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Two Methods on Rubidium Extraction from Boron Clays

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Abstract: Two methods were emerged as a result of the extraction studies of the boron clay wastes (CW) in Emet/Kütahya region in Turkey and they were presented as a flow sheet. The first one was direct acid leaching process with H_2SO_4 and the other was roasting operation then acid leaching with HF. 43.8% of rubidium extraction was achieved the direct H_2SO_4 leaching and the rubidium extraction can reach 87.43% under the same mass ratio of CW/$CaSO_4$/$CaCO_3$ at 950°C for an hour then acid leaching with 1 M HF for two hours at room temperature. The two methods were compared and discussed in all their aspects. Although the results are quite different from each other, it has been shown that the sulfuric acid leaching method can also be used as an alternative.

Key words: Boron clay wastes, Extraction, Roasting, Leaching, Rubidium

1. Introduction

Turkey has about 73% of the world's boron reserves. The Emet-Espey plant is one of the largest boron deposited area in Turkey [1]. Colemanite, is a calcium borate mineral (theoretically, 50.8% B_2O_3) with monoclinic crystal structure and a chemical composition of $Ca_2B_6O_{11}.5H_2O$, is concentrated to produce boric acid in sulfuric acid solutions in this plant. During this mining operation large volumes of colemanite wastes are discharged and this situation causes a serious environmental problem. The wastes contain boron oxide in quite high concentrations. So many researchers tried to recover boron from tailings and the others used the wastes as an additive material in some sectors such as cement [2, 3], concrete [3, 4], brick [5-8], tile [9, 10] and ceramic [11, 12]. It was also used as an adsorbent material for removal the synthetic textile dyes [13, 14]. On the other hand, boron clay wastes contain some valuable metals. Lithium was determined in boron clay wastes first, and extracted using natural limestone and gypsum that the waste material of boric acid production. $LiCO_3$

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was obtained by precipitated at the end of the study [15]. Using the tailings in different sectors after separating these metals can reduce economic losses [16].

Rubidium is an alkali metal that has some special properties like softness, malleability, low melting point and ionization energy, high dielectric constant, strong chemical and photo emissive activity. Rubidium and its compounds are used in biomedical and academic research, quantum computing devices, electronics, specialty glass and pyrotechnics [17]. Due to many of applications, demand of rubidium has been growing since 1990 and its price has increased in the world [18, 19]. Rubidium is more abundant element in the Earth but there is no mineral that is the main component of rubidium; it is produced in small quantities of natural brines and as a byproduct of cesium, lithium, and strontium mining. Rubidium and cesium are used together or interchangeably in many applications because of their same specifications. Rubidium is found in lithium minerals such as lepidolite and zinnwaldite [20, 21]. There are some studies about extraction of rubidium from natural resources (natural brines, minerals and mine tailings). Inorganic ion-exchange sorbents were used for the extraction of metals found in low concentrations in brines. Encapsulated an organic polymer, polyacrylonitrile (PAN) with potassium copper hexacyanoferrate and substituted phenol, 4-butyl-2(α-methylbenzyl) phenol (BAMBP) was used as a selective sorbent for lithium and rubidium extraction from natural brines [22, 23]. Lıu et al. (2015) extracted ions (like Mg^{+2}, K^{+} and Na^{+}) that coexist with target metals using washing and precipitation for the efficient rubidium and cesium extraction from salt lake brine with t-BAMBP−kerosene solution [24]. Chemical roasting at high temperature then water or acid leaching processes were used to extraction of rubidium from minerals and tailings. Yan et al. (2012b) extracted rubidium (93.6 %) from lepidolite, the lithium mineral, using roasting process with $Na_2SO_4/CaCl_2$ at 880°C for 0.5 h and water leaching [25]. Vu et al. (2013) achieved 91 % of rubidium extraction from zinnwaldite, lithium–rich mica mineral [26], using $CaCO_3$ as a roasting agent at 825°C for 1 h then water leaching at 95°C for 1 h [27]. Shan et al. (2013) achieved (90.1%) rubidium extraction from roasted muscovite $[KAl_2(AlSi_3O_{10})(OH)_2]$ mineral with the mass ratio of muscovite/NaCl/$CaCl_2$ of 1.00/0.25/0.25 at 850°C for 30 min and then water leaching at room temperature for an hour [28]. Zheng et al obtained 96.95 % of rubidium extraction from distinctive kaolin ore using $CaCl_2$ as a roasting agent at 800°C for 0.5 h and water leaching at 60°C for 3 h [29]. Zhou et al. (2015) obtained rubidium from kaolin clay wastes using two methods. They were direct acid leaching with fluorination agent and chlorination roasting using $CaCl_2$ then water leaching [30]. CaF_2 was used as a fluorination agent and rubidium extraction was increased with increasing CaF_2 content. At the end of the process HF gas was generated and it is harmful. So chlorination roasting then water leaching method was preferred. Three-step process (acid washing, followed by salt roasting and water leaching) was used to extracted rubidium from gold wastes by Tavakoli Mohammadi et al. (2015) Acid washing with 5 M nitric acid was used to remove the impurities and Na_2SO_4 and $CaCl_2$ were used as roasting agents [31].

In this study two methods were used to extraction of rubidium from boron clay wastes. The first one is direct acid leaching using H_2SO_4 and the second one is roasting with $CaCO_3$ and $CaSO_4$ at 950°C for an hour then acid leaching with 1 M HF for two hours. At the end of this study, the separation of the extracted rubidium was described in another article [16].

2. Materials and Methods

Preparation and characterization of the sample

The boron clay waste used in this study was obtained from Emet/Kütahya region. The sample was dried at 110°C for 2 hours, ground in a ball mill and screened to 63 µm sieve. Atomic absorption spectrometry (Varian AA240FS) and X-ray fluorescence (XRF) spectrometer (Rigaku ZSX Primus) were used for the determination of chemical composition of the boron clay waste. Table 1 shows that the result of chemical analysis of CW. Crystal phases in the boron clay were determined with XRD (Rikagu Miniflex). According to the XRD result of the sample, the main phases are colemanite ($Ca_2B_6O_{11}.5H_2O$), muscovite ($KAl_2[(OH,F)AlSi_3O_{10}]$), quartz ($SiO_2$) and phlogopite ($KMg_3AlSiO_{10}(F,OH)_2$). The reagents used in this study are all analytically grade.

Table 1

Chemical compositions of CW (mass fraction %)						
SiO_2	Al_2O_3	MgO	Fe_2O_3	K_2O	B_2O_3	CaO
55.2	16.2	8.93	7.77	6.05	3.060	2.33
TiO_2	**SrO**	**As_2O_3**	**Cs_2O**	**P_2O_5**	**MnO**	**Rb_2O**
0.821	0.317	0.259	0.256	0.233	0.195	0.159

Leaching operation

1 g boron clay was put into a teflon beaker then 100 mL of 0.1 M acid was added slowly in a shaker with a mixing speed of 200 rpm at room temperature for 2 hours. After the leaching operation, liquid and solid phase were separated by filtration. Rubidium content of the liquid phase was analyzed using ICP-OES (Perkin Elmer 4300DV)

Roasting operation

The boron clay, gypsum ($CaSO_4$) and limestone ($CaCO_3$) were mixed and put into the crucible that can resist high temperature at the same mass ratio. The mixture was roasted set temperature in electrical furnace for an hour. After cooling it was applied leaching.

Table 2

Effect of kind of solvent on rubidium extraction from boron CW.					
Solvent	Pure water	HCl	HNO_3	H_2SO_4	HF
%Rb Extraction	1.46	5.48	4.88	25.56	29.78

3. Results and Discussion

Table 2 shows % rubidium extraction in boron clay with leaching in different solvents without roasting process. In literature roasting of minerals or clays with limestone, gypsum, alkali salts or sulphates was used to reduce of melting point, increase the fluidity and convert the metals into the lattice of alumina or silicate to soluble form before leaching operation [32-35]. Gypsum and limestone were used as roasting agent in the study of lithium extraction in boron clays. Gypsum is used to convert lithium that assumed to be in the clay as a silicate form to lithium sulphate and CaO that form by heating limestone of over 800°C (3) react with SiO_2 to prevent the formation of silicate form, because second reaction is reversible [15]. So we roasted the boron clay with gypsum and limestone to convert water soluble form of rubidium (Rb_2SO_4 solubility is 42.4 g/100 g water, in 10°C) [36], because it is an alkali metal such as lithium.

$$CaSO_4.2H_2O + SiO_2 \rightarrow CaSiO_3+SO_2+½O_2 + 2H_2O \quad (1)$$

$$Rb_2Si_2O_5+SO_2+½O_2 \leftrightarrow Rb_2SO_4+2SiO_2 \quad (2)$$

$$CaCO_3 \rightarrow CaO+CO_2 \quad (3)$$

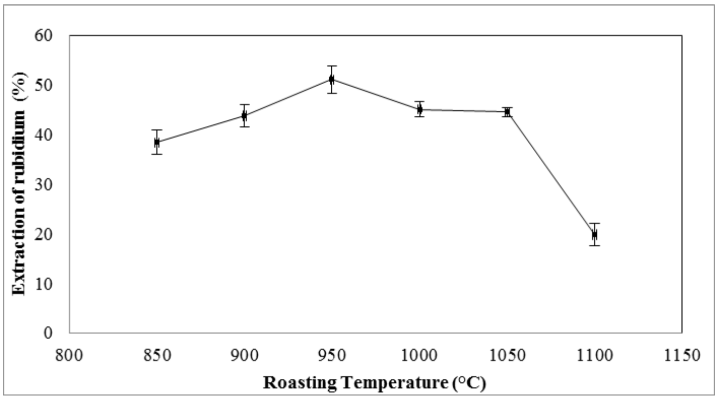

Fig. 1. Effect of roasting temperature on rubidium extraction

Fig. 1 presents % rubidium extraction at increase of temperature from 850°C to 1100°C. Duo to the realization of the 3rd reaction and the nature of clays, this temperature range was selected to the study. The parameter of roasting time was not studied because roasting time depends on the roasting temperature strictly [26]. So it is adjustable that the higher temperature for the shorter time or the lower temperature for the longer time. The optimal roasting conditions were determined as 950°C for an hour.

Leaching process was continued separately with two acids (HF and H_2SO_4) according to the best results in the Table 2.

Experiments with HF

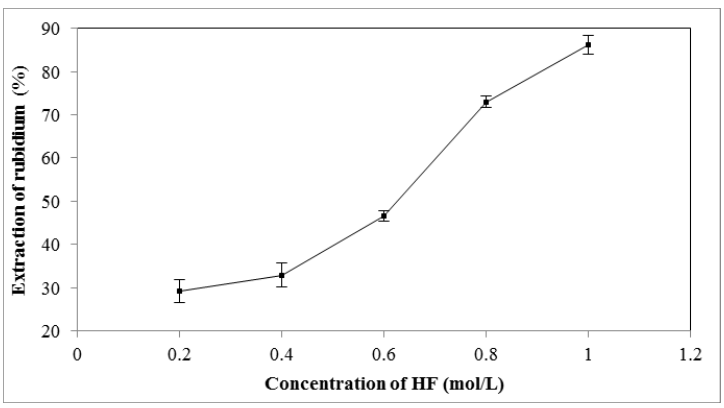

Fig. 2. Effect of HF concentration on rubidium extraction

As seen the Fig. 2, if concentration of acid was increased, % rubidium extraction was increased, too. Rubidium extraction in hydrofluoric acid is generally high due to its ability to solvation of silicate compounds.

The effect of solid/liquid ratio on the leaching operation is shown Fig. 3. Solid/liquid ratios were ranging between 0.001 to 0.04 and the optimal ratio was determined at 0.02.

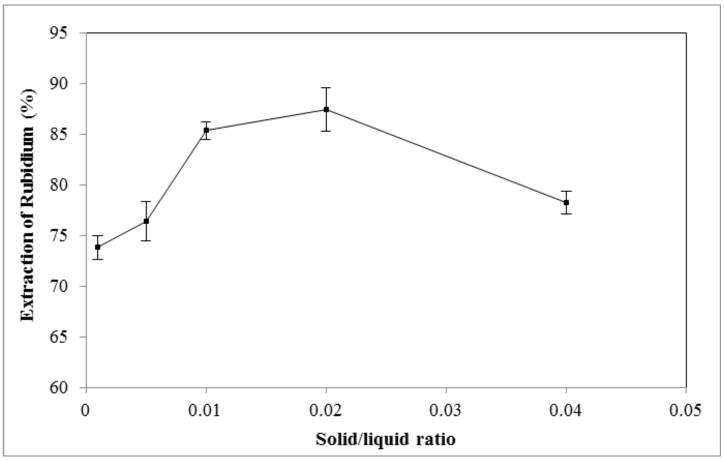

Fig. 3. Effect of solid/liquid ratio on rubidium extraction

Experiments with H_2SO_4

14.29% of rubidium extraction was obtained when using boron clay that roasted under the optimal conditions. However, rubidium extraction was 25.85% using unroasted boron clay. This is because the roasting material "gypsum" and sulfuric acid increased the sulphate rate in media and reduced the solvation of rubidium. Therefore unroasted boron clay was used in the experiments with H_2SO_4.

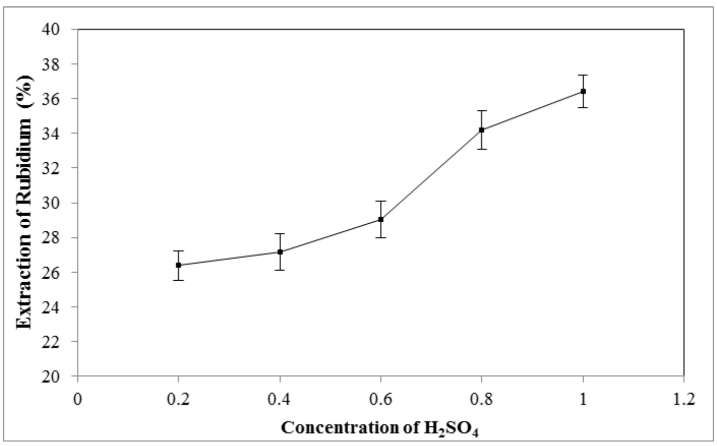

Fig. 4. Effect of H_2SO_4 concentration on rubidium extraction

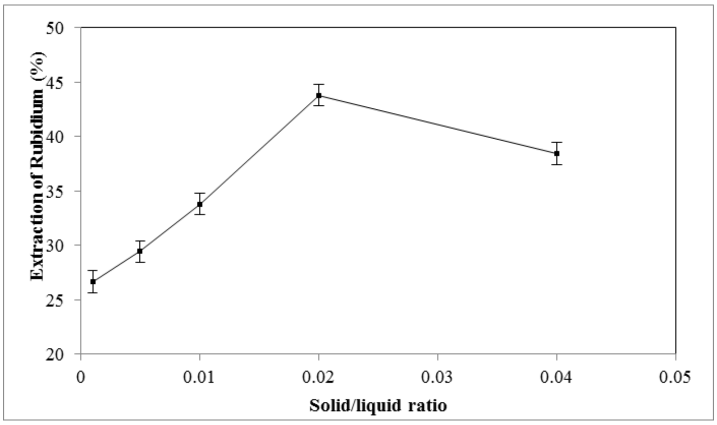

Fig. 5. Effect of solid/liquid ratio on rubidium extraction

In Fig. 4 % rubidium extraction increased with increasing acid concentration. When 1M H_2SO_4 was used, 36.42% of rubidium extraction was realized. According to the Fig. 5 the highest value of % rubidium extraction was 43.8 in S/L ratio of 0.02 and the lowest value of % rubidium extraction was 26.63 in S/L ratio of 0.001. While increasing the liquid amount means S/L rate was decreased, solubility of the other sulphate compounds were increased. The amount of sulfate that the water can solve was reached the saturation degree.

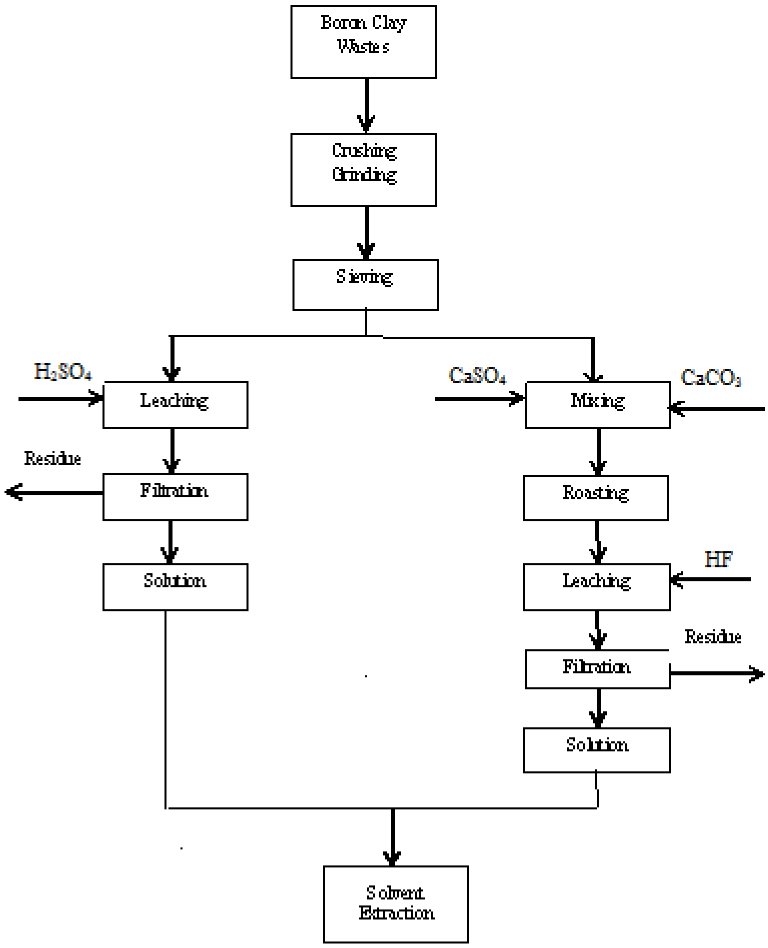

Fig. 6. The flow sheet of this study

4. Conclusion

The rare element "rubidium" in boron clay wastes was aimed to extract with two methods and a flow sheet of this study was formed. In the direct acid leaching method and the roasting then hydrofluoric acid leaching method, rubidium was extracted 43.8%, 87.43% respectively. It is not need to compare these results that extremely different. Because hydrofluoric acid has capable of dissolution of silicate that the main component of minerals and clays. But it is corrosive to glass materials. So we had to use plastic materials in experiments. On the other hand hydrofluoric acid is damage for human and environment. When all this is taken into account, the sulfuric acid leaching method can be used as an alternative. The absence of rubidium's own mineral and existence of rubidium together with the other metals into the lattice structure of mineral or clay make it difficult to extracted rubidium from natural sources. So it is necessary to obtain rubidium from different sources and investigate efficient, low cost and environmental friendly methods. The boron clay waste used in this study contained 1292 mg/kg rubidium. We thought that this obtained value was enough to try about gaining rubidium from boron clays. We advised that valuable elements in boron clays should be extracted. Then, the tailings can be used in many sectors as an additive material.

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