

## Short communication

# Preparation of rare earth oxides from Synchysite oxidized ore by acid leaching

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### ABSTRACT

Mixed rare earth oxides have been prepared from synchysite ore from the Lugiin gol rare earth deposit (Mongolia) which contains about 6% of cerium light rare earth elements. Ore powders were leached for up to 60 min using 80-120 g/l sulfuric acids at an acid to powder ratio of 20, agitation was performed by magnetic stirring followed by precipitation and calcination at 700°C for 1h. The highest leaching of REEs equal to 85% of the total REE was observed in the acid solution of 80 g/l. Obtained mixed rare earth oxides represent a layered type structure.

**Keywords:** Synchysite, leaching, calcination, mixed rare earth oxides

### INTRODUCTION

The rare earth elements comprise 16 naturally occurring metals and are an essential component in the modern industrial development which used in metal alloys/ batteries, catalysts, luminescence, magnets/.

There are many rare earth minerals, but a few are present at economic grades. The minerals occur as carbonate (e.g. bastnaesite  $(\text{Ce, La})(\text{CO}_3)\text{F}$ , parasite  $\text{Ca}(\text{Ce, La})_2(\text{CO}_3)_3\text{F}_2$  and synchysite  $\text{Ca}(\text{Ce, La})(\text{CO}_3)_2\text{F}$ ), phosphate (e.g. monazite  $(\text{Ce, La, Nd, Th})\text{PO}_4$ , xenotime  $\text{YPO}_4$ , apatite  $\text{Ca}_5(\text{PO}_4)_3(\text{F, Cl, OH})$ ) and silicate (e.g. gadolinite  $(\text{Ce, La, Nd, Y})_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$ ) [1, 2].

The main rare earth processing steps comprised mining to obtain ore with rare earth oxides content of <1 - 10%, milling and flotation to obtain a rare earth concentrate with total RE-oxide content of 30-70% for further processing. The carbonate rare earth concentrates are mainly processed by acid leaching after roasting. Published research on rare earth ore processing covers the various aspects of processing such beneficiation technique [2, 3], processing parameters such as temperature, mixing speed, acid concentration [4-6] or heating source [7, 8]. In Mongolia, there are several known rare earth deposits, namely Lugiin gol, Mushgia khudag, Khotgor and Khalzan burgedtei. The Lugiin gol rare earth deposit consisting of the cerium carbonate minerals synchysite and parasite were studied extensively [9, 10]. Preliminary roasting of the rare earth concentrate at 700°C followed by leaching with  $\text{HNO}_3$  resulted in 97% dissolution of the

rare earths [9]. In this research we have aimed at applicability of synchysite oxidized ore by a simple acid leaching on recovery of rare earth elements from the ore.

### EXPERIMENTAL

The major chemical composition of the ore and calcined mixed rare earth elements was determined by ICP-OES (Optima 7300DV) and Perkin Elmer ICP-OES 8300 instruments. XRD patterns were obtained by X-ray diffraction, instruments (D/MAX-2500V, Rigaku and MAXima-X XRD-7000, Shimadzu).

The ore and calcined powders were coated with gold and characterized by SEM (Topcon SM-300 electron microscope operated at 20 kV) attached with the EDS (C10012 (Thermo Noran)).

For the research a beneficiated ore from the Lugiin gol deposit was obtained. The chemical composition of the ore and the rare earth elements are shown in Tables 1 and 2. The X-ray diffraction of the concentrate indicated that calcite and dolomite were the main crystalline phases present.

5 grams of the concentrate were agitation leached in 100 g/l sulfuric acid ( $\text{H}_2\text{SO}_4$ ) for up to 60 min. The leach solution was filtered and the residue washed, dried and retained. The solubilized rare earths in the leach solution were precipitated using a saturated solution of oxalic acid, filtered and dried at 105°C prior to calcination at 700°C for 1h. In order to determine effects of acid concentration on the rare earth dissolution was used same acid

Table 1. The main chemical composition of the ore, wt.%

Si	Al	Fe	Ca	Mg	K	Mn	Sr	Zn	Pb	P	Ti	Th
4.29	0.85	6.69	19.83	2.99	0.68	2.51	0.21	0.1	0.40	0.09	0.06	0.069

Table 2. The content of the rare earth elements in the ore, wt.%

La	Ce	Pr	Nd	Sm	Gd	Eu	Dy	total REE
2.06	3.05	0.24	0.74	0.07	0.030	0.014	0.010	6.21

solution with concentration of 80 g/l, 100 g/l and 120 g/l, respectively. The leaching residues also were filtered and dried at 105°C for 5 h in the further investigation.

## RESULTS AND DISCUSSION

XRD patterns of the oxidized ore indicated the presence of quartz, calcite and dolomite as the main mineralogical constituents with a minor content of synchysite (not shown). Residue of leaching consists of mostly with bassanite  $\text{Ca}_2(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  (PDF-24-1068) or gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (PDF-36-0432).

Figure 1 shows the weight change of leaching residues and weight percentage of rare earth oxides in calcined precipitates as a function of leaching time.

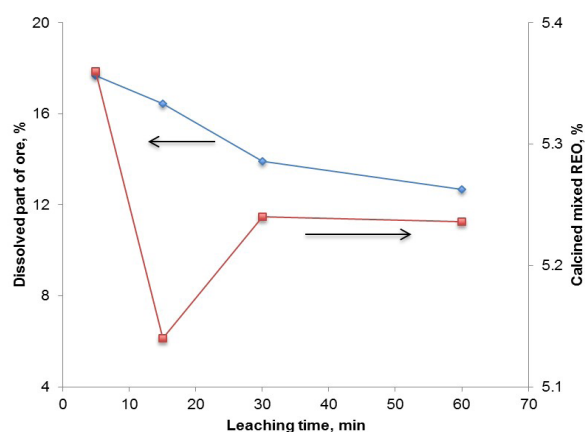
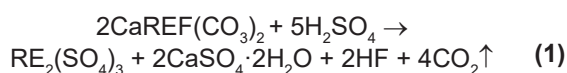


Fig. 1. Weight changes of ore and rare earth oxides content in the calcined precipitates with leaching time.

With increasing of leaching time decreases dissolution rate of the rare earth ore in results of dissolution precipitation reaction. Gypsum is soluble to a small level and requires supersaturation in order to precipitate and the rapid dissolution of the carbonates was followed by a slow precipitation of the calcium.

However, the weight change of the rare earth oxide precipitates did not change much with the leaching time. It's an indication that the synchysite can be easily dissolved in sulfuric acid for a short time. Dissolution of the synchysite can be written as:



It shows also rare earth sulfates did not precipitate with the gypsum during the leaching. SEM micrograph of the leaching residues indicated the presence of a needle like

gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) particles (not shown).

For the comparative characterization XRD patterns of the 5 and 60 min oxalate precipitates and calcined products are shown in Figure 2. Oxalates were precipitated according to following reaction:

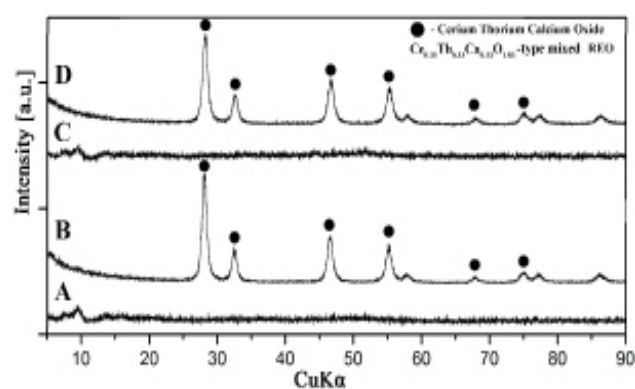
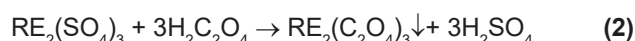


Fig. 2. XRD patterns of the precipitated and calcined samples: (A) - 5 min. magnetic stirred and precipitated, (B) - 700°C calcined sample of (A), (C) - 60 min. magnetic stirred and precipitated, (D) - 700°C calcined sample of (C)

XRD of the oxalate precipitates after 5 and 60 min showed they were amorphous, after calcination crystalline cerium thorium calcium oxide  $\text{Ce}_{0.33}\text{Th}_{0.33}\text{Ca}_{0.33}\text{O}_{1.83}$  (PDF-078-0742) was formed both samples. Recovery rate of rare earth oxides in 5 min dissolved sample was 82.4% while in the 60 min dissolved sample was 83.2%, respectively.

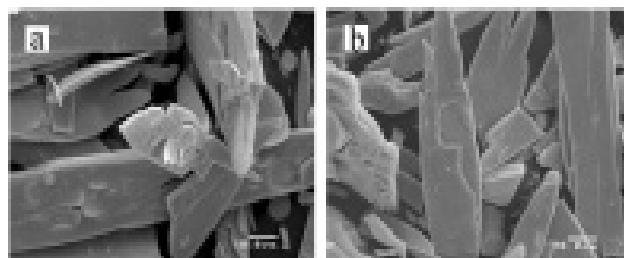


Fig. 3. SEM micrographs of the calcined samples. 5 minute magnetic stirred and calcined at 700°C (a), 60 minute magnetic stirred and calcined at 700°C (b)

SEM micrographs of the calcined rare earth oxides are shown in Figure 3. SEM micrographs indicate that regardless with the leaching procedures all samples are having a layered structure.

Figure 4 shows a change of Ce, La, Nd and Pr recovery at 60 minute of leaching with acid concentration.

Recovery of rare earth elements shows that the praseodymium recovers with higher rate which accounts over 99% of the total praseodymium in the ore. The lanthanum shows the lowest recovery among the main rare earth oxides. The highest recovery was observed for the acid concentration of 80 g/l. Total relative recovery of REEs in 80 g/l solution was 92.7%, in 100 g/l solution 82.9%, in 120 g/l solution 89.4%, respectively. The thorium content within rare earth elements was approx. 1%.

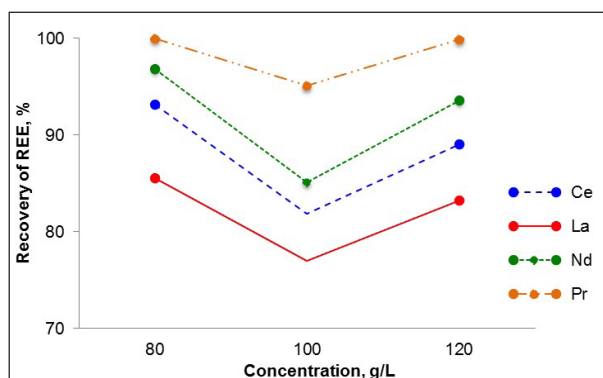


Fig. 4 Recovery of rare earth oxides

One can see that apparently lower recovery of REEs at 100 mg/L than at either 80 or 120 g/L. This is very unusual behavior and we don't have any explanation at this time. However, this behavior is subject to further study. Within the same acid concentration the content of rare earth elements not much differs each other.

All sample's ICP analyses and SEM-EDS analysis (not shown) indicated almost all light rare earth elements present in this sample. The content of the heavy rare earth elements in the mixed oxide is no more than 1%. However, the recovery rate of the heavy rare earth elements was over 95% in the 80 g/l acidic solution.

XRD patterns (Figure 2) of the calcined rare earth oxides showed that there is only a single phase present. Therefore it can be suggested that the cerium thorium calcium oxide type rare earth oxides represent the layered microstructure. The low temperature calcined oxide powders generally kept their original morphology of the precipitated oxalates [11]. Cerium oxalate with the layered structure, which mostly kept its morphology by calcination up to 1000°C, was also showed previously [12]. Therefore, it can be suggested that the mixed rare earth oxalate could show layered structure, though; we haven't observed it by an analytical technique. Mixed rare earth oxalate is very rare but not unusual compound. Presence of mixed rare earth oxalate mineral coskrenite-Ce ((Ce, Nd, La)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)·8H<sub>2</sub>O) in a soil or a rock has been described elsewhere [13].

Chemical analyses of the calcined rare earths suggest that the Ca<sub>0.33</sub>Th<sub>0.33</sub>Ce<sub>0.33</sub>O<sub>1.83</sub> is most unlikely as the Ce:Th:Ca far too high for there to be enough thorium present, it is more likely a structurally similar phase with different composition. Obviously low thorium it is an

advantage of the present result, because one of the big problems in REO processing is to reduce the radioactivity in the product to a low levels.

The crystallized part of the rare earth elements represents approximately 5.3% of the ore. This value is a bit lower than that of in the raw ore.

The raw oxidized ore contained about 6.2% of rare earth elements. It indicates about 85% of the total rare earth elements were leached out. Further optimization of the leaching procedure to increase the leached rare earth wasn't performed.

It was described that the synchysite more readily soluble in nitric acid solution [10]. However, the present research indicates that the synchysite can be dissolved in sulfuric acid solution same as bastnaesite. According to equation (1) in the synchysite ore the cerium oxide exists as Ce<sup>3+</sup>. However, in the present oxidized ore cerium should exist as the oxidized cerium (Ce<sup>4+</sup>). Such oxidized rare earth elements possibly were dissolved in the sulfuric acid more readily.

## CONCLUSIONS

Synchysite from the Lugiin gol rare earth deposit can be processed using sulfuric acid leaching. The total content of rare earths in the ore represents approximately 6.2 wt.%. Mixed rare earth elements obtained after precipitation and calcination represent rare earth oxide mixture with the same structure of Ce<sub>0.33</sub>Th<sub>0.33</sub>Ca<sub>0.33</sub>O<sub>1.83</sub>. Leaching of the synchysite ore by the 80 g/l concentrate sulfuric acid for 60 min allows dissolution of about 85 % rare earth elements from the ore.

## REFERENCES

1. Kumari A., Panda R., Jha M. K., Kumar J.R., Lee J.Y. (2015) Process development to recover rare earth metals from monazite mineral. A review, *Miner. Eng.*, **79**, 102-115.
2. Study on Rare Earths and Their Recycling, Final Report for The Greens/EFA Group in the European Parliament (accessed 20 March 2016) [http://www.resourcefever.org/publications/reports/Rare%20earths%20study\\_Oeko-Institut\\_Jan%202011.pdf](http://www.resourcefever.org/publications/reports/Rare%20earths%20study_Oeko-Institut_Jan%202011.pdf).
3. Jordens A., Cheng Y.P., Waters K.E. (2013) A review of the beneficiation of rare earth element bearing minerals. *Miner. Eng.*, **41**, 97-114.
4. Yukun H., Tingan Z., Zhihe D., Jiang L., Fangfang T. (2015) Study on leaching rare earths from bastnaesite treated by calcification transition. *Rare Earths*, **32**, 1043-1047.
5. Feng X.L., Long Z.Q., Cui D.L., Wang L.S., Huang X.W., Zhang G.C. (2013) Kinetics of rare earth leaching from roasted ore of bastnaesite with sulfuric acid. *Trans. Nonferrous Met. Soc. China*, **23**, 849-854.
6. Yorukoglu A., Obut A., Girgin I. (2003) Effect of thiourea on sulphuric acid leaching of bastnaesite. *Hydrometal.*, **68**, 195-202.
7. Jie L., Chengyuan L., Baowei L., Shaobing W., Jicheng H., Jieliang W. (2014) Acid leaching of low grade rare earth concentrate by microwave heating.

- Chinese J. Rare Met.*, **38**, 839-845.
8. Peelman S., Sun Z.H.I., Sietsma J., Yang Y. (2014) Leaching of rare earth elements: past and present. *1<sup>st</sup> European Rare Earth Resources Conference ERES2014*, Milos, Greece, 446-456.
  9. Burmaa G., Temuujin J., Welham N.J. (2007) Effect of pretreatment on synchysite-Ce ( $\text{CaCe}(\text{CO}_3)_2\text{F}$ ) leaching. *Miner. Eng.*, **20**, 807-809.
  10. Temuujin J., Burmaa G., Jadambaa Ts., Munkhtsetseg B., Mackenzie K.J.D. (2008) *Processing of synchysite, a potential source of rare earth elements in rare earths: Research and Applications*, Ed: Delfrey K.N., New York, Nova Science Publishers, 391-406.
  11. Xiu Z., Li J.G., Li X., Huo D., Sun X., Ikegami T., Ishigaki T. (2008) Nanocrystalline Scandia powders via oxalate precipitation: The effect of solvent and solution pH. *J. Am. Ceram. Soc.*, **91**, 603-606.
  12. Almeida L.De, Grandjean S., Vigier N., Patisson F. (2012) New insights on the thermal decomposition of lanthanide(III) and actinide(III) oxalates: from neodymium and cerium to plutonium. *Eur. J. Inorg. Chem.*, **31**, 4986-4999.
  13. Peakor D.R., Rouse R.C., Essene E.J. (1999) Coskrenite-(Ce),  $(\text{Ce,Nd,La})_2(\text{SO}_4)_2(\text{C}_2\text{O}_4)\cdot 8\text{H}_2\text{O}$  a new rare-earth oxalate mineral from alum cave bluff, Tennessee: characterization and crystal structure. *Canad. Mineral.*, **37**, 1453-1462.