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Research Article

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Characterization of coal gangue for recovery of lithium as a fusion fuel

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HIGHLIGHTS

- Two samples of coal gangue labeled B_1 and B_2 were characterized through XRD, XRF and ICP analysis.
- The XRD analysis results indicated that the primary minerals of B_1 and B_2 were montmorillonite and quartz.
- The ash percentage of B_1 and B_2 samples were 33.31 and 50.94% at 700 °C, respectively.
- The lithium content of B_1 and B_2 ash samples were 279 and 214 ppm, respectively.

ABSTRACT

Lithium is the lightest alkali metal with unique chemical properties, such as high electrochemical activity, high reduction potential, and high specific heat capacity. This element has a wide range of applications in various industries, including the nuclear industry. For instance, lithium-6 is a source of tritium for nuclear fusion fuel by absorbing neutrons. Therefore, the separation of lithium from relevant sources is highly important. Since the separation of lithium from these resources is not possible without knowledge of its inventory, in this report, the characterization of the coal gangue is done using XRF and ICP-OES analysis for geochemical studies and measurement of major and minor oxides, as well as XRD analysis for determining the crystalline phases present in the samples. Due to the ICP-OES analysis, the amount of Li in B_1 and B_2 samples are 279 and 214 ppm, respectively, which makes the B_1 sample a suitable source for the extraction of this element. Moreover,as XRD analysis shows, both samples have similar structural minerals, with montmorillonite and quartz being the primary minerals.

KEYWORDS
Lithium
Coal gangue
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ICP-OES analysis
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1 Introduction

The need for specific materials with unique features and cutting-edge technologies in the current industry makes it clear that geological resources must be carefully evaluated while taking future technologies into account. Lithium is one of these elements that is used in cutting-edge technologies such as medical, pharmaceuticals, electronics, battery production, ceramics, glass, aerospace alloys, and nuclear industries. Lithium has two stable isotopes, Li-6 and Li-7, which have abundances of 7.5% and 92.5%, respectively. The thermal neutron absorption cross-sections of lithium isotopes Li-6 and Li-7 are 940 and 0.037 barns, respectively. Li-6 is used to produce tritium as a fuel for fusion reactors. Since Li-7 has a lower thermal neutron absorption cross-section, is employed as an additive in PWR (Pressurized Water Reactor) primary coolant, at about 2.2 ppm, for maintaining water chemistry, counteracting the corrosive effects of boric acid (used as neutron absorber) and minimizing corrosion in steam generators of PWRs (Giegerich et al., 2016; Zhang et al., 2018).

Lithium is primarily found in three different sources: lithium-containing minerals such as spodumene and lepidolite, aqueous sources like brines and seawater, and ultimately in coal gangue. Lithium-bearing minerals can serve as a suitable extraction source for lithium, but increasing extraction of these resources leads to resource depletion. Seawater and brines account for over 60% of total lithium resources. Currently, lithium-rich resources are located in countries such as Chile, Bolivia, China, and the United States. The process of extracting lithium from aqueous solutions is relatively easier and less costly operationally than minerals. Today, the development of efficient technologies for extracting lithium from aqueous solutions is underway (Shao and Jin, 2020; Zhao et al., 2020).

Another resource for lithium extraction is coal gangue

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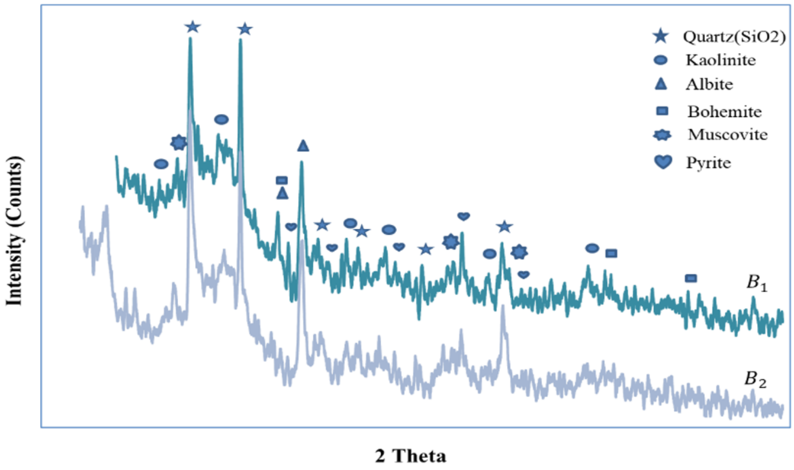

Figure 1: XRD analysis of two coal samples B_1 and B_2 before ash.

and its by-products. For example, in coal basins such as Kirensk and Verkhne-Bikin in Russia, the inventory of lithium oxide ranges from 0.22 to 0.65%. Lithium predominantly exists in coal as aluminosilicate compounds and clay minerals. Currently, coal gangue is one of the most significant environmental challenges that can contaminate soil and water resources. If coal can be utilized as a source of rare metals such as lithium, many of these environmental problems can be mitigated. Additionally, it has been discovered that many coal fields are secondary resources for rare elements (Zhang et al., 2020).

This article evaluates the lithium resource of coal gangue in a national mine to select an appropriate method for the separation and purification of lithium among the interfering elements. It should be noted that there are a few papers and researches in the field of Li extraction from the coal in the world. Its the first time that the extraction of lithium from the secondary resources such as coal gangue is investigated in Iran. Identification of coal gangue was conducted through XRD, XRF and ICP analyses.

2 Experimental

Two representative samples were collected from different sections of the national coal mine. Characterization of the samples was performed before and after ashing. The most important analyses included XRF (OXFORD ED200, UK) and ICP-OES (Optima 7300 DV, USA) for geochemical studies and measurement of the main and secondary oxides in coal gangue samples, as well as XRD analysis (Philips PW 1800, USA) for determining the crystalline phases present in the samples. These analyses were carried out at the central laboratory of the Nuclear Science and Technology Research Institute.

3 Results and Discussion

The XRD results of coal samples B_1 and B_2 before ashing are presented in Fig. 1. The results show that the main mineral phases in the raw materials include quartz (SiO_2, Ref. code : 083-0539), clay (kaolinite) ($Al_2Si_2O_5(OH)_4$), muscovite ($KAl_2[(OHF)_2\text{-}AlSi_32O_{10}]$, Ref. Code: 007-0025), pyrite (FeS_2, Ref. Code: 071-0053), albite ($NiALSi_3O_8$), and boehmite (AlOOH). Coal gangue mainly consists of kaolinite and quartz, along with small amounts of albite, boehmite, and other compounds. The kaolinite and quartz content in coal gangue is nearly 80%. In other words, the predominant mineral in coal samples is kaolinite. As seen in this figure, the most prominent peaks correspond to quartz and kaolinite. Additionally, identical peaks indicate that the compositions of samples B_1 and B_2 are the same. This conclusion aligns with reported studies (Chen et al., 2022; Xie et al., 2023; Hu et al., 2018).

In the next stage, both coal samples B_1 and B_2 were ashed at temperatures of 700 °C and 1000 °C for four hours in a furnace (according to standard D 3174 - 11). The obtained results are presented in Table 1 (ASTM, 2004).

Table 1: The ash percentage of B_1 and B_2 samples at different temperatures.

Sample	Ash content (%)	Temperature (°C)
B_1	33.31	700
B_2	50.94	700
B_1	31.08	1000
B_2	46.99	1000

After ashing the samples, XRD and XRF analyses were conducted on the samples. As shown in Fig. 2, the ashed coal samples B_1 and B_2 at a temperature of 700 °C exhibit a 2θ peak corresponding to the mineral montmorillonite with the chemical formula $[(Na,Ca)0.33(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O]$. Montmorillonite is a group of minerals that include illite, kaolinite, and halloysite. With the increase in temperature, the crystal structure of this mineral is destroyed, leading to its absence in the coal samples B_1 and B_2 ashed at 1000 °C. Peaks at 2θ equal to 40, 26, 50, and 55 correspond to the mineral quartz seen in both coal samples B_1

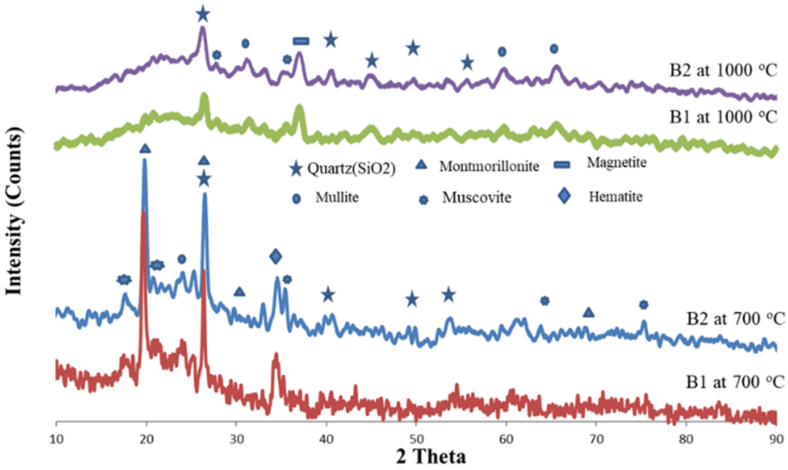

Figure 2: XRD analysis of two coal samples B_1 and B_2 after ash.

and B_2 at both temperatures. Peaks at 2θ equal to 35 and 17 in coal samples B_1 and B_2 ashed at 700 °C correspond to the mineral mullite with the chemical formula $3Al_2O_3.2SiO_2$. Additionally, at 1000 °C, peaks at 2θ equal to 60, 33, and 65 correspond to mullite (Xu et al., 2021). Furthermore, peaks appearing at 2θ 34 in coal samples B_1 and B_2 ashed at 700 °C are attributed to the mineral hematite with the chemical formula Fe_2O_3. With the temperature increase, the intensity of these peaks decreases, and hematite transforms into magnetite, leading to new peaks at 2θ equal to 87.36. Muscovite, with the chemical formula $KAl_2(AlSi_3O_{10})(FeOH)_2$, a group of minerals, appears at 2θ equal to 27, 18, 36, 65, and 77 in the samples.

XRF analysis was also performed elementally on the ashes of samples B_1 and B_2, and the results are reported in weight percent in Table 2. The results indicate that the amount of lithium in coal sample B_1 is higher than in coal sample B_2. Additionally, the concentrations of other elements such as aluminum, calcium, iron, and magnesium are greater in coal sample B_1 compared to coal sample B_2. Therefore, despite the identical mineral structures of the two coal samples, there is a difference in lithium concentration between the two samples.

Table 2: XRF analysis of ashed coal samples B_1 and B_2.

Component wt%	B_1 samples at 700 °C	B_2 samples at 700 °C
Al_2O_3	13.21	15
SiO_2	59.4	66.09
K_2O	4.44	5.01
CaO	1.25	0.76
Fe_2O_3	10.28	7.1

Table 3: Results of ICP analysis for B_1 ash sample.

Element	Content in ash (ppm)
Li	279
Al	131800
Ca	15763
Fe	51193
Mg	9788

Table 4: Results of ICP analysis for B_2 ash sample.

Element	Content in ash (ppm)
Li	214
Al	12042
Ca	9690
Fe	12278
Mg	7980

In the next stage, a digestion test was conducted on the coal samples to determine the lithium content following the standard method (Standard D 6357 - 2011) (ASTM, 2000). The results of the lithium analysis are reported in Tables 3 and 4.

According to the results, it can be seen that despite the same structure of the minerals in the samples B_1 and B_2, the amount of lithium and related elements in B_1 sample is far more than B_2 sample, which is due to taking samples from different parts of the coal gangue.

4 Conclusions

Two representative samples labeled B_1 and B_2 were obtained from various sections of the coal gangue, and characterization tests were conducted on them. The XRD analysis results indicate that both samples have similar structural minerals, with montmorillonite and quartz being the primary minerals. Montmorillonite is a group of minerals that include illite, kaolinite, and halloysite. Despite the structural similarity, the chemical compositions of these samples were different. According to the results, sample B_1 had the highest lithium content of 279 ppm, likely due to sampling from different sections of the coal gangue. Additionally, sample B_2 has the highest ash content, reaching approximately 51% by weight, with a lithium content of around 214 ppm. This makes lithium extraction from this sample challenging due to increased energy consumption, time, and costs associated with higher raw material consumption.

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Conflict of Interest

The authors declare no potential conflict of interest regarding the publication of this work.

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