Determination of Optimum Extraction Conditions for Lithium, Rubidium, and Cesium From Boron Industrial Waste and Analysis by FAAS

Ferda Özmal^{a,*}, Yunus Erdogan^b, and Melike Kale^a

^a Dumlupınar University, Science and Art Faculty, Biochemistry Department, 43100 Kütahya, Turkey

^b Dumlupınar University, Science and Art Faculty, Chemistry Department, 43100 Kütahya, Turkey

INTRODUCTION

Turkey has the largest boron reserves in the world with approximately 50% in the Emet-Hisarçık region. The ore is called colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). The Emet Boron Process Management Company has one concentrator in Hisarçık and another in Emet, including two boron factories in Emet, each with a production capacity of 120,000 tonnes of H_3BO_3 per year. While the colemanite ore is being enriched in concentrators, nearly half of it becomes waste, such as hand-sorting waste, -25 mm solid waste, and -3 mm dam waste (1). The analysis of macro elements in these wastes and the boron minerals is performed routinely, but few studies have reported the determination of micro elements. Some studies have reported that a significant amount of lithium (Li), rubidium (Rb), and cesium (Cs) is in these wastes (2-4).

According to our research, industrial boron waste contains at least 300-600 mg/kg lithium (3). Lithium and its compounds have become of strategic importance for today and tomorrow. It is used for the production of light alloy in the manufacture of aircrafts, for the development of environmentally friendly cars, according to the ${}^6\text{Li} + n \rightarrow {}^3\text{H} + {}^4\text{He}$ reaction for nuclear fusion, is the alternative energy fuel of the future, and for rechargeable batteries of mobile devices (5, 3). The selling price of lithium carbonate is listed as \$6.4/kg (6).

*Corresponding author.
E-mail: ferda.ozmal@dpu.edu.tr,
gpmelike@hotmail.com
Tel: +90 274 2652051 / 3705

ABSTRACT

In this study, boron waste (-25 mm solid waste) obtained during the enrichment process of colemanite mineral at Emet-Espey was analyzed and Li, Rb, and Cs determined by atomic absorption spectrometry. Although these valuable metals have extremely important and strategic use, they are not found in Turkey. Since they are present at fairly high amounts in boron waste, an efficient and economical extraction method has been investigated. In order to increase the extraction yield of these metals by water leaching process, boron waste was roasted with chlorinating agents (NaCl and CaCl_2). The parameters used to determine the optimum extraction conditions were roasting temperature, weight ratio of the chlorinating agents to boron waste, roasting time, leaching temperature, leaching time and solid-to-liquid (S/L) ratio. The maximum extraction values achieved for Li, Rb, and Cs were 75.01%, 84.15%, and 89.90%, respectively, with a mass ratio of boron waste/ $\text{NaCl}/\text{CaCl}_2$ of 1:0.6:0.4 at 700 °C for 120 minutes, at the leaching temperature and time of 60 °C and 45 minutes, and a S/L ratio of 0.4. This method can also be applied to minerals, clays, and other types of inorganic wastes containing Li, Rb, and Cs.

Rubidium is mainly used for specialty glasses in fiber optic telecommunication systems, for night vision devices, in photoelectric cells, and in photomultiplier tubes owing to its photoemissive properties. Rubidium use in medical sciences is also of great importance. Rubidium salts are used in epilepsy

treatment and rubidium-82 in positron emission tomographic imaging as a blood-flow tracer (7). Rubidium has no minerals of its own and is found in pegmatites. A number of studies have been published on the extraction of rubidium from minerals or different kinds of wastes with the methods such as direct acid leaching, salt roasting and water leaching. (8-13). According to reports from the U.S. Geological Survey, the price of 1 g and 100 g of 99.75%-grade metallic rubidium is \$80.30 and \$1,472.00, respectively (14).

Non-radioactive cesium is mostly used for petroleum exploration and as a high-density component in drilling mud for lubrication of drill bits and for maintaining pressure on the oil-bearing strata. Other uses are for television image devices, night-vision equipment, solar photovoltaic cells, photoelectric cells, and for the super-accurate atomic cesium clock. It is also used in the chemical process industry, for medical treatments, specialty glasses, and in fiber optics (15). In 2015, one company offered 1 g ampoules of 99.98% (metal basis) cesium for \$73.40 (16).

Cesium and rubidium have similar physical properties and atomic radii which enables their interchangeable use in many applications. Because cesium is more electropositive than rubidium, it is especially used in areas such as photosensitive materials (16). Thus, recovering these metals from boron wastes is of great economical value.

The aim of this study was to determine these metals in boron wastes by using a chlorination process (17). Boron waste samples

TABLE I
WDXRF Results for
-25 mm Solid Waste

Components	%(W)	Detection Limit (%)
Na ₂ O	0.219	0.0072
MgO	6.770	0.0074
Al ₂ O ₃	10.90	0.0068
SiO ₂	37.40	0.0092
P ₂ O ₅	0.205	0.0010
SO ₃	0.243	0.0012
Cl	0.014	0.0017
F	0.661	0.0530
K ₂ O	3.770	0.0022
CaO	6.390	0.0023
TiO ₂	0.528	0.0058
Cr ₂ O ₃	0.0213	0.0027
MnO	0.106	0.0181
Fe ₂ O ₃	4.750	0.0027
NiO	0.0188	0.0013
ZnO	0.0186	0.0010
GeO ₂	0.0035	0.0011
As ₂ O ₃	0.334	0.0052
SrO	0.618	0.0007
BaO	0.0632	0.0126
PbO	0.0076	0.0019
Y ₂ O ₃	0.0190	0.0007
CuO	0.0060	0.0011
*B ₂ O ₃	18.60	-
Ignition loss	8.030	-

*B₂O₃ analysis was performed at Emet Boric Acid Plant by volumetric method.

TABLE II
Li, Rb, and Cs Composition
in -25 mm Solid Waste by AAS

Components	(mg/kg)
Li	547±8
Rb	679±5
Cs	1416±27

*The results are the average of 3 repetitions.

were roasted with chlorinating agents (NaCl, CaCl₂) and leached with water. The amount of extracted Li, Rb, and Cs was determined by AAS from the aqueous solution. This study will be a preliminary work for researchers interested in the recovery of valuable metals from minerals, clays, or wastes.

EXPERIMENTAL

Samples and Characterization

Boron waste, obtained during the enrichment process of colemanite as -25 mm solid waste, was analyzed. The sample was first dried in an oven at 110 °C for 12 hours, then crushed and ground in a ring mill and sieved to sizes lower than 63 µm. The chemical analysis was performed using a Model ZSX Primus wavelength dispersive X-ray fluorescence instrument (WDXRF) (Rigaku, U.S.) and a Model ContrAA 300 atomic absorption spectrometer (AAS) (Analytikjena, Germany).

The analysis results are listed in Tables I and II. The crystalline phases of the waste were determined by X-ray diffraction (XRD)

analysis (PAN Analytical Empyrean, Holland) at a speed of 2°/min and 0.01° steps by using CuKα radiation between 2 and 70° (see Figure 1). The main minerals are colemanite (2CaO·3B₂O₃·5H₂O), muscovite (KAl₃Si₃O₁₀(OH)₂), quartz (SiO₂), and dolomite (CaMg(CO₃)₂). Li, Rb, and Cs concentrations of leach liquors were measured by AAS.

WDXRF analysis was carried out at the Emet Boric Acid Plant, and the AAS and XRD analyses at Dumlupinar University, Advanced Technologies in Design, Research and Development and Application Center, Turkey.

Roasting and Leaching Process

In this study, the chlorination roasting-water leaching process was used. To extract Li, Rb, and Cs from boron waste, the optimum roasting temperature (500, 600, 700, 800, 900 °C) was determined in an electrically heated furnace. The waste sample (5 g) was roasted at the chosen temperature (700 °C) with NaCl and CaCl₂ (determined by preliminary experiments) at different ratios (the ratios of chlorinating agents to boron waste were

Fig. 1. XRD patterns of -25 mm solid waste.

0.2, 0.4, 0.6, 0.8, 1.0), then the optimum ratios of the two chlorinating agents (NaCl:0.6, CaCl₂:0.4) were mixed into the waste and roasted together. The roasted mixtures (boron waste and chlorinating agents) were leached with 25 mL deionized water for one hour, then filtered with glass funnel filters with a pore size of 10–16 µm, and metal analysis was performed from the leach liquors of the mixtures. Roasting time (15–180 minutes) of the waste sample with the mixture of chlorinating agents at the optimum ratios and at the chosen temperature was another studied parameter. Because the roasting process is heat-dependent, the period of this process is quite important in order to avoid economical loss. Then the roasted mixtures were leached ranging from 15 to 75 minutes at 30 °C, 60 °C, and 90 °C, respectively. The S/L ratio

was changed from 0.1 to 1.0 in order to see the effect of this parameter on the extraction process.

RESULTS AND DISCUSSION

Effect of Roasting Temperature

The effect of roasting temperature from 500 to 900 °C on metal extraction was investigated (see Figure 2). For the three metals, the extraction efficiency increases to its maximum value at 700 °C and then decreases. The reason can be ascribed to the sample losing its plasticity property above this temperature. Therefore, further experiments were carried out at 700 °C.

Effect of Mass Ratio of Chlorinating Agents to Waste Sample

In order to increase the extraction efficiency of Li, Rb, and Cs, a series of chlorination roasting experiments were conducted at

different mass ratios of NaCl or CaCl₂ to boron waste at 700 °C for 2 hours. The results in Figures 3 and 4, are discussed below.

As seen in Figures 3 and 4, the mass ratio of 0.6 and 0.4 is most favorable for NaCl and CaCl₂, respectively. At the 0.6 mass ratio of NaCl, the maximum extraction yields were 16.61%, 7.39%, and 11.80% for Li, Rb, and Cs, at the same order and at the 0.4 mass ratio of CaCl₂ the efficiencies increase to 23.09%, 37.98%, and 46.57%, respectively. In comparison it can be seen that CaCl₂ is more effective with the higher extraction efficiencies.

The reactions that occur during the extraction process were as follows (R=Li, Rb, Cs) (8):

Eq. 1

Eq. 2

Eq. 3

The SiO₂ and Al₂O₃ content in boron waste was 37.4% and 10.9%, respectively, and the molar ratio of SiO₂ to Al₂O₃ in the waste was 5.8. This ratio indicates that CaCl₂ is more effective for decomposing boron waste.

Fig. 2. Effect of roasting temperature on metal extraction (roasting time : 2 hours).

Fig. 3. Effect of mass ratio of NaCl to waste sample (roasting temperature : 700 °C, roasting time: 2 hours).

Fig. 4. Effect of mass ratio of CaCl₂ to waste sample (roasting temperature : 700 °C, roasting time: 2 hours)

When sodium chloride and calcium chloride are used together in the roasting process, the extraction yield of the three metals is higher than with the chlorinating agents alone. This condition is as a result of a lower melting point when the chlorinating agents are used. This situation increases the fluidity of the chloride melt while decreasing the viscosity of the liquid phase. In this case, the chloride mixture covers the surface of the boron waste and results in easy extraction of Li, Rb, and Cs (8).

The mixture (waste: NaCl:CaCl₂) was prepared by maintaining the

mass ratio at 1:0.6:0.4 and roasted at 700 °C for 2 hours. Then the mixture was leached with deionized water for 1 hour at room temperature. The obtained results for Li, Rb, and Cs were 72.5%, 70.64%, 73.69%, respectively. It shows that the extraction yield of Li, Rb, and Cs is much higher when NaCl and CaCl₂ are used together in the roasting process.

Figure 5 shows the XRD patterns of the roasted waste sample with and without chlorinating agents at 700 °C. It can be seen that Na(Si₃Al)O₈, KCl, CaAl₂Si₂O₈ and NaCl are the products of chlorina-

tion roasting. These products verify Eq. 1 and 3. When the waste sample was roasted alone, the Li, Rb, and Cs extraction efficiencies were 16.99%, 4.66%, and 3.65%, respectively. After addition of chlorination agents and roasting, extraction yields reached up to 72.5%, 70.64%, 73.69%.

Effect of Roasting Time With Chlorination Process

The mixtures prepared with the determined ratios roasted at 700 °C for 15-180 minutes. Figure 6 shows that the maximum extraction efficiency is obtained at 120 minutes. Therefore, further experiments were carried out for 120 minutes.

Effect of Leaching Time and Temperature

The sample mixture roasted at 700 °C for 120 minutes at the mass ratio of m(boron waste) : m(NaCl): m(CaCl₂) = 1:0.6 : 0.4 was then subjected to water leaching. During the leaching tests, the solid-to-liquid ratio held steady at the ratio of 1:2.5 and the tests were carried out at different temperatures (30, 60, 90 °C). The effect of leaching time and temperature on Li, Rb, and Cs extraction were investigated and are shown in Figures 7, 8, and 9 for each metal.

Figure 7 shows that the leaching time of 45 minutes at 90 °C for

Fig. 5. XRD patterns of roasted waste sample with and without chlorinating agents. (Roasting temperature: 700 °C, roasting time: 2 hours, mixture ratio (m(waste sample):m(NaCl):m(CaCl₂)) = 1:0.6:0.4).

Fig. 6. Effect of chlorination roasting time on metal extraction (roasting temperature: 700 °C, m(waste sample): m(NaCl):m(CaCl₂) = 1:0.6:0.4).

Fig. 7. Effect of leaching time and temperature on lithium extraction.

lithium extraction is the most suitable condition. But Figures 8 and 9 show that the most reasonable temperature for Rb and Cs extraction is 60 °C and 45 minutes to reach equilibrium. In addition, extraction of the three metals was studied together from the same sample with the same method and showed that 60 °C for 45 minutes is the most economical condition.

Effect of Solid-to-Liquid Ratio

The solid-to-liquid (S/L) ratio was changed from 0.1 to 1.0. The mass ratio of boron waste to NaCl to CaCl₂ was kept constant at 1:0.6:0.4. The chlorination roasting temperature of 700 °C and chlorination roasting time of 120 minutes were the stable conditions and 45 minutes leaching time at 60 °C was also the steady situation for the leaching process. Figure 10 shows

the effect of the S/L ratio on the extraction of Li, Rb, and Cs.

Figure 10 shows that the extraction yield seems to be stable up to the ratio of 0.4 for the three metals. After this point, the extraction efficiencies decrease slightly. At the ratio of 0.4, the Li, Rb, and Cs extraction efficiencies were 75.01%, 84.15%, and 89.90% respectively. Thus, this ratio is considered to be most favorable and economical.

CONCLUSION

In this study, a chlorination roasting-water leaching process was used to optimize the extraction conditions of Li, Rb, and Cs from industrial boron waste. The conditions used were as follows: Chlorinating roasting temperature 700 °C, mass ratio of boron waste to NaCl to CaCl₂ 1:0.6:0.4, chlorinating

roasting time of 120 minutes, leaching temperature and time 60 °C and 45 minutes, solid-to-liquid ratio of 0.4. The extraction efficiencies of Li, Rb, and Cs reached peak values of 75.01%, 84.15%, and 89.90%, respectively. Thus this study shows that future researchers can use this method to recover these valuable metals from the leach liquors of waste samples and is also a precursor for recovery studies.

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Fig. 8. Effect of leaching time and temperature on rubidium extraction.

Fig. 9. Effect of leaching time and temperature on cesium extraction.

Fig. 10. Effect of solid-to-liquid ratio in leaching process.

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