nikulicheva: Metodology, Writing – original draft, Writing – review & editing, Dmitry A. Kolesnikov: Investigation, Alexey O. Vyugin: Investigation, Nikita V. Anosov: Metodology, Writing – original draft, Writing – review & editing.

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