

LEACHING OF RARE EARTH ELEMENTS FROM BASTNASITE ORE (SECOND PART)

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Summary:

Dissolution of rare earth elements from bastnasite ore was studied using different leaching agents such as sulfuric acid, hydrochloric acid, acetic acid, citric acid and sodium hydroxide at 70°C, with 1 mol/L, solid/liquid ratio of 0.05 between 30 and 180 min. The one-step direct leaching strategy was applied under atmospheric pressure aiming at selective leaching of rare earth elements from a matrix of iron oxides in which the rare earth elements – carbonates & fluorides – are embedded.

Key words: rare earth elements, hydrometallurgy, bastnasite, acids.

Introduction

Rare earth elements are a group of metallic elements of the periodic table, often overlooked, but very significant in today's industrial landscape and modern lifestyle. Like other metals, rare earths are silvery-gray, malleable, ductile, and they conduct electricity.

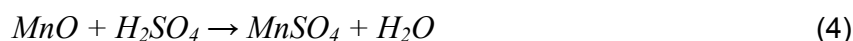
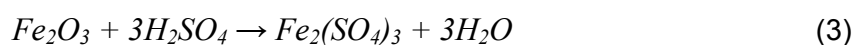
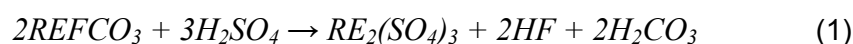
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They appear in nature in the form of oxides and other compounds, but with one particularity – the chemical similarity between all of them is so astounding that they all occur together in their bearing minerals, substituting one another at the molecular level (Gupta & Krishnamurthy, 2005), (Castor & Hedrick, 2006, pp.769-772).

Development of new advanced materials based on oxidic powders is of high importance for different applications in modern life (Kuburović et al, 2018, pp.771-835).

Bastnasite (La,Ce)CO₃F is a fluororcarbonate of the cerium group found in ore deposits, metamorphic zones and pegmatites. In average, it contains 70% rare earth oxides, most of them belonging to the light fraction and in particular lanthanum, cerium and neodymium (Stopić & Friedrich, pp.757-770). A sulfuric acid leaching process was studied for the processing of roasted ore of Dechang bastnasite in Sichuan, China, in order to obtain rare earth elements (Feng et al, 2013, pp.849-854). With a particle size of 0.074-0.100mm, 1.5mol/L sulfuric acid concentration, a liquid to solid mass ratio of 8 and a stirring speed of 500rpm, the reaction rate of the leaching process can be controlled by diffusion through the product/ash layer, as described by the shrinking-core model, and the calculated activation energy of 9.97, which is typical for a diffusion controlled process.

The main equations ruling dissolution in sulfuric acid are described as:



The aim of this work is to compare the leaching efficiency of different leaching agents such as sulfuric acid, hydrochloric acid, acetic acid, citric acid and sodium hydroxide at 70°C, using 1mol/L, solid/liquid ratio of 0.05 between 30 and 180 min in order to recover rare earth elements.

Experimental work, material, parameters and procedure

The Rodberg ore sample used in these trials was analyzed and the results are given in Table 1 and Figure 1. The amount of iron of about 10.63 was smaller in comparison to the one of 73.1 % mentioned in our previous work (Stopić & Friedrich, 2018, 757-770), where the RE-content seems to be fairly lower than in the representative Rodberg samples.

Table 1 – Chemical composition of the “Rodberg bastnasite ore” sample

Таблица 1 – Химический состав образца «Родбергский бастнезит – минерал, содержащий, фторкарбонат»

Табела 1 – Хемијски састав узорка „Родберг руда које садрже флуорокарбонатни минерал“

Element	Fe	Ca	Mg	Mn	La	Ce	Nd	Sm	Y	Th
(%)	10.63	15.15	4.28	1.50	0.22	0.43	0.18	0.025	0.0124	0.057

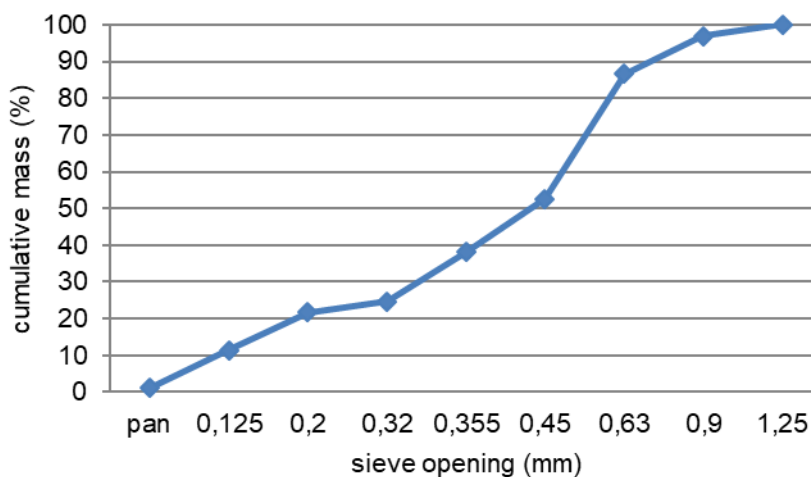


Figure 1 – Particle size distribution of the Rodberg ore

Рис. 1 – Распределение величины частиц «Родбергской руды»

Слика 1 – Расподела величине честица руде „Родберг“

Table 2 – Leaching trial design with sulfuric-, hydrochloric-, acetic and citric acid and sodium hydroxide

Таблица 2 – Разработка пробного выщелачивания с использованием серной, соляной, уксусной и лимонной кислот и гидроксида натрия

Табела 2 – План експеримената лужења сумпорном, хлороводоничном, сирћетном и лимунском киселином и натријум-хидроксидом

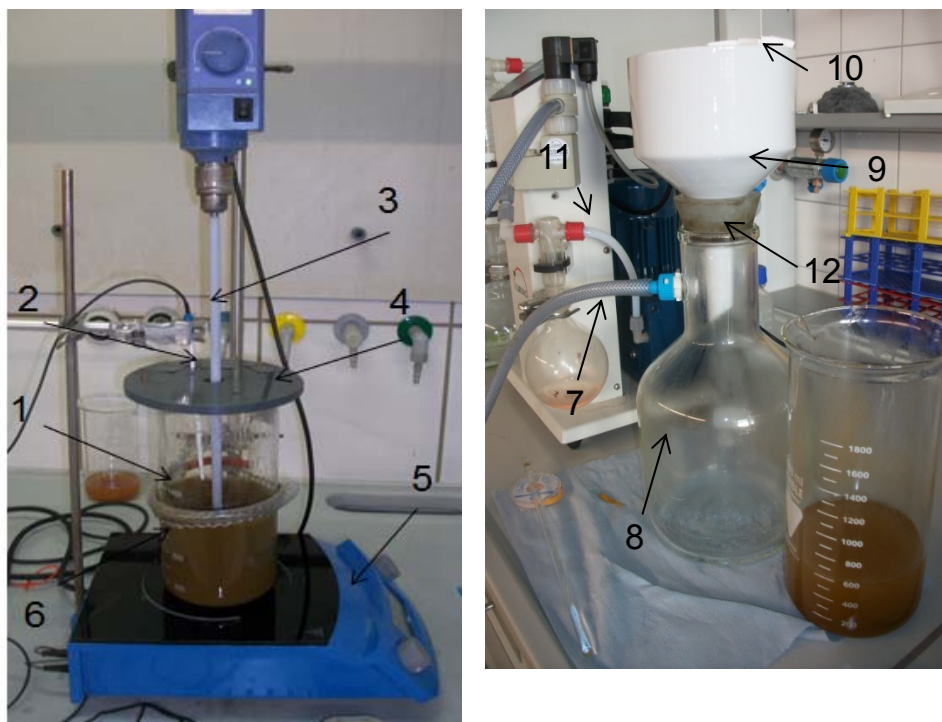
Parameter	set value
Concentration (mol/L)	1 (0.5)
Temperature (°C)	70
Solid-liquid ratio (g/L)	50
Time(min)	30, 60, 120, 180
Stirring rate (rpm)	300

A sample of the Rodberg ore was submitted to a series of preliminary trials where the leaching parameters were kept constant in all experiments and only the leaching agent was changed. The aim of these experiments was to obtain information about the general behavior of the Rodberg ore under acid and alkali attacks, and to choose a route for further experimentation. The desired leaching agent should not dissolve much of the iron oxide matrix and should attack the carbonate rare earth bearing minerals instead. However, this means that the non-rare earth bearing carbonates present in the ore will almost inevitably dissolve as well.

As well as the standard mineral acids, sulfuric and hydrochloric acid, and the base sodium hydroxide, two organic acids, acetic and anhydrous citric acid, were used as leaching reagents. The purpose of the organic acid trials was to investigate whether or not calcium carbonate and ankerite (a carbonate of iron, magnesium and manganese), which add up to 17% of the ore, could be selectively leached from the ore in the first leaching step. This would allow for the removal of most of the ore's impurities. The second step involving strong mineral acid leaching could then be performed to recover the rare earth elements in a solution of higher purity.

The experiments were carried out in a laboratory fume cabinet, as shown in Figure 2. A 2L beaker was placed on top of a heating induction plate and filled with one liter of the previously prepared diluted acid or reagent. A temperature measuring device was connected to the induction plate for adequate temperature control. The temperature was set at 70°C. The stirring equipment was fixed to a clamp above the beaker and

connected at a speed of 300rpm. Rod stirrers were used instead of magnetic stirrers because of the magnetic nature of the ore.



Where: 1. Beaker containing Rodberg ore + leaching agent, 2. Thermocouple, 3. Stirrer, 4. Cover, 5. Heating plate, 6. Security chain, 7. Pipe connected with a vacuum pump, 8. Glass container, 9. Ceramic filtering cone, 10. Fine filtering paper, 11. Vacuum filtering machine, 12. Rubber adapter.

Figure 2 – Equipment for leaching and filtration
Рис. 2 – Оборудование для выщелачивания и фильтрации
Слика 2 – Апаратура за лужење и филтрацију

After reaching the desired temperature, the weighed 50g of the Rodberg ore were added, and the stop watch started. A cover was placed over the beaker to avoid excessive evaporation. The samples were taken from the leaching mixture by means of a syringe at several intervals: 30, 60, 120 and 180 min.

The taken samples were filtered using the previously weighed fine filter papers and the leachate was collected in the test tubes. Each sample gave about 40ml. The used filter papers were then placed over a

vacuum filtering machine were they were neutralized with distilled water before being introduced into a drying cabin at 105°C for three hours.

After the 3h sample was taken, the stirrer and heating plate were disconnected and the beaker content was filtered using the above mentioned filtering machine. The filtrate was collected in a bottle and the neutralizing of the solid residue and the filter was carried out before drying in the same conditions as for the rest of the samples. After the drying time had elapsed, the solid residue was weighed and the results were noted down.

Results and discussion

The summarized results are presented in Tables 3 and 4 and Figures 3 to 6.

Table 3 – Amount of the solid residue after leaching
Таблица 3 – Количество твердого остатка после выщелачивания
Табела 3 – Износ чврстог остатка након лужења

Trial No	leaching agent	net mass of solid residue (g)	mass dissolved (%)
1	sulphuric acid	33.798	32.404
2	hydrochloric acid	9.475	81.050
3	acetic acid	29.257	41.486
4	anhydrous citric acid	12.898	74.205
5	sodium hydroxide	49.635	0.730

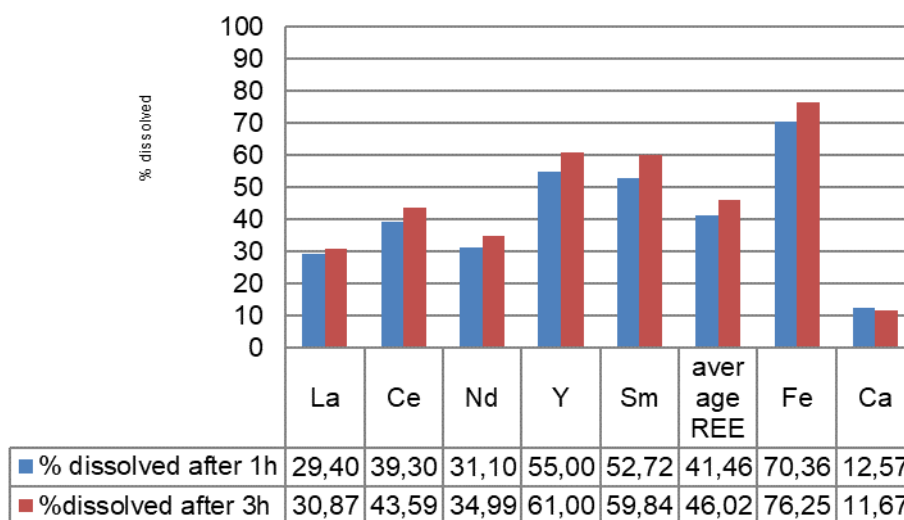


Figure 3 – Trial No1: Dissolution of rare earths and impurities during leaching with sulphuric acid

Рис. 3 – Эксперимент №1: Растворение редкоземельных элементов и примесей при выщелачивании серной кислотой

Слика 3 – Експеримент бр. 1: Растварање елемената ретких земаља и нечистоћа за време лужења сумпорном киселином

After a few hours from the leaching operation with sulfuric acid, a fine, white precipitate appeared at the bottom of test tubes and the bottle. The samples were re-filtered and the white precipitate was sent for analysis. The results are shown in Table 4.

Table 4 – Chemical composition of the precipitate produced in H₂SO₄ leaching

Таблица 4 – Химическиј састав осадка, образујућег се при выщелачивании H₂SO₄

Табела 4 – Хемијски састав преципитата добијеног растварањем сумпорном киселином

Element	Fe (ppm)	Ca (%)	Ce (ppm)	La (ppm)	Nd (ppm)	Pr (ppm)	Sm (ppm)	Gd (ppm)	Tb (ppm)	Y (ppm)
Amount	11/ <1 (inhomogeneous)	29,7	600	302	146	<1	<1	<1	<1	<1

As shown in Fig. 4, leaching with hydrochloric acid had higher leaching efficiency in comparison to that with sulfuric acid.

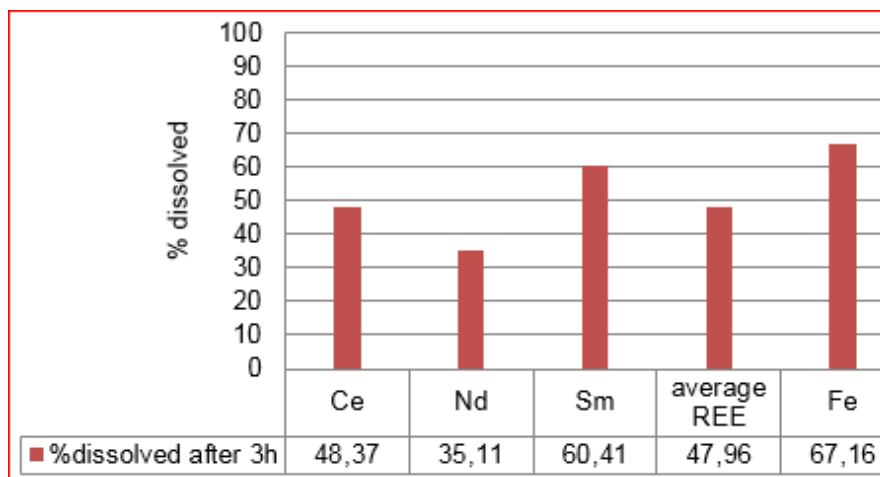
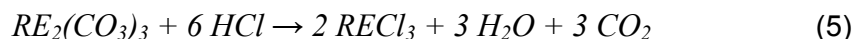


Figure 4 – Trial No 2: Dissolution of rare earths and impurities during leaching with hydrochloric acid

Рис. 4 – Эксперимент № 2: Растворение редкоземельных элементов и примесей при выщелачивании соляной кислотой

Слика 4 – Експеримент бр. 2: Растварање елемената ретких земаља и нечистоћа за време лужења хлороводоничном киселином

The chemical reactions ruling carbonate and fluoride dissolution are described as:



Leaching with organic acids was performed using acetic and citric acid, as shown in Figs. 5 and 6.

The results show that the extraction of rare earth elements was higher with mineral acids than with organic acids. Sulfuric acid dissolved 46% REE after 3 hours while hydrochloric acid dissolved 48%. However, the dissolution of large quantities of iron took place in parallel, 76% in the case of sulfuric acid and 67% in the case of hydrochloric acid. Hydrochloric acid also dissolved the totality of calcium present in the ore (an error in the chemical analysis or inhomogeneity of the ore gives a percentage superior to 100). Indeed, the rare earth acid carbonate minerals seem to be more resistant to acid attack than the other gangue carbonate minerals. In the sulfuric acid leachate, the dissolution values of

calcium are much lower due to the removal of the white precipitate, identified as calcium sulfate or gypsum (CaSO_4). The precipitate also contains small quantities of rare earth elements that have been absorbed in its crystals, namely 13.9% of cerium, 13.7% of lanthanum and 8.1% of neodymium.

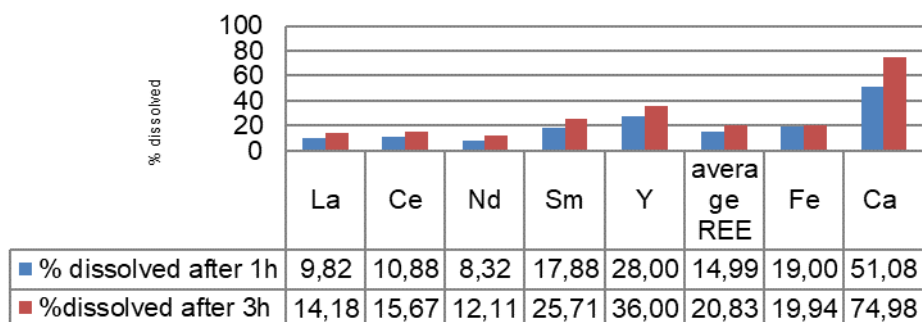


Figure 5 – Trial No 3: Dissolution of rare earths and impurities during leaching with acetic acid

Рис. 5 – Эксперимент № 3: Растворение редкоземельных элементов и примесей при выщелачивании уксусной кислотой

Слика 5 – Експеримент бр. 3: Растварање елемената ретких земаља и нечистоћа за време лужења сирћетном киселином

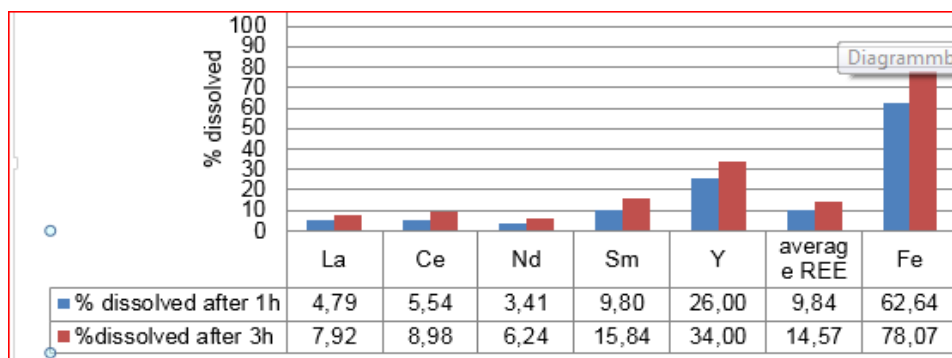


Figure 6– Trial No 4: Dissolution of rare earths and impurities during leaching with citric acid

Рис. 6 – Эксперимент № 4: Растворение редкоземельных элементов и примесей при выщелачивании лимонной кислотой

Слика 6 – Експеримент бр. 4: Растварање елемената ретких земаља и нечистоћа за време лужења лимунском киселином

The amount of solid residue left in sulfuric acid leaching is also inferior to that of hydrochloric acid (32% versus 81%), although different minerals, including iron oxide, are dissolved to a similar degree. There is a possibility that a part of gypsum is precipitating too during the leaching operation with sulfuric acid, and is collected together with the solid residue counted as undissolved material.

The organic acids failed to remove the carbonate gangue minerals without dissolving the rare earth carbonate minerals. Acetic acid leached an average of 21%REE together with 20% of iron and 75% of calcium after 3 hours. Citric acid left most rare earths untouched, but dissolved a great quantity of the gangue minerals containing iron and calcium. The likelihood of a selective leaching of gangue carbonates with organic acids was overall not encouraging.

As to the base NaOH, the total mass of ore dissolved, lower than 1%, already pointed toward little rare earth recovery. Fe dissolved in 0.03% and 0.02% after 1 and 3 hours, respectively. Calcium dissolved in 0.28% and 0.13%. All rare earths dissolved to give less than 1mg/l in the solution.

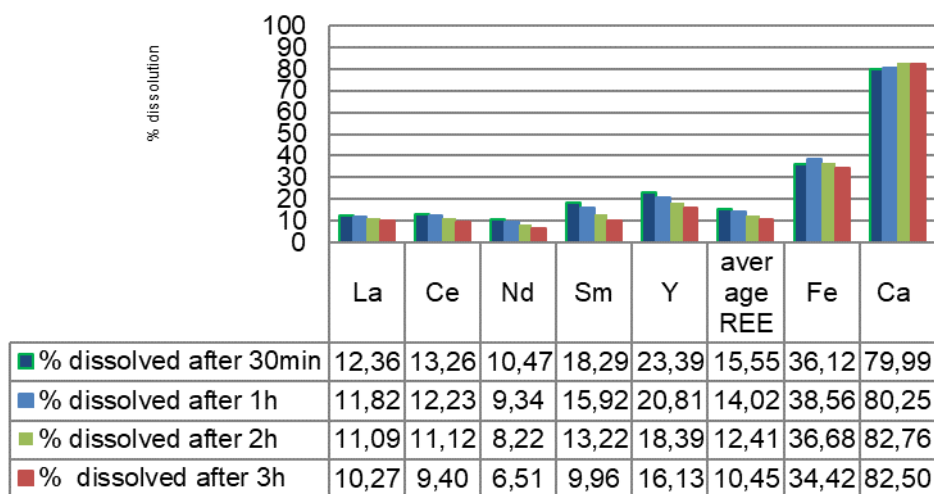


Figure 7 – Leaching in hydrochloric acid (0.5mol/L) - Dissolution of rare earths and impurities

Рис. 7 – Выщелачивание в соляной кислоте (0,5 моль/л). Растворение редкоземельных элементов и примесей

Слика 7 – Лужење хлороводоничном киселином (0,5 mol/L) – растварање елемената ретких земаља и нечистоћа

In an additional leaching experiment, a possibility of selective leaching was attempted with a lower concentration of hydrochloric acid of 0.5mol/L, leaving the rest of the parameters as previously determined. The results are shown in Figure 7.

A peculiarity of this hydrochloric acid trial is that all rare earths give larger values of dissolution after 30 minutes of leaching and the lapse of time reduces their quantity in the leachate. This does not happen with iron and calcium, which reach maximum dissolution levels after 1 and 2 hours, respectively. After 30 minutes, an important quantity of calcium, 80%, was leached, versus 16%REE, 10% in the case of neodymium. The amount of iron present in the leachate was 36%.

When comparing the trial No1 done with 1M HCl and this extra trial where the concentration has been halved to 0.5M, it can be concluded that the dissolution of rare earths has decreased drastically in 78.21%. Calcium remained with high dissolution rates, decreasing only in 17.50% in respect to the 1M trial, while iron was 48.75% less dissolved. This means that reducing the acid concentration was more selective toward dissolving the gangue calcium based minerals and not the rare earth bearing minerals. Reducing the concentration further, and varying other parameters, for instance leaching at lower temperatures, with higher solid to liquid ratios and longer times, could give more accurate results, and the possibility of a two-step leaching process.

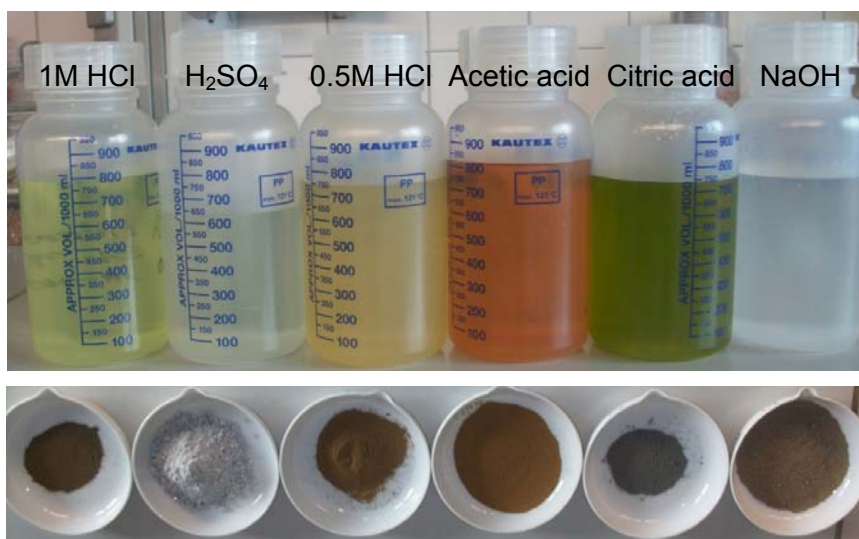


Figure 8 – Leachates and their corresponding solid residues

Рис. 8 – Полученные растворы и соответствующие твердые остатки

Слика 8 – Добијени раствори и њима одговарајући чврсти остаци

Conclusion

The dissolution of rare earth elements from bastnasite ore was performed using different leaching agents such as sulfuric acid, hydrochloric acid, acetic acid, citric acid and sodium hydroxide at 70°C, using 1mol/L, solid/liquid ratio of 0.05 with duration between 30 and 180 min. The maximal leaching efficiency was about 48% under the above mentioned conditions using hydrochloric acid and sulfuric acid in contrast to 20 % obtained using acetic and citric acid. A decrease in the concentration of hydrochloric acid from 1.0 to 0.5mol/L leads to a decrease in the leaching efficiency to 11%.

In order to increase the leaching efficiency of rare earth elements, an additional study of the increased concentration and higher pressure and temperature in an autoclave will be performed. The minimal leaching efficiency was obtained using sodium hydroxide for dissolution of rare earth elements from a bastnasite ore. Higher dissolution of iron and calcium under the above mentioned conditions is a serious problem for the leaching process selectivity.

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ВЫЩЕЛАЧИВАНИЕ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ ИЗ ПОРОД, СОДЕРЖАЩИХ ФТОРКАРБОНАТЫ – ВТОРАЯ ЧАСТЬ

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Резюме:

При исследовании процесса растворения редкоземельных рудных пород, содержащих фторкарбонат применялись различные виды выщелачивания: серной кислотой, соляной кислотой, уксусной кислотой, лимонной кислотой и гидроксидом натрия, при температуре 70° С, концентрация: 1 моль / л, соотношение твердость/жидкость: 0,05, в промежутке времени от 30 до 180 минут. Одностадийное выщелачивание проводилось с целью селективного выщелачивания редкоземельных элементов, в виде фторидов и хлоридов, находящихся в матрице оксида железа.

Ключевые слова: редкоземельные элементы, гидрометаллургия, фторкарбонат, серная кислота.

РАСТВОРАЊЕ ЕЛЕМЕНАТА РЕТКИХ ЗЕМАЉА ИЗ РУДА КОЈЕ САДРЖЕ ФЛУОРОКАРБОНАТНИ МИНЕРАЛ (ДРУГИ ДЕО)

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ОБЛАСТ: хемијске технологије
ВРСТА ЧЛАНКА: оригинални научни рад
ЈЕЗИК ЧЛАНКА: енглески

Сажетак:

Растварање елемената ретких земаља из руда које садрже флуорокарбонатни минерал проучавано је коришћењем разних реагенаса за лужење, као што су сумпорна, хлороводонична, сирћетна и лимунска киселина и натријумхидроксид, концентрације 1mol/L, на 70°С у времену од 30 до 120 минута и односом чврсто/течно од 0,05. Директно лужење у једном кораку извођено је са циљем селективног лужења елемената ретких земаља у облику флуорида и хлорида, који су заробљени у матрици гвожђе оксида.

Кључне речи: елементи ретких земаља, хидрометалургија, флуорокарбонатни минерал, сумпорна киселина.

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