EXPERIMENTAL AND STATISTICAL STUDY OF LEACHING OF NIOBIUM PENTOXIDE FROM PAKISTANI ORE

Article Highlights

• Review of various processes for extraction of niobium from its ores
• Selection of a sustainable and energy efficient process for extraction of niobium products
• Experimental investigation of leaching of niobium pentoxide from a pyrochlore ore
• Determination and statistical analysis of significant process parameters
• Normal vs. residual plot demonstrates the noise factor and outliers in the experimental data

Abstract

The growing demand for niobium pentoxide, based on its use in separation processes, established its prominent significance as a leading candidate in the field of separation science and technology. This study reports the extraction of niobium pentoxide from pyrochlore ore occurring in Sillai Patai, KPK, Pakistan. It is difficult to recover niobium pentoxide from Pakistani ore due to its low concentration. Niobium pentoxide is an important material used in manufacturing industries for different purposes. Most of the commercially employed extraction processes are associated with serious environmental impacts and are not efficient in extracting niobium pentoxide from low concentration pyrochlore. Alkali potash has been used for separation and purification of niobium pentoxide because it is efficient and an environmentally friendly process. The leaching of niobium pentoxide is carried out in a batch reactor using alkali potash as a leachant. Various process parameters, including ore particle size, reaction temperature, reaction time and alkali to ore mass ratio, were examined statistically during the leaching process. It was observed that reaction temperature and ore particle size were more significant compared to other parameters. The maximum percent recovery of niobium pentoxide (95%) was obtained at 280 °C in 90 min, while keeping the ore particle size 44 μm and alkali to ore mass ratio of 7:1.

Keywords: pyrochlore ore; process selection; statistical studies; process optimization.

Nobium is a transition metal that has a metallic grey color in its natural solid state and belongs to the fifth group of the periodic table. Niobium is mostly commercially available in the form of niobium pentoxide. Niobium pentoxide is widely used in metallurgical and nuclear industries. It is also employed in stainless steel to enhance its strength at elevated temperatures. Niobium pentoxide is typically used in various components of automobiles, capacitors, lithium niobate and optical glasses [1]. Niobium pentoxide alloys are used in aerospace applications due to their low density and good workability. The superconductivity of niobium-tin and niobium-titanium alloys is very high [2]. Niobium pentoxide is also used in the form of super alloys in gas turbines, turbocharger systems, combustion equipment and rocket subassemblies [3]. In Pakistan, niobium was discovered in the form of a pyrochlore mineral in a small...
village of Arondu. Arondu is located along the upper Basha valley [4]. Kazmi and Abbas [5] reported the occurrence of niobium in the form of different minerals in Pakistan. The expanding market and numerous applications of niobium attracted academic researchers from various industries to develop new processes for the recovery of niobium from indigenous ores and concentrates. Recently, the extraction of niobium pentoxide from pyrochlore has drawn great attention due to their promising properties such as strength, conductivity, and unreactivity. Complicated factors such as low-grade, complex mineral composition, and fine-grained dissemination are the major challenges encountered in niobium pentoxide extraction processes.

Worldwide, several mining companies have established various processes to extract niobium and its product from the ore. The objective of these methods was to fulfill the growing demand of the niobium products for their potential applications and financial encouragement of industries. It is quite strange that niobium is usually associated with tantalum and thus various methods are reported for the separation of these metals. However, the lack of appropriate methods for niobium extraction from pyrochlore in existing literature and the nature of low-grade Pakistani ore took us closer to the process selection [6-9].

Toromanoff and Habash [10] have worked on niobium oxide production from pyrochlore concentrates by using 10 M HCl at 200 °C in a pressure reactor for 4 h. Yang et al. demonstrated over 98% leaching of niobium with sulphuric acid under pressure using oxygen [11]. These processes mainly used highly toxic acids (HCl as well as H2SO4), which are dangerous to human health, processing vessels and ecosystems. Over the past years, the conventional hydrometallurgical processes have been extensively used for the extraction and purification of niobium and tantalum. Niobium and tantalum were extracted from ferro-columbite by using hydrofluoric acid pressure leaching process [12]. Processing of niobium ores was mostly carried out by employing hydrofluoric acid (HF) [13]. The alkaline solution with pressure dissolutions has been proposed as a promising process for leaching of niobium [14,15], and the use of a combination of H2SO4 and HF was also developed [16]. In order to produce the niobium products, the Marigniac process was totally replaced by solvent extraction processes [17,18]. Bhattacharyya and Ganguly in their review article discussed the extraction of niobium and tantalum from niobium-tantalum ore by various reagents [19]. A more recent review was presented by Zhu and Cheng, focusing on methyl isobutyl ketone (MIBK), and other extractants for extraction of niobium and tantalum [20]. Most of the above methods use acid or a hazardous solvent for extraction. These methods and solvents are dangerous, non-sustainable, hazardous for human health, less energy efficient and difficult to handle during the process.

Recently, the alkaline processes have received attention for niobium and tantalum recovery from ore, because of high solubility of these metals in KOH and NaOH. These processes were proved to have lower environmental impacts compared to processes involving fluoride [21,22]. Zhou and Zheng proposed the leaching of niobium in a molten alkali hydroxide solution [23]. Eramet et al. purified niobium and tantalum concentrates by using concentrated NaOH, followed by water leaching [24]. The product was recovered and separated from impurities such as iron, tantalum and magnesium. Deblonde et al. extracted niobium and tantalum from low-grade industrial concentrate by using NaOH (aq) at atmospheric pressure [25].

This work mainly focuses on the alkali potash process. The feasible process selection for niobium pentoxide extraction from low-grade Pakistani ore can provide clues for further developments. The effect and percent contribution of process parameters on niobium pentoxide extraction can provide a novel trend for future applications. The aim of this study is to evaluate the extraction of niobium pentoxide from Pakistani ore by using the selected process and the experimental results are statistically analyzed and interpreted with that objective in mind. Moreover, the optimal operational conditions are investigated for the recovery of niobium pentoxide from pyrochlore ore.

**EXPERIMENTAL**

**Material**

Potassium hydroxide of analytical grade, deionized water and concentrated sulphuric acid (98%)
were purchased from Haq Chemicals. The pyrochlore ore samples were collected from Sillai Patai, located in KPK, Pakistan. The solid phase was dried at 100 °C, crushed and grinded. The niobium concentration in the ore was increased before the experiments by a magnetic separator as denoted by concentrate, and its elemental compositions were as follows (in mass%): Nb 10.34, C 8.11, O 38.87, Mg 0.97, P 1.25, Ca 27.80 and Fe 12.63. The elemental compositions were determined through EDX (energy dispersive X-ray) analysis. An analytical sieve shaker was used to obtain the various size fractions (125-500, 63-125 and 38-63 μm) of the concentrate (Table 1).

<table>
<thead>
<tr>
<th>Element</th>
<th>38-63 μm</th>
<th>63-125 μm</th>
<th>125-500 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.81</td>
<td>7.98</td>
<td>8.54</td>
</tr>
<tr>
<td>O</td>
<td>39.13</td>
<td>37.87</td>
<td>39.61</td>
</tr>
<tr>
<td>Mg</td>
<td>0.91</td>
<td>0.89</td>
<td>1.13</td>
</tr>
<tr>
<td>P</td>
<td>0.72</td>
<td>1.24</td>
<td>1.79</td>
</tr>
<tr>
<td>Ca</td>
<td>28.17</td>
<td>28.15</td>
<td>27.10</td>
</tr>
<tr>
<td>Fe</td>
<td>13.10</td>
<td>12.97</td>
<td>11.84</td>
</tr>
<tr>
<td>Nb</td>
<td>10.15</td>
<td>10.89</td>
<td>9.98</td>
</tr>
</tbody>
</table>

**Experimental setup**

The reaction was performed in a batch reactor as shown in Figure 1a. The experimental setup consisted of a hot plate with a magnetic stirrer, glass reactor, silicon oil bath, and reflux condenser. During the reaction, the temperature was controlled manually by adjusting the heating rate of the hot plate and cross-checked with the temperature inside the reactor. It was observed that the heating rate remained constant throughout the reaction, as silicon oil acts as a uniform heating medium. The reaction temperature was maintained within ±10 °C of the desired temperature. The muffle furnace was used for drying of the residue, and a heated water bath was used for filtrate evaporation.

**Experimental procedure**

Initially, the ore samples were dried, crushed and grinded up to the desired size. Niobium is a paramagnetic material, so its concentration in the ore was increased by processing the crushed ore in a magnetic separator. The resultant concentrate was screened into various fractions. Typically, about 8 g of concentrate was treated with different amounts of KOH solution (84%) at various temperatures in a batch reactor with a controlled heating system, a mechanical stirrer and a reflux condenser. The reaction was carried out for a specific period of time, after which the reacting mixture was cooled. Deionized water was added to wash the residue and to obtain the desired product in soluble form. The obtained solution was filtered in order to get the leached solution. The resultant solution then underwent evaporation to increase the concentration of the desired solid components in the leached solution. Finally, the solid crystals were formed by crystallization from the leached solution. The product, niobium pentoxide, was obtained after a phase transformation process during which a sulphuric acid solution (10%) was added. The whole process flow sheet is shown in Figure 1b.

To conduct statistical analysis, four process parameters were selected: reaction temperature,
reaction time, ore particle size, and alkali to ore mass ratio. Two levels were chosen for each factor, as shown in Table 2.

Table 2. Natural and codified values for each factor (process parameter)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Natural values</th>
<th>Codified values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>140 – 280</td>
<td>-1 – +1</td>
</tr>
<tr>
<td>Time, min</td>
<td>30 – 90</td>
<td>-1 – +1</td>
</tr>
<tr>
<td>KOH:ore mass ratio</td>
<td>3:1 – 7:1</td>
<td>-1 – +1</td>
</tr>
<tr>
<td>Particle size, µm</td>
<td>44 – 230</td>
<td>-1 – +1</td>
</tr>
</tbody>
</table>

The fractional factorial \((2^k - 1)\) was chosen as the experimental design for statistical analysis. This test required only \((2^{k} - 1) = 2^3 - 8\) eight experimental runs. Additional three central runs were performed at the same conditions to investigate the effect of replication on product recovery. Hence, the total number of experiments for the design matrix was eleven, as shown in Table 3. The percent leaching of niobium pentoxide obtained during the experiments is considered to be the response of process parameters and the results are shown in Table 3. The process parameters were statistically analyzed using Design Expert 8.0.6 trial version.

RESULTS AND DISCUSSION

Analysis of experiments

The extraction of niobium pentoxide is affected by the concentration of the KOH solution. The recovery of niobium pentoxide was increased with the increase in concentration of the KOH solution. The increase in solution concentration above 84 wt.% decreased the extraction [23]. Therefore, 84 wt.% of KOH solution was used for each experimental run. The leaching of niobium pentoxide was also affected by the agitation speed. In the case of fine solids, the leaching rate can be increased by agitation in order to decrease the solid and liquid film resistance during the leaching process [26]. Furthermore, niobium pentoxide recovery was increased when increasing the stirring speed. It was observed that the leaching rate was almost independent of the agitation rate when the stirring speed was higher than 1100 rpm [23]. The stirring speed during the reaction was therefore kept constant at 1300 rpm throughout the experiments. Moreover, when the reaction temperature was increased, the rate of the reaction also increased. This causes the formation of soluble \(K_8[(Ta,Nb)_6O_{19} \cdot nH_2O]\) during the reaction [27-29]. In addition, the particle size also had a significant effect on niobium pentoxide extraction. When the ore particle size was decreased, the surface area of the ore was increased. This increase in surface area increased the contact surface of particles that results in the enhancement of reactivity and recovery of niobium pentoxide. It was also observed that alkali to ore mass ratio makes a significant contribution to niobium pentoxide extraction. The increase in alkali to ore mass ratio increased the amount of KOH solution for the extraction of the desired component from the specific amount of ore. Thus, the solid film resistance decreased and enhanced the leaching rate of niobium pentoxide. Additionally, the effect of reaction time on the extraction was also studied. It was observed that the extraction of niobium pentoxide increased in the first 60 min and then remained constant afterwards. The reaction kinetics were such that during the reaction, 90% extraction occurred in the first 30 min [23]. Statistical analysis was conducted to investigate the effects of process parameters using Design-Expert 8.0.6 trial version. The results indicate that temperature and particle size were more significant in niobium pentoxide extraction than the other two parameters.

Table 3. Fractional factorial experimental design matrix

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>KOH:ore mass ratio</th>
<th>Particle size, µm</th>
<th>(Nb_2O_5) leached, %</th>
<th>Niobium content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>140</td>
<td>30</td>
<td>3:1</td>
<td>44</td>
<td>63.62</td>
<td>44.4701</td>
</tr>
<tr>
<td>2</td>
<td>280</td>
<td>30</td>
<td>3:1</td>
<td>230</td>
<td>81.24</td>
<td>56.7864</td>
</tr>
<tr>
<td>3</td>
<td>140</td>
<td>90</td>
<td>3:1</td>
<td>230</td>
<td>55.03</td>
<td>38.46572</td>
</tr>
<tr>
<td>4</td>
<td>280</td>
<td>90</td>
<td>3:1</td>
<td>44</td>
<td>89.85</td>
<td>62.80475</td>
</tr>
<tr>
<td>5</td>
<td>140</td>
<td>30</td>
<td>7:1</td>
<td>230</td>
<td>58.64</td>
<td>40.9891</td>
</tr>
<tr>
<td>6</td>
<td>280</td>
<td>30</td>
<td>7:1</td>
<td>44</td>
<td>95.15</td>
<td>66.50942</td>
</tr>
<tr>
<td>7</td>
<td>140</td>
<td>90</td>
<td>7:1</td>
<td>44</td>
<td>71.27</td>
<td>49.81741</td>
</tr>
<tr>
<td>8</td>
<td>280</td>
<td>90</td>
<td>7:1</td>
<td>230</td>
<td>86.36</td>
<td>60.36525</td>
</tr>
<tr>
<td>9</td>
<td>210</td>
<td>60</td>
<td>5:1</td>
<td>137</td>
<td>73.71</td>
<td>51.52296</td>
</tr>
<tr>
<td>10</td>
<td>210</td>
<td>60</td>
<td>5:1</td>
<td>137</td>
<td>72.23</td>
<td>50.48845</td>
</tr>
<tr>
<td>11</td>
<td>210</td>
<td>60</td>
<td>5:1</td>
<td>137</td>
<td>72.87</td>
<td>50.9358</td>
</tr>
</tbody>
</table>
Effect of process parameters

The interaction effect of the two main factors (reaction temperature and ore particle size) was studied from the contour plot, as shown in Figure 2A. It was observed from the contour plot that percent leaching of niobium pentoxide was increased with increases in reaction temperature. Meanwhile, the recovery of niobium pentoxide showed a reverse trend in the case of ore particle size. It is worth to mention that the increase in temperature enhanced the kinetic rate, and a decrease in particle size reduced solid film resistance during extraction.

Figure 2B shows the interaction effect of reaction temperature and reaction time. The contour plot shows that leaching of niobium pentoxide was increased with the increase of reaction temperature, while reaction time had a negligible effect. This is due to approximately 90% of the reaction occurring in the first 30 min [23]. In addition, the effects of ore particle size and alkali to ore mass ratio have been studied from the contour plot as shown in Figure 2C. The contour plot showed that the percent leaching of niobium pentoxide was increased with the increase in alkali to ore mass ratio and decrease in ore particle size. This increase in alkali to ore mass ratio enhanced the extraction chances for alkali to extract niobium oxides from its ore. Furthermore, the effect of alkali to ore mass ratio on the extraction process was also studied with respect to reaction time as shown in Figure 2D. The percent leaching of niobium pentoxide was increased with the increase in alkali to ore mass ratio and reaction time. Overall, reaction time made a small contribution to the extraction process compared to alkali to ore mass ratio.

Morphology of the ore and the product

Morphological investigations of the ore and the product are presented in Figure 3, where (A) and (B) show the surface of ore and surface of product, respectively. It can be observed from the SEM micrograph, that the surface of unreacted ore was compact and flat, and some agglomeration was present on the surface. This agglomeration was due to the various organic and inorganic metals present in the ore. On the other hand, the SEM image of the product showed that the surface of the leached product was rough and porous, indicating the confirmation of the leached product.

Statistical analysis of process parameters

Based on the regression analysis in terms of codified values of process parameters, a correlation was developed and is given by the following equation:
where $A$, $B$, $C$ and $D$ are the temperature, time, alkali to ore mass ratio, and ore particle size, respectively. The $R^2$ value of this correlation is 0.9980, showing the strength and consistency of the developed correlation. Moreover, the normal plot for process parameters is shown in Figure 4A. The normal plot illustrates that factor $D$ (ore particle size) lies on the left side of normal plot, showing a negative effect of the specified factor on percent recovery of niobium pentoxide. Hence, the percent leaching of niobium pentoxide decreased with the increase in ore particle size. The reaction temperature factor ($A$) lies far from the normal plot showing its maximum effect on the percent recovery of niobium pentoxide compared to other two factors (alkali to ore mass ratio and reaction time). Furthermore, the outliers and variability in the experimental data were investigated from the normal plot of residuals as shown in Figure 4B. The plot showed that all the experimental data lies on the diagonal or near the diagonal and is not too scattered. This observation concludes that there are less noise factors and outliers in the experimental results, suggesting consistence of the data.

The contribution of the process parameters was evaluated by a Pareto chart in terms of t-values, as shown in Figure 4C. The chart showed that temperature makes the maximum contribution to the recovery of niobium pentoxide, while ore particle size is the second highest contributor and has the reverse effect on niobium pentoxide extraction among the pro-
cess parameters. In addition, the responses of process parameters at different levels were showed using a response cube plot, as shown in Figure 4D. The percent recovery of niobium pentoxide is shown using a response cube plot, as shown in Figure 4D. The percent recovery of niobium pentoxide from pyrochlore ore was investigated. An efficient and sustainable process was adopted to selectively extract niobium pentoxide from pyrochlore. The process is based on the formation of potassium hexaniobate by the reaction between pyrochlore and a concentrate solution of KOH at atmospheric pressure. The effect of various process parameters such as reaction temperature, reaction time, ore particle size, and alkali to ore mass ratio were investigated. It was found that leaching of niobium pentoxide increased with increase in reaction temperature, reaction time and alkali to ore mass ratio. In contrast, the reverse trend has been observed in the case of particle size. The percent leached of niobium pentoxide decreased with increase in particle size due to the availability of small surface area and less contact surface. It was observed that the effect of reaction temperature and ore particle size on niobium pentoxide recovery was much greater than that of the other two factors. The fractional factorial design and statistical analysis were performed for the experimental results to investigate the effects and to optimize the process parameters. The results proved promising and can provide clues for further developments and future applications for the recovery of niobium pentoxide from pyrochlore ore.

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REFERENCES

EKSPERIMENTALNA I STATISTIČKA ANALIZA IZLUŽIVANJA NIOBIJUM PENTOKSIDA IZ PAKISTANSKE RUDE


Ključne reči: pyrochlore ore, process selection, statistical studies, process optimization.