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# LEACHING OF RARE EARTH ELEMENTS FROM BASTNASITE ORE (THIRD PART)

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## Summary:

*Sulfuric acid dissolution of rare earth elements from bastnasite ore was studied after reductive smelting with carbon as a reducing agent at 1600°C. The two-step strategy: 1.carbothermic reduction, and 2.dissolution with sulfuric acid at 70°C was applied under atmospheric pressure aiming at an increased selective extraction of rare earth elements from slag containing rare earth elements.*

*Key words: rare earth elements, smelting, leaching, acid.*

## 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. 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

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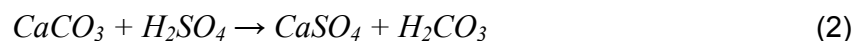
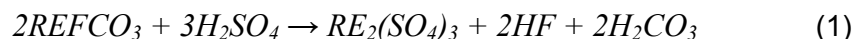
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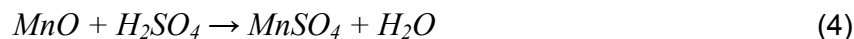
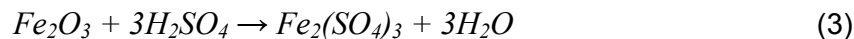
another at the molecular level (Gupta & Krishnamurthy, 2005), (Castor & Hedrick, 2006, pp.769-772). Bastnasite (La,Ce)CO<sub>3</sub>F is fluorocarbonate of the cerium group found in ore deposits, metamorphic zones and pegmatites. In average, it contains 70% rare earth oxides, most of them belonging to the light fraction and in particular lanthanum, cerium and neodymium (Stopić & Friedrich, 2018, pp.757-770). The 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, 1.5 mol/L sulfuric acid concentration, a liquid to solid mass ratio of 8 and a stirring speed of 500 rpm, 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 kJ/mol, which is typical for the diffusion controlled process.

A stepwise carbochlorination-chemical vapor-transport-oxidation process was developed for the green rare earth extraction from a bastnasite concentrate using carbon as a reductant, chlorine gas as a chlorination agent, gas as a defluorination agent, aluminium chloride as a vapor complex former and a mixture from oxygen and hydrogen as an oxidant (Zhang et al, 2004, pp.217-221). After carbochlorination for an efficient rare earth extraction and thorium free volatile by-product release, thorium was removed by chemical vapor transport at 800°C for 0.5 hours in the chlorine-, silicon chloride-, and aluminium chloride atmosphere and alkaline earths were separated from rare earth by oxidation at 700°C to 1000°C in the mixture of oxygen and water atmosphere for 0.5 hours, followed by water leaching at room temperature. Their proposed treatment reached a clean and efficient rare earth extraction from the bastnasite concentrate.

A process for rare earth recovery from the Baotou bastnasite concentrate was developed by fixing fluorine and chlorinating with ammonium chloride in the ore (Shi et al, 2003, pp.438-442). The optimum conditions were determined as follows: the MgO/ore ratio of 3 at 600 °C; chlorinating the fixed fluorine calcine in 80 min, with ammonium chloride/ore ratio of 2 at 500°C.

The main equations concerning a dissolution of rare earth elements from bastnasite ore in sulfuric acid are described as:





According to the “Recovery behavior of rare earth from Bayan Obo Complex Iron ore” (Ding et al, 2013, pp.28-36) a two step strategy with a carbothermic reduction in an electric furnace and a subsequent sulfuric acid leaching of the formed slag was proposed. As already mentioned, the rare earth elements such as Ce and La which are more fully crystallized when the cooling rate of the liquid slag is decreased, were leached by hydrochloric acid to evaluate the relations between the leaching efficiency of rare earth elements and the cooling conditions. This method would allow a separation of the produced iron and the formed slag containing REE. Once smelted, the slag should contain a high fraction of rare earth elements together with other compounds that normally appear in slags. Therefore, the slag can be considered as a rare earth concentrate suitable for leaching operations using sulfuric acid and for a subsequent recovery of REEs.

The formation of slag during iron manufacture is the result of a number of complex operations between silica, oxides, other oxidation by-products from melting and reactions with refractory linings, etc. It is therefore a complex liquid phase made of oxides of iron, manganese, magnesium, silicon, silicates and sulfides plus other complex compounds that may include alumina, calcium oxides and sulfides, and rare earth oxides. Depending on the elements present in bastnasite ore, the formed slag will probably contain MgO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, and MnO as well as rare earth compounds.

An advantage of reduction smelting of bastnasite ore with high iron oxides grades is that the mineral already contains calcium carbonate which is normally used as an additive in iron smelting. A popular additive is limestone with small quantities of calcium fluoride.

The main aim of the following experimental study was to compare the leaching efficiencies of rare earth elements from bastnasite ore by smelting and a subsequent leaching of the slag using sulfuric acid.

The proposed strategy for the treatment of bastnasite ore was shown in Figure 1. In this paper, we will be focused only on reductive smelting and acidic leaching.

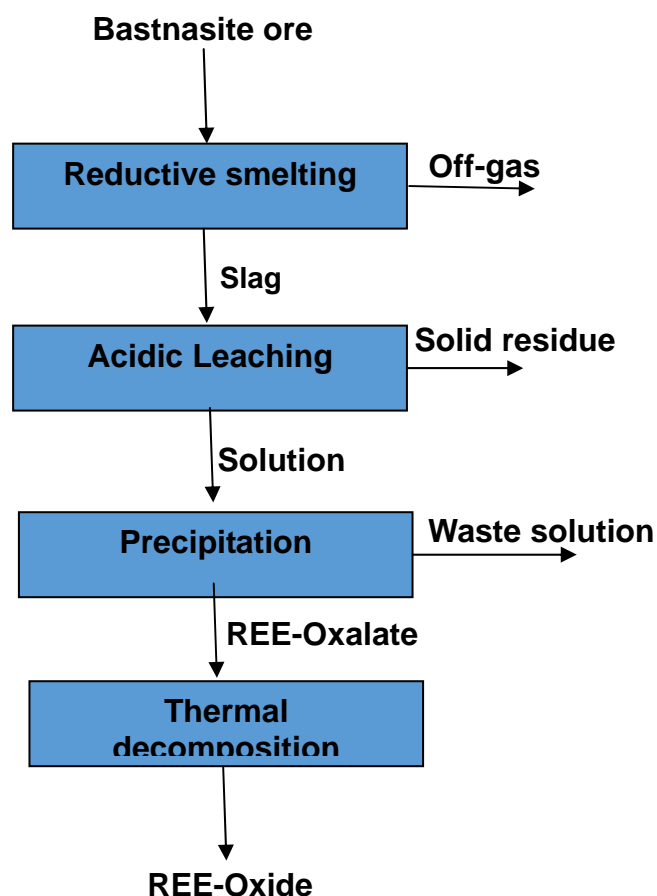


Figure 1 – Research strategy from bastnasite ore to rare earth oxide  
 Рис. 1 – Исследовательская стратегия от бастнезитовой руды до оксидов редкоземельных элементов  
 Слика 1 – Стратегија истраживања од бастнезитне руде до оксида ретке земље

The precipitation was performed using oxalic acid in order to produce rare earth oxalate. Finally, rare earth oxides were prepared after thermal decomposition of rare earth oxalate at 800°C in a muffle furnace.

## Experimental work, material, parameters, and procedure

The chemical composition of bastnasite ore was shown in Table 1.

*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 руде бастнезит која садржи флуорокарбонатни минерал”*

Compound	Fe <sub>3</sub> O <sub>4</sub>	CaCO <sub>3</sub>	MgCO <sub>3</sub>	MnO	TREO	ThO <sub>2</sub>	SiO <sub>2</sub>
(%)	78.1	11.0	6.0	0.5	1.5	0.1	2.8

The reduction smelting of bastnasite ore was carried out in a small electric arc furnace and carbon was added as a reducing agent.



*Figure 2 – Reduction smelting of the Rodberg ore in an electric arc furnace (left) and a ladle with the resultant slag (right)*

*Рис. 2 – Восстановительная плавка образца Родберга в электродуговой печи (слева) и ковш с полученным шлаком (справа)*

*Слика 2 – Редуктивно топљење узорка Родберг у електролучној пећи (лево) и кутлача с добијеном шљаком (десно)*

The bastnasite sample was a high iron grade ore used for reductive smelting. The initial mass of bastnasite ore added to the furnace was 1480 g. The furnace was kept at 1600°C for 45 minutes. After this time, the slag formed at the top of the furnace was poured onto a ladle and left to cool. Both the slag and the reduced portion of iron were weighed after cooling. The mass of the produced metallic iron after reduction was of 816 g. The mass of the produced slag was of 58 g.

*Table 2 – Chemical composition of the produced slag*  
*Таблица 2 – Химический состав полученного шлага*  
*Табела 2 – Хемијски састав добијене шљаке*

Compound (%)	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	La <sub>2</sub> O <sub>3</sub>	Nd <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>
Amount	11.4	15.4	30.2	0.78	1.43	2.62	2.59
Compound (%)	Y <sub>2</sub> O <sub>3</sub>	Sc <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>	Gd <sub>2</sub> O <sub>3</sub>	Pr <sub>2</sub> O <sub>3</sub>	Sm <sub>2</sub> O <sub>3</sub>	Total
Amount	0.15	0.059	0.94	0.30	0.64	0.28	66.79

The slag was then crushed and ground to powder with a comparable particle size similar to direct leaching. The leaching agent used was sulfuric acid. The apparatus and the experimental procedure were the same as in the first set of experiments (Stopić & Friedrich, 2019, pp 241-254). Once the 1L acidic solution had been prepared and heated on an induction plate, the available mass of slag, 49g, was added into the beaker. The samples were collected every 1, 2 and 3h. The leaching parameters are very similar to the ones used in the first set of experiments.

*Table 3 – Parameters for the leaching of slag with sulfuric acid*  
*Таблица 3 – Параметры для выщелачивание шлаков с помощью серной кислоты*  
*Табела 3 – Параметри за лужење шљаке помоћу сумпорне киселине*

Parameter	set value
Concentration of sulfuric acid (mol/L)	1
Temperature (°C)	70
Solid -liquid ratio (g/L)	49
Time (h)	1, 2, 3
Stirring rate (rpm)	400

## Results and discussion

The chemical analysis results show that the slag became a rare earth concentrate with 6.67% of REE in comparison to original bastnasite ore which contained 1.36% REE.

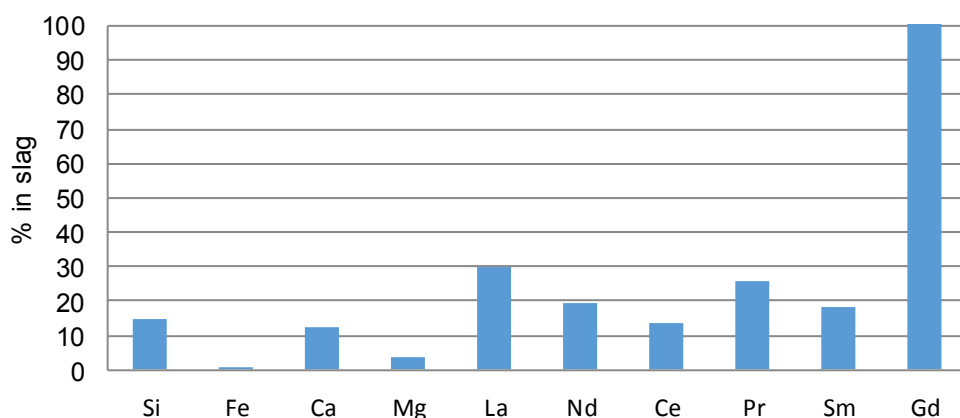


Figure 3 – Percentage of elements that have passed from bastnasite ore to slag

Рис. 3 – Доля елементов, перешедших из бастнезита в шлак

Слика 3 – Процент елемената који су прешли из бастнезитне руде у шљаку

Figure 3 shows the percentage of REEs that the slag has acquired from the bastnasite ore. Only 0.58% of iron was passed onto the slag, together with 15.02% Si, 12.53% Ca and 3.69% Mg. The proportion of lanthanide elements that were passed onto the slag was greater: 29.87% La, 13.55% Ce, 25.79% Pr and 19.56% Nd, but still not very high. All of gadolinium, a representative of heavier rare earths, went into the slag. The average of rare earth incorporation into the slag is 34.54% (La+Ce+Nd+Pr+Sm+Gd). In general, it can be said that important amounts of REEs are not incorporated into the slag and will be lost for further processing. In order to establish the content of REE, the analysis of the formed iron metal was performed. The ground slag was dissolved in 1mol sulfuric acid at 70°C, as shown in Figure 3.



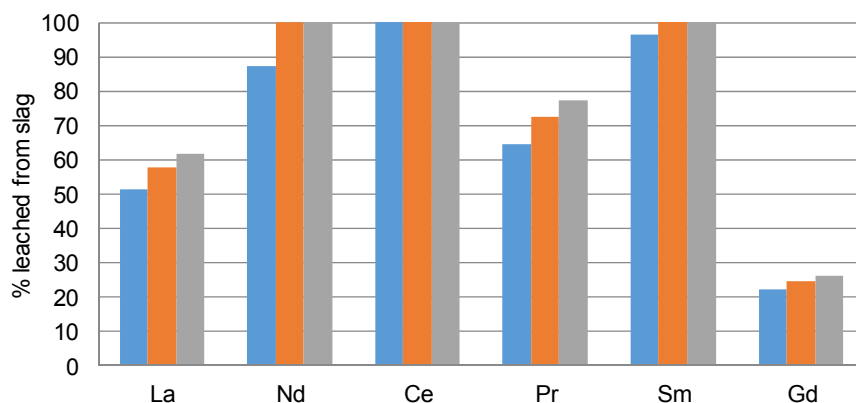


Figure 4 – Percentage of rare earth elements dissolved from slag in sulfuric acid after 1 hour (blue color), 2 hours (orange color) and 3 hours (gray color) using 1mol/L sulfuric acid

Рис. 4 – Доля элементов редкоземельных руд, выделенных из шлаков в растворе серной кислоты, по истечении одного часа (синий столбик), двух часов (оранжевый столбик) и трех часов (серый столбик), с использованием 1mol/L серной кислоты

Слика 4 – Процент елемената ретких земаља растворен из шљаке у сумпорној киселини после једног сата (плава боја), два сата (наранџаста боја) и три сата (сива боја) уз коришћење 1mol/L сумпорне киселине

The pH-values of the solution during the leaching process between 1 and 3 hours amounted to between 0.44 and 0.53. As shown in Figure 3, the proportions of REEs leached from the slag using the sulfuric acid solution after 1h, 2h and 3h are sufficient. The maximum leaching efficiencies are 100% for cerium, neodymium and samarium. The minimum leaching efficiency is about 25 % for gadolinium. The differences in the leaching efficiency for single rare earth elements can be explained via the inhomogeneity of the produced slag.

In all cases, the leaching efficiency was increased with time from 1 hour to 3 hours, as it happened in direct leaching. For instance, the recovery of cerium and neodymium is around 18% higher after 3h than after 1h. The biggest proportion of rare earths is leached out after the first hour, then the rate of extraction decreases but does not reach a steady state rate within 3h of the experiment.

Gadolinium is the least dissolved element, followed by lanthanum and praseodymium. After 1h, the percentage of Gd extracted from the slag is 22.27%, followed by 51.22% La and 64% Pr. The rest of the elements, cerium, neodymium and samarium, exhibit large dissolution ratios. 87% Nd and 96% Sm dissolve within the first hour. Cerium is

completely dissolved according to these results. The average percentage of the REEs (La+Nd+Ce+Pr+Sm+Gd) dissolved after 1h and 3h is 73.76% and 88.68%, respectively.

Finally, if we compare the leaching efficiency of the two step strategy: the smelting and slag leaching process with the direct leaching of bastnasite ore from the first set of experiments, (see Figure 5), we find that the direct leaching process is not more efficient. Direct leaching of bastnasite ore with sulfuric acid at 70°C gives the leaching efficiency between 16 of 20 % for rare earth elements (La+Ce+Nd+Sm) between 1 and 3 hours in comparison to 30 % and 60 % in the two step strategy. The best leaching efficiencies are obtained for samarium during 1hour smelting and the 3-hour leaching process. The reason for this behavior is that rare oxides are in a form more suitable for leaching. On the other hand, iron was removed during the smelting process as metallic iron. Finally, the leaching of the formed concentrate is more favorable than the leaching of bastnasite ore.

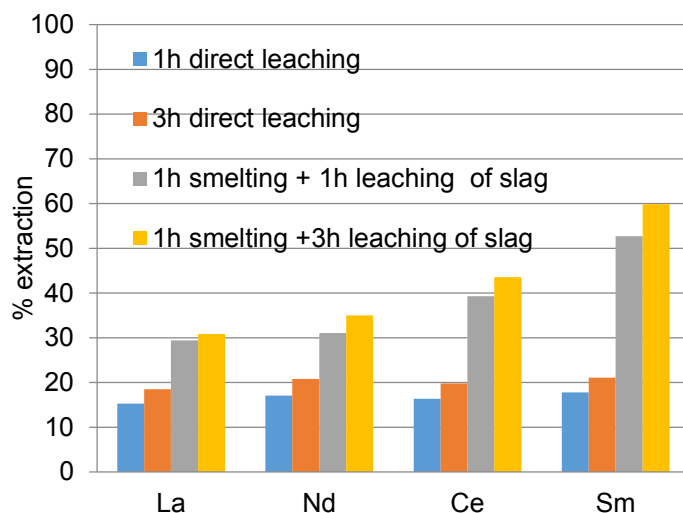


Figure 5 – Percentage of rare earth recovery by direct leaching in comparison to the two step strategy: smelting and leaching of slag

Рис. 5 – Доля восстановления редкоземельных руд, прямым выщелачиванием в

сравнении с двухэтапным методом: плавление и выщелачивание из шлага

Слика 5 – Процент опоравка ретких земаља директним лужењем у поређењу са стратегијом у два корака: топљење и лужење шљаке

The real advantage of the smelting method is the reduction of acid consumption. If we were to use the same amount of solid to liquid ratio, this means the smelting strategy would allow us to save 86% of the acid. Given the low prices of sulfuric acid, it is evident that the most favorable strategy for REE extraction is direct leaching for the bastnasite ore with a decreased content of iron. Rare earths are critical metals and, above all, a priority strategic resource, indispensable in economic well-being, industrial production and national security affairs.

## Conclusions

The followings findings:

1. Two step strategy: carbothermic reduction of bastnasite ore with a high content of iron oxide and a subsequent leaching of the formed slag with sulfuric acid has shown some advantages (high leaching efficiencies of REE in sulfuric acid and the newly formed slag as a concentrate of REE with 8 % TREO) with some disadvantages (a high percentage of thorium is present in the slag).
2. The direct leaching process will be used for bastnasite ores with a decreased content of iron oxide.
3. Removal of thorium from the solution during precipitation after leaching will be considered using sodium pyrophosphate of different pH-values in the future work.
4. The future work will be continued in order to improve a transfer of rare earth elements from bastnasite ore to slag via changing the parameters for reductive smelting.

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## ВЫЩЕЛАЧИВАНИЕ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ ИЗ ПОРОД, СОДЕРЖАЩИХ ФТОРКАРБОНАТЫ – ТРЕТЬЯ ЧАСТЬ

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РУБРИКА ГРНТИ: 61.13.21 Химические процессы

ВИД СТАТЬИ: оригинальная научная статья

ЯЗЫК СТАТЬИ: английский

### Резюме:

При исследовании процесса выщелачивания редкоземельных рудных пород, содержащих фторкарбонат, применялся метод восстановительного плавления в углеродной среде при температуре 1600° С, состоящий из двух этапов: 1) карботермическое восстановление и 2) растворение в серной кислоте при атмосферном давлении, с целью увеличения селективного извлечения редкоземельных элементов из шлака, содержащего редкоземельные элементы.

Ключевые слова: редкоземельные элементы, плавление, выщелачивание, серная кислота.

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

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ОБЛАСТ: хемијске технологије

ВРСТА ЧЛАНКА: оригинални научни рад

ЈЕЗИК ЧЛАНКА: енглески

## Сажетак:

*Растварање елемената ретких земаља из бастнезитне руде (руде која садржи флуорокарбонатни минерал) проучавано је после редуктивног топљења угљеником на 1600°C. Стратегија у два корака: 1. редукција угљеником, и 2. растварање помоћу сумпорне киселине примењено је на атмосферском притиску са циљем да се повећа екстракција елемената ретких земаља из шљаке која садржи елементе ретких земаља.*

*Кључне речи: елементи ретких земаља, топљење, лужење, киселина.*

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