Rare Met. (2013) 32(6):632–635
DOI 10.1007/s12598-013-0068-3

RARE METALS
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Modified calcination conditions of rare alkali metal Rb-containing muscovite ($KAl_2[AlSi_3O_{10}](OH)_2$)

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Received: 17 October 2012 / Revised: 27 November 2012 / Accepted: 5 December 2012 / Published online: 17 October 2013

Abstract Muscovite mineral was roasted in different conditions. Rubidium leaching rate was a standard to examine the impact of various factors on calcination effect, including the agent types, roasting time, mass ratio, and roasting temperature. The results indicate that the best agent is the combination of sodium chloride and calcium chloride, and its mass ratio of muscovite/NaCl/$CaCl_2$ is 1.00:0.25:0.25. Calcined at 850 °C for 30 min, the rubidium leaching rate is up to 90.12 %. The reaction of muscovite ore with the chlorinating agent $CaCl_2$ was studied by TG/DSC, and the surface morphology before and after leaching was characterized by SEM. Rubidium chloride products can be obtained using t-BAMBP extraction, hydrochloric acid re-extraction, and purification.

Keywords Modified calcination; Muscovite ore; Chlorinating agent

1 Introduction

Rubidium is one of rare alkali metals, which was found in 1981 by Germans R.W. Bunsen and G. R. Kirchhof. Rubidium includes the following features: atomic number 37, atom weight 85, the body-centered cubic lattice, each unit cell having two metal atoms, and density 1.532 $g\cdot cm^{-3}$. The properties of low melting point (312.46 K) and malleability make rubidium have a strong chemical activity and photoemission. Rubidium provides a main material for manufacturing phototube with a wide range of light waves, which possess high sensitivity and stability. Efforts are being made to carry out research on rubidium ion engine, magnetic flux generators, and thermoelectric transducer. Rubidium exists in muscovite ore ($KAl_2[AlSi_3O_{10}](OH)_2$ (monoclinic system and hexagonal layered structure) as an isomorphism and replaces the large radius of the potassium atoms as well as part of rubidium located between structure layers. The complex components bring great difficulty in comprehensive recycling.

Ion exchange, precipitation, and extraction are the three main methods in the rubidium resource recovery from muscovite ore [1, 2]. Inorganic ion exchange agent and organic resin are two main materials used in ion exchange methods. The development of inorganic ion agent is limited for its high solubility in the water. While, the resin has a poor anti-interference ability, so its application in practical production and analysis of basic sample is also limited [3]. Its main disadvantage of precipitation method is high reagent consumption. It must be through several precipitation and separation cycles to get high-purity substances. Rubidium can be easily separated from mother liquor by solvent extraction technology [4]. Thorat and Tripathi [5] found a new technique of decomposing beryl ore at low temperature with ammonium hydrofluoride. The recovery of rubidium and potassium alums from lithium-bearing minerals was studied and it was found that rubidium could be efficiently isolated from the mother liquor after Li_2CO_3 crystallization and conversion to sulfate solution [6–9]. The extraction of Rb from lepidolite was studied, in which a optimum process conditions were found [10–13]. During rubidium production process, modified calcination is the

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Table 1 Chemical composition of muscovite

Composition	SiO_2	Al_2O_3	K_2O	N_2O	MgO	TiO_2	CaO	MnO	Fe_2O_3	Rb_2O	Li_2O	Cs_2O
Content/%	49.84	24.00	9.97	0.62	0.23	0.15	0.60	0.28	0.09	0.83	0.024	0.028

key process. Its aim is to maximize rubidium leaching rate and determine the mutual correlations among the various factors [14, 15].

Therefore, it is important to develop an efficient method for extracting rubidium from its ore and it has been a thrust area of research and development [16].

2 Experimental

2.1 Chemical analysis of muscovite

Chemical compositions are listed in Table 1. Gangue minerals are mainly quartz and sialic acid salt mineral. The content of calcium and magnesium matrix is relatively less. The elements that can be developed and utilized are mainly rubidium, titanium, and potassium.

2.2 Procedures and analysis instruments

The muscovite in this study is a concentrate product of flotation, and the particle size is less than 0.3 mm. X-ray diffraction analysis shows that the raw material is primarily muscovite and quartz. All samples are heated in a muffle furnace at temperatures ranging from 550 to 950 °C for 0.5 h. The mass ratios of muscovite/NaCl/$CaCl_2$ were 1.00:0.25:0.10, 1.00:0.25:0.15, 1.00:0.25:0.25, 1.00:0.25:0.35, and 1.00:0.25:0.45, respectively. After heating sequence, the residue was leached with water at room temperature for 1 h, and then the undissolved residue was filtered out. The content of rubidium in the leaching liquor was analyzed by atomic absorption spectrometry (AAS; Rayleigh, China). The intermediates and final phases of the products were identified using X-ray diffraction spectrometer. Before and after leaching, the surface morphology of residue is characterized by scanning electron microscope (SEM; JSM6460LV, Japan).

3 Results and discussion

3.1 Effect of calcination time

The effect of calcination time on the extraction of Rb is shown in Fig. 1. The extraction rate increases as the reactions proceed. When calcination time is more than 30 min, the leaching rate changes very little and the sintering situation is worse. Part of Rb was not be leached. Therefore, the time should be controlled in 30 min.

3.2 Effect of calcination temperature

Calcium chloride and sodium chloride were used as solid chlorination agents in the study, the former was also as a sintering agent. The two kinds of salt react with the water vapor in the air in high-temperature conditions. Rb_2O is converted into water-soluble RbCl by hydrogen chloride generated in reaction process, and then sodium ions displaced rubidium existing in the form of isomorphous. The roasting reactions are seen in Eqs. (1)–(4). The $CaCl_2$ is also thought to aid the composition of the muscovite by formation of the stable mineral $CaSiO_3$.

$$CaCl_2 + SiO_2 + \frac{1}{2}O_2 = CaSiO_3 + Cl_2 \quad (1)$$

$$CaCl_2 + SiO_2 + H_2O = CaSiO_3 + 2HCl \quad (2)$$

$$CaCl_2 + SO_2 + O_2 = CaSO_4 + Cl_2 \quad (3)$$

$$2HCl + Rb_2O = 2RbCl + H_2O \quad (4)$$

The effect was investigated when roasting temperature on rubidium extraction ranged from 550 to 950 °C. The result is shown in Fig. 2. Clearly, the calcination temperature of 850 °C is an optimum temperature. The reactions are slower in the low-temperature phase. Two kinds of salt did not yet reach the molten state, and the leaching rate increases significantly when the temperature changes from 750 to 850 °C. The rubidium is fully

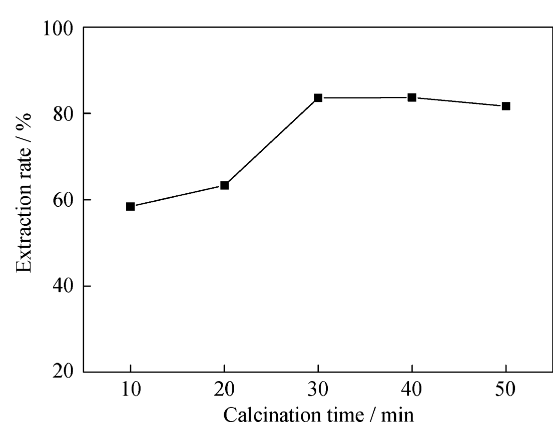


Fig. 1 Effect of calcination time on extraction of Rb (ore/$CaCl_2$/NaCl = 1.00:0.25:0.25; temperature = 850 °C)

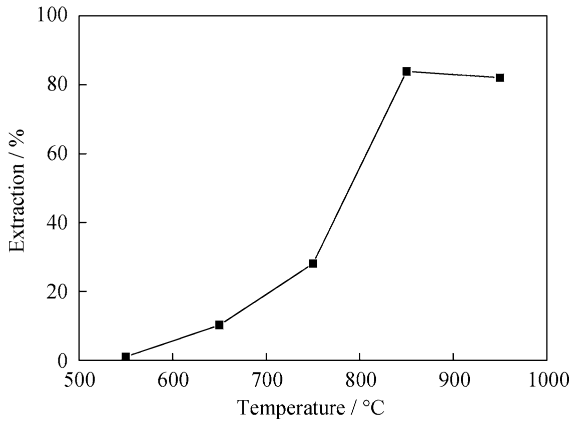


Fig. 2 Effect of temperature on extraction of rubidium (ore/$CaCl_2$/NaCl = 1.00:0.25:0.25, 0.5 h)

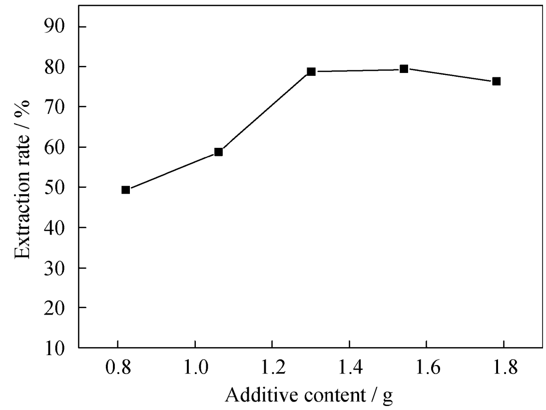


Fig. 4 Effect of calcination time on extraction of Rb (muscovite/$CaCl_2$/NaCl = 1.00:0.25:0.25; temperature = 850 °C)

chlorinated. NaCl/$CaCl_2$ is not completely dissolved and existed in the form of clusters at 750 °C, and the surface of particles become uniform at 850 °C, which can be seen from Fig. 3. It can be deduced that the wrapped muscovite reacts with the molten salt completely. The final products of the reactions are $CaSiO_3$, $NaAlSi_3O_8$, and SiO_2.

The melting points of the two kinds of salt will reduce due to molten salt effect, and the differential scanning calorimetry (DSC) of the single muscovite sample shows one exothermal peak at 800 °C (Fig. 4). Chlorination of muscovite ore takes place at high rate, and the reaction is completed substantially at 850 °C. At 900 °C, RbCl is wrapped by calcium silicate generated due to high temperature, and there is no need to increase the temperature. This is confirmed by the TG curve (Fig. 5), which shows that the change of weight is not obvious.

3.3 Effect of $CaCl_2$/NaCl addition

The effect of mass ratio of muscovite to the salts was researched by calcining at 850 °C for 0.5 h. Five different ratios were selected. The result is shown in Fig. 4. Rb extraction ratio increases with the increase of $CaCl_2$, but it has no obvious change after getting to 90.12 %, and it is not necessary to increase the amount of $CaCl_2$. The presence of large amounts of calcium will bring difficulty to subsequent decalcification step. The rubidium has two main trends to be converted into RbCl in the calcination process: the first one is calcium salt chlorination calcination and the second one is sodium ion substitution. XRD result indicates that the main calcination products are $CaSiO_3$ and $NaAlSi_3O_8$. The mass ratio of muscovite and NaCl (1.00:0.25) suggests that the molar ratio of Na:(K, Rb, Cs) is approximately 2:1. According to ion replacement mechanism, there are sufficient sodium ions present to exchange with the alkali metal ions in the muscovite.

3.4 Extraction of leaching solution

The contents of lithium, rubidium, and cesium in experimental muscovite ore are 0.048, 0.260, and 0.013 %, respectively. The concentration of rubidium in leaching solution is 0.534 $g \cdot L^{-1}$. First, a series of process including decalcification, purification, and concentration are carried out for the leaching solution, and then the solution is subjected to solvent extraction using t-BAMBP as extractant.

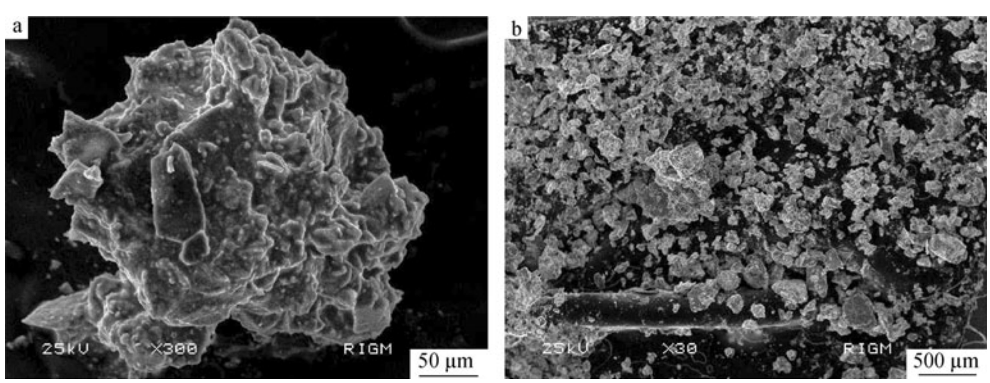


Fig. 3 Calcined minerals images: **a** 750 °C and **b** 850 °C

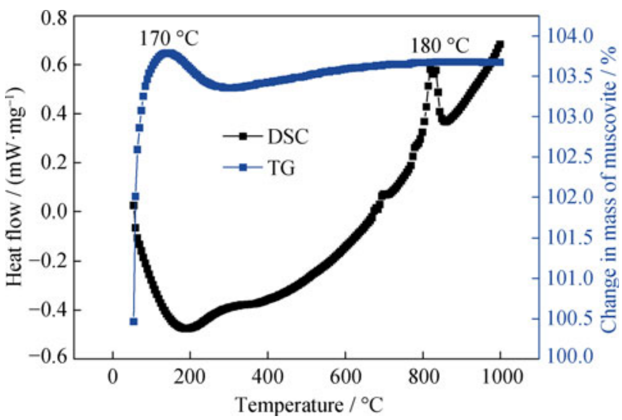
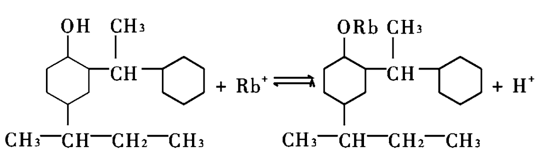


Fig. 5 TG-DSC curves of single muscovite ore

The Rb extraction reaction is seen in Eq. (5). $[H^+]$ is replaced by Rb^+. Removing $[H^+]$ in the solution is necessary to make the reaction proceed smoothly, so the solution pH value is adjusted by NaOH. When the concentration gets to 2 $mol \cdot L^{-1}$, the t-BAMBP has a high viscosity and its fluidity gets bad. The literature [16] shows that low temperature is conducive to extraction rate. Taking into account all the factors above, orthogonal test of 3-factors and 4-levels including the extractant (t-BAMBP) concentration, pH value, and the ratio of the aqueous phase and the organic phase is arranged. The optimum extraction conditions are as follows: the extractant concentration 1 $mol \cdot L^{-1}$, pH 14, and phase ratio (O/A = 1:1), and the extraction rate can get to 93 %. RbCl products with a purity of 92 % can be obtained using hydrochloric acid re-extraction and purification.



(5)

4 Conclusion

NaCl and $CaCl_2$ are found to be a potential chlorination agent for the processing of muscovite ore. The above studies showed that the method of chlorination calcination using two kinds of salt to extract rubidium from muscovite is feasible. The various factors in the calcination process were studied systematically. A valuable and promising technological scheme for preparing high-purity RbCl from muscovite was proposed. The optimum conditions are as follows: the mass ratio of muscovite/NaCl/$CaCl_2$ = 1.00:0.25:0.25; calcination temperature = 850 °C; calcination time = 30 min.

In the extraction section, the extractant (t-BAMBP) concentration is 1 $mol \cdot L^{-1}$, the organic phase/aqueous phase = 1:1, the pH of multistage extraction is 14. In the conditions above, the extraction rate could get to 93 %. Eventually, the rubidium chloride products with a purity of 92 % can be obtained. The studies provide a theoretical basis for the comprehensive utilization of muscovite, which contains rubidium resource.

Acknowledgments This study was financially supported by the Chinese Nonferrous Guilin Research Institute of Geology for Mineral Resource (No. ky20101372000001).

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