

# Chemical Beneficiation of Zircon Sand: A Review

<sup>1</sup>Mohammed, A., <sup>1</sup>Kareem, S. A. and <sup>1</sup>Chiroma T. M.

<sup>1</sup>Chemical Engineering Department, Modibbo Adama University, Yola, Nigeria

## Paper History

Received: 21<sup>st</sup> May, 2024

Accepted: 21<sup>st</sup> July, 2024

Published: July, 2024

## Abstract:

Zircon sand ( $\text{ZrSiO}_4$ ) is a valuable mineral resource widely used in industries such as ceramics, refractories, and nuclear reactors due to its unique properties. As demand for high-quality zircon sand and its derivatives have increased in recent years, effective beneficiation processes that can meet these demands have been explored. Conventional processing of zircon sand involves physical separation methods, such as gravity, magnetic and electrostatic separation. However, these techniques may have limitations in achieving the desired levels of purity required for certain applications. Chemical beneficiation methods, such as alkali fusion, acid leaching and chlorination present alternative pathways for improving zircon sand quality. This review paper examines existing literature on the chemical beneficiation of zircon sand and provides a detailed analysis of the methodologies employed to enhance the purity and quality of zircon sand. Reviews detailing the various studies undertaken on the chemical beneficiation of zircon sand are scarce, hence the need for this paper. This review thus aims to provide a comprehensive overview of the chemical beneficiation techniques applied to zircon sand. This review further highlights the effectiveness, challenges, and limitations of the various chemical beneficiation methods, as well as future research and development directions in enhancing the beneficiation of zircon sand.

Corresponding author

Mohammed, A.

[amajalingo@mau.edu.ng](mailto:amajalingo@mau.edu.ng)

**Keywords:** Alkali fusion, Beneficiation, Zirconia, Zircon

## 1. Introduction

Zirconium silicate ( $\text{ZrSiO}_4$ ), commonly known as zircon is a major neosilicate mineral and the primary source of zirconium metal. Zircon occurs mostly along with other minerals such as ilmenite ( $\text{Fe.TiO}_3$ ), leucosene ( $\text{FeTiO}_3.\text{TiO}_2$ ), rutile ( $\text{TiO}_2$ ), and monazite ( $\text{Ce,La,Nd,Th}(\text{PO}_4)$ ) which are collectively referred to as mineral sands or heavy mineral sands [1]. Zircon can also be obtained as part of tailings during the processing of mineral ores such as cassiterite [2,3]. Over 90% of zircon in the world is however, obtained from heavy mineral sands mining [1,4].

Zircon ideally consists of about 67% zirconia ( $\text{ZrO}_2$ ) and 33% silica ( $\text{SiO}_2$ ), but naturally occurring zircon typically contains lower amounts due to impurities like Fe, Al, P, Ti, U, Th, and rare earth elements (e.g., Ce, Y, Nd) in trace amounts. These impurities are more often present as discrete contaminant grains such as inclusions, alteration products or unseparated components. High levels of uranium and thorium in zircon may be due to the presence of minerals such as monazite ( $\text{Ce,La,Nd,Th}(\text{PO}_4)$ ), thorite ( $[\text{Th,U}]\text{SiO}_4$ ), or uraninite ( $\text{UO}_2$ ) as either discrete minerals or as inclusions within individual zircon grains. Uranium and thorium decay in zircon minerals, releasing energetic particles and rays that damage the mineral lattice, a process known as metamictisation. Impurities in zircon concentrates are significant, but most contamination arises

from the failure to properly separate impurities during beneficiation [5].

The chemical compositions of zircon sand vary by source as shown in Table 1, necessitating different treatment methods and process conditions. Studies are essential to determine the optimal beneficiation methods and conditions for achieving desired purity levels. However, comprehensive reviews of zircon sand beneficiation studies are scarce, making research more challenging. This review aims to fill that gap by providing a thorough overview of chemical beneficiation techniques for zircon sand, evaluating their effectiveness, challenges, and limitations, and suggesting future research directions to enhance zircon sand beneficiation.

## 1.1 Properties of Zircon Sand

Zircon is generally unreactive to strong mineral acids but is attacked by concentrated  $\text{H}_2\text{SO}_4$  at high temperatures and pressures, and fluorides like HF and potassium bifluoride [ $\text{K}(\text{HF}_2)$ ] can convert it into complex zirconium fluoride and silica; it is paramagnetic, non-conductive, highly resistant to thermal shock, chemically inert when in contact with molten slag and glass, has a low and uniform thermal expansion coefficient ( $4.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  from room temperature to  $1700^\circ\text{C}$ ), and low thermal conductivity ( $5.1 \text{ Wm}^{-1} \text{ }^\circ\text{C}^{-1}$  at room temperature and  $3.5 \text{ Wm}^{-1} \text{ }^\circ\text{C}^{-1}$  at  $1000^\circ\text{C}$ ) [7,8]. Some other important physical properties of zircon are presented in Table 2.

Table 1: Typical assay of zircon sand from different locations [6]

Assay Constituents	Sri Lanka	India	Nigeria	South Africa	United States	Australia
(Zr + Hf)O <sub>2</sub>	64.9	64.4	58.2	65.0	65.3	65.7
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.23	0.90	0.18	0.07	0.06
Al <sub>2</sub> O <sub>3</sub>	0.20	0.60	0.65	0.15	0.17	0.14
TiO <sub>2</sub>	0.71	0.16	0.05	0.08	0.10	0.17
P <sub>2</sub> O <sub>5</sub>	0.18	0.13	0.39	0.13	0.05	0.07
U <sub>3</sub> O <sub>8</sub>	0.03	0.04	0.11	0.03	0.03	0.03
Nb <sub>2</sub> O <sub>3</sub>	<0.01	<0.01	2.0	<0.01	<0.01	<0.01
Hf/Hf+ Zr	2.2	2.3	6.8	2.3	2.2	2.2

Table 2: Physical properties of zircon sand

Property	Value
Density	4200 – 4800 kg/m <sup>3</sup>
Specific gravity	4.60 – 4.71
Mohs hardness	7.0 – 7.5
Melting point	2100 – 2500°C
Refractive index	1.80 – 1.99

## 1.2 Uses of zircon

Zircon is primarily utilized as an important raw material in the ceramics industry, particularly in the production of various ceramic bodies, glazes, enamels, frits, and pigments. It is extensively used in traditional ceramics such as wall and floor tiles, porcelain tiles, sanitaryware, tableware, special porcelains, and industrial tiles[1]. In ceramics, zircon enhances whiteness and opacity, producing glossy white finishes.

Zircon is also used in the foundry industry, either directly as sand in sand casting or in milled form as flour used in investment and similar castings. Its high refractoriness and low thermal expansion coefficient makes it ideal for producing accurate castings free from scabbing defects, and its excellent heat conduction and strength ensure reliable mold performance [9 - 13].

Zircon finds extensive use in refractory production owing to its exceptional heat resistance and chemical inertness. It is utilized in the fabrication of refractory mortar, firebricks, and linings for furnaces in the glass and metal industries. Additionally, zircon is incorporated into various applications such as fibers, nozzles, slide gates, valves, and grouts [14, 15].

An increasing portion of zircon mined globally is directed towards extracting zirconium and hafnium metals, as well as the production of zirconium based chemicals. Zirconium chemicals produced include Zirconium oxychloride ZrOCl<sub>2</sub>·8H<sub>2</sub>O, (ZOC), Zirconium basic sulfate Zr<sub>5</sub>O<sub>8</sub>(SO<sub>4</sub>)<sub>2</sub>H<sub>2</sub>O (ZBS), Ammonium zirconium carbonate (NH<sub>4</sub>)<sub>2</sub>Zr(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>, (AZC), Zirconium fluoride ZrF<sub>4</sub> among others. Furthermore, zircon is sometimes added to the glass used in cathode ray tubes in televisions and computer monitors to absorb X-rays and enhance the glass's refractive index. It is also used in the glass of LCD and plasma displays at lower concentrations [1].

## 1.3 Zircon Quality

The suitability of zircon for various industrial uses depends on its quality, which is typically assessed based on its zirconia (ZrO<sub>2</sub>) content (reported as ZrO<sub>2</sub> + HfO<sub>2</sub>), along with levels of iron (Fe<sub>2</sub>O<sub>3</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), titania (TiO<sub>2</sub>), and uranium and thorium. For applications requiring

ceramic opacifiers, a 'premium grade' zircon with iron content below 0.08% is necessary. Conversely, 'standard grade' zircon, which can have iron levels up to 0.3%, is generally adequate for refractory and foundry purposes [15]. Table 3 presents the two important grades of zircon sand and their quality requirements.

Table 3: Zircon Grade quality specifications and properties [1, 14]

Chemical composition		
Specification/Property	Standard Grade zircon	Premium Grade zircon
% ZrO <sub>2</sub> + HfO <sub>2</sub>	65.00 min	66.50 min
% SiO <sub>2</sub>	32.50 max	32.50 max
% Fe <sub>2</sub> O <sub>3</sub>	0.3 max	0.08 max
% Al <sub>2</sub> O <sub>3</sub>	1.50 max	0.15 max
% TiO <sub>2</sub>	0.30 max	0.15 max
U + Th (ppm)	500 max	500 max
Free silica	0.20 max	0.05 max
Mineral composition		
% Zircon	97	99.3
% Kyanite	2.0 max	0.5 max
% Rutile	0.35 max	0.1 max
Misc. minerals	1.0 max	0.1 max

## 2. Zircon Physical Beneficiation

In order to separate heavy minerals such as zircon, cassiterite, rutile, magnetite, and monazite from light minerals (such as quartz and clay), gravity separation methods are normally first used [16]. Subsequently, magnetic separation can be used to remove all magnetic minerals (such as magnetite and cassiterite) from the zircon concentrate. Conductive minerals such as rutile can further be separated from the zircon concentrate by electrostatic separation [17]. Froth flotation can also be used for separation of zircon from other minerals [15, 18 - 20].

### 2.1 Zircon Chemical Beneficiation

Zircon concentrate obtained through physical beneficiation typically contains discoloured zircon grains covered in iron oxide, titanium, or clay mineral coatings, which can limit its suitability for various applications. To remove these impurities, processes such as attritioning in water or chemical solutions have been used, although more intensive chemical treatments are often necessary to meet industry standards. Various chemical leaching methods have been explored to eliminate contaminants and enhance the purity of the zircon concentrate [15]. In some cases, however the impurities in zircon may be partly embedded within the crystal structure and partly in the

growth bands of zoned zircon grains. In zircons with high impurity levels, these growth bands are often microporous, a condition typically caused by metamictisation from radioactive impurities. Metamictisation also facilitates the entry of other impurities into the zircon's porous microstructure, indicating that these impurities, both within the zoned and altered regions and on the grain surfaces, could potentially be removed through leaching treatments.

The removal of impurities, particularly uranium and thorium, from zircon lattice is challenging, with Hot Acid Leaching (HAL) being effective for surface impurities but not for embedded ones. Finely milling zircon sand can enhance leaching by increasing surface area but poses health risks due to radioactive particle inhalation, is energy-intensive, leads to significant zirconia dissolution, and complicates subsequent processing stages, making non-comminuted treatment preferable in some cases [15].

There are at least three distinct methods for eliminating impurities from zircon grains through chemical beneficiation, these include:

- Complete zircon decomposition, achieved by reacting the sand with a flux, typically NaOH (alkali fusion), or the use of halogens such as chlorine.
- Acid leaching treatments, typically conducted at elevated temperatures.
- Partial decomposition and leaching techniques designed to preserve the structural integrity of the zircon crystalline lattice.

### 2.1.1 Zircon Alkali Fusion

Alkali fusion is particularly effective for refractory ores or those with complex mineral structures that hinder conventional leaching, as it breaks down the mineral matrix and enhances the efficiency of subsequent hydrometallurgical processes; it is versatile, simple, and low-cost due to minimal equipment and reagent requirements, and involves four main stages: decomposition with an alkali, water leaching to extract silicates, acid leaching of insoluble solids, and precipitation of zirconium compound ( $ZrO_2$ ).

Sodium hydroxide (NaOH) is the most commonly used reagent for this process, as cited in multiple studies [22 - 28]. The use of reagents such as potassium hydroxide (KOH) and sodium carbonate ( $Na_2CO_3$ ) have also been reported [29 - 33].

Zircon reacts with NaOH at a temperature above 600°C according to the following reactions [34].



The reactions are heavily influenced by the quantity of NaOH employed. In equation (1), an amount of NaOH less than the stoichiometric requirement is used, whereas in equation (2), the exact stoichiometric amount is utilized. In equation (3), 1.5 times the stoichiometric amount of NaOH needed is reacted with zircon. Numerous studies indicate that using excess reagents can lead to optimal decomposition of zircon sand [24, 29, 34 - 37].

A typical alkali fusion process using NaOH to obtain zirconia ( $ZrO_2$ ) is shown in Figure 1.

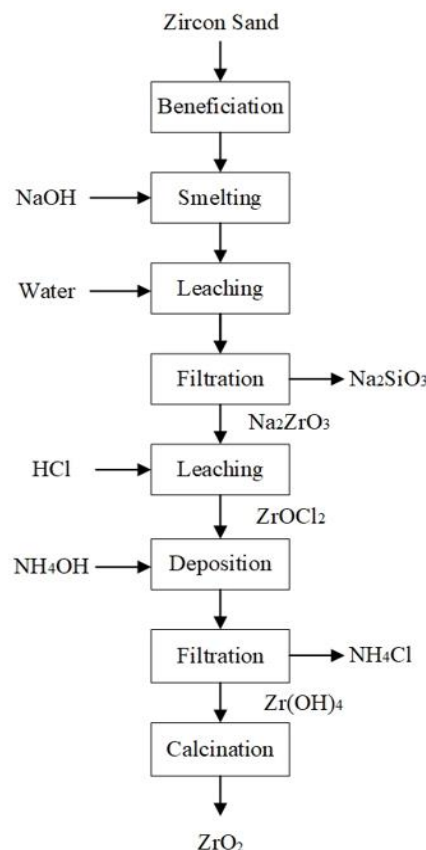


Figure 1: Zircon alkali fusion using NaOH [38]

One of the challenges in the zircon alkali fusion process is the formation of the water insoluble by-product,  $Na_2ZrSiO_5$ , which largely affects NaOH recovery and can result in the formation of silicon slags, thus necessitating the control of  $Na_2ZrSiO_5$  formation. Most of the water-soluble  $Na_2SiO_3$ ,  $Na_4SiO_4$ , and unreacted NaOH dissolve in water, whereas the insoluble  $Na_2ZrO_3$  is hydrolyzed to  $ZrO(OH)_2$  during the washing process. Thus, the majority of the NaOH remains in the washing water and can be recovered after silicon removal by adding CaO. However,  $Na_2ZrSiO_5$  is water insoluble and does not hydrolyze in water; it reacts with HCl in the transition process, leading to  $Na^+$  wastage.

A study carried out by Liu et al. [34] to limit the formation of  $Na_2ZrSiO_5$  in alkali fusion process using NaOH, showed that the reaction temperature, NaOH/zircon mole ratio, and particle size of zircon sand all had effects on  $Na_2ZrSiO_5$  formation. According to the study, the optimum reaction parameters are a reaction temperature of 750°C, NaOH/zircon mole ratio of 6:1, and zircon sand average particle size  $\leq 95 \mu m$ . To avoid an uneven reaction temperature during alkali fusion, the use of a rotary kiln reactor was also recommended. The amount of  $Na_2ZrSiO_5$  was significantly limited under these optimum conditions.

In research by El-Barawyet al.[29], zircon sand from El-Bardaweel Lake, Egypt, was processed using

electrostatic and magnetic separation, then treated with anhydrous  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  as fusion agents under varying conditions, followed by acid leaching with  $\text{HCl}$ . During the fusion process with  $\text{Na}_2\text{CO}_3$ , zircon sand was mixed in ratios ranging from stoichiometric to twice the stoichiometric amounts and placed into a nickel crucible for heating in an electric furnace. The temperature ranged from  $900^\circ\text{C}$  to  $1200^\circ\text{C}$ , and the heating lasted between 0.5 to 2 hours. After cooling, the mixtures were weighed and subjected to  $\text{HCl}$  leaching with concentrations from 1.2M to 8M to dissolve the alkali zirconium compounds and precipitate silica as silica gel. The resulting filtrate, containing a soluble zirconium salt, was treated with ammonia to produce zirconium hydroxide, subsequently calcined to generate  $\text{ZrO}_2$ . The optimal conditions identified were using 1.2 times the stoichiometric amount of  $\text{Na}_2\text{CO}_3$  at  $1100^\circ\text{C}$  for 2 hours. The best leaching results were achieved with 4M  $\text{HCl}$ , a solid/liquid ratio of 2/15, at  $90^\circ\text{C}$  for 1 hour, yielding a 91% recovery of  $\text{ZrO}_2$  at a purity exceeding 99%.

In the subsequent phase of the study,  $\text{NaOH}$  was mixed with the sand in proportions from 0.5 to 1.5 times the stoichiometric amount. These mixtures were heated for up to 2 hours at temperatures ranging from  $350^\circ\text{C}$  to  $700^\circ\text{C}$ . XRD analysis was employed to explore the impact of the  $\text{NaOH}$  quantity on the fusion outcome. It was found that samples with 0.5 times the stoichiometric amount of  $\text{NaOH}$  primarily contained zircon, with weak indications of sodium zirconate. Samples with an equal stoichiometric amount of  $\text{NaOH}$  displayed XRD patterns featuring both zircon and sodium zirconate. At 1.5 times the stoichiometric amount, no zircon was detected, and sodium zirconate was the dominant phase. Sodium silicate was not observed due to its amorphous nature. An optimal temperature of  $600^\circ\text{C}$  and duration of 2 hours were selected for complete reaction. The fused products were leached with water at room temperature and filtered to separate soluble  $\text{Na}_2\text{SiO}_3$ . The residue was dissolved in 5 M  $\text{HCl}$  at  $90^\circ\text{C}$  with a solid to liquid ratio of 1:5 to remove remaining  $\text{SiO}_2$ , producing a clear  $\text{ZrOCl}_2$  solution. This was neutralized with ammonia to precipitate zirconium hydroxide, which was then calcined at  $900^\circ\text{C}$  for 1 hour to produce pure zirconia, assaying greater than 99.5% purity and exhibiting a monoclinic structure.

In the preparation of high purity  $\text{ZrO}_2$  and  $\text{SiO}_2$  powders via wet process reported in Yamagata et al. [39], a 50 wt% solution of  $\text{NaOH}$  was used to decompose zircon sand. The prepared solution and the zircon sand were mixed in wt/wt ratio of 1.0; 1.2 and 1.5  $\text{NaOH}/\text{ZrSiO}_4$ . The alkaline fusion reaction was conducted by first heating at a rate of  $20^\circ\text{C}/\text{min}$  up to  $100^\circ\text{C}$ , remaining at this temperature for 1 hour and then heating at a rate of  $20^\circ\text{C}/\text{min}$  up to  $200^\circ\text{C}$ , for 1 hour and finally the temperature was increased to  $600^\circ\text{C}$  for 2 hours. The fused mass obtained was washed with water and leached in 8M  $\text{HCl}$  at  $80^\circ\text{C}$  to obtain an impure zirconyl chloride solution. The zirconyl chloride solution was kept overnight at room temperature to precipitate silica in the form of silica gel which was filtered out. The remaining  $\text{ZrOCl}_2$  solution, now free from  $\text{SiO}_2$ , was concentrated on a hot plate until crystals were formed which were isolated by filtration and

washed with ethanol. The white crystals formed were dissolved in water to create a clear  $\text{ZrOCl}_2$  solution, which was neutralized with  $\text{NH}_4$  to precipitate zirconium hydroxide. This precipitate was dried and calcined at  $550^\circ\text{C}$  for one hour. XRD patterns of the fused products showed optimal zircon decomposition at a  $\text{NaOH}$  to  $\text{ZrSiO}_4$  wt/wt ratio of 1.5.

A similar method to that of [39] was used by Subuki [37] to produce  $\text{ZrOCl}_2$  from Amang zircon using  $\text{NaOH}$  and  $\text{HCl}$ . They determined the optimum  $\text{NaOH}/\text{ZrSiO}_4$  ratio to be 1.2, fusion temperature  $670^\circ\text{C}$  and time 2 hours. The conditions for water and acid leaching using  $\text{HCl}$  were however not reported. [40], tried to enhance the yield of  $\text{ZrOCl}_2$  by performing water and acid leaching with  $\text{HCl}$  twice, but they ultimately found that this approach did not offer any additional advantages.

A novel zircon decomposition method was researched by Abdelkader [30], they used an equimolar ratio of  $\text{KOH}$  and  $\text{NaOH}$  in the study. They explored the effect of alkali quantity, temperature of the reaction, and the duration of the reaction. For each experimental run, a 183 g sample of zircon was combined with an equimolar mixture of  $\text{KOH}$  and  $\text{NaOH}$ , ranging from the stoichiometric amount to 1.5 times the stoichiometric amounts. An electric furnace heated the mixture to the desired fusion temperatures, ranging from  $350$  to  $600^\circ\text{C}$ , with the duration of heating varying between 60 and 150 minutes to explore the effects of time. The reaction products were allowed to cool overnight before being milled. The fused sand was weighed and then leached with hot water to dissolve any soluble  $\text{Na}_2\text{SiO}_3$ ,  $\text{K}_2\text{SiO}_3$ , and excess  $\text{NaOH}$  or  $\text{KOH}$ . The solid hydrous zirconium was separated from the silicate solution via filtration and subsequently dried in an oven at  $200^\circ\text{C}$ . The dry powder was then leached with an excess of various concentrated acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$ ) to extract the acid-soluble zirconium from the unreacted zircon, which was filtered out, dried, and weighed; the degree of decomposition was calculated by assessing the percentage weight difference before and after the process. It was found that using a 20% excess of alkali mixture at  $550^\circ\text{C}$  for a 60-minute reaction led to optimal (96%) decomposition of zircon. However, assessing the success of their approach is challenging since analytical techniques were not employed to identify the decomposition products accurately.

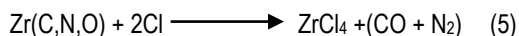
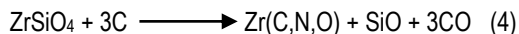
Some researchers used  $\text{KOH}$  alone to decompose zircon, Yustanti [31] for example used  $\text{KOH}$  fusion,  $\text{HNO}_3$  leaching and coprecipitation to produce zirconia. Alkali fusion with  $\text{KOH}$  was done with stoichiometric ratio  $\text{ZrSiO}_4/\text{KOH}$  of 1:1.5 at  $700^\circ\text{C}$  for 3 hours. Water leaching was carried out at  $25^\circ\text{C}$  and  $95^\circ\text{C}$ , while  $\text{HNO}_3$  concentrations 4M and 6M were used for leaching. A water leaching temperature of  $25^\circ\text{C}$  and  $\text{HNO}_3$  concentration of 4M gave the best results.

## 5.1.2 Zircon Chlorination

Chlorination of zircon sand is a chemical process used to extract zirconium metal from zirconium-bearing minerals, with zircon sand being a common source. Historically, the production of zirconium tetrachloride from



zircon involved first reducing the zircon to carbide nitride by reaction it with coke in an electrical arc furnace at 2500°C as shown in equation (4). Subsequently, the highly exothermic reaction of the crushed carbide nitride with chlorine gas occurred in a water-cooled vertical shaft furnace, operating at temperatures ranging from 700 to 1200°C (equation 5).



In modern practices however, chlorination of a mixture of zircon and carbon to produce  $\text{ZrCl}_4$  directly has become the most popular method for producing  $\text{ZrCl}_4$ . The Kroll reduction process originally developed for the production of titanium is universally adopted for large scale production of zirconium [6, 41]. Milled zircon and coke are chlorinated in fluidized beds at about 1100°C using chlorine as the fluidizing medium according to equation 6



Extra energy required to maintain the endothermic reaction is supplied either through the introduction of silicon carbide grain or through electrical means such as electrothermal fluidized beds, induction heating, or resistance heating. The resulting product gases are initially cooled to temperatures below 200°C to selectively condense zirconium tetrachloride using a spacious condenser. Following this, silicon tetrachloride is condensed in a quench condenser, where the warm gases are scrubbed in a countercurrent manner with liquid silicon tetrachloride at -20°C. Typically, factors such as particle size of coke and zircon, coke and zircon intimacy, the ratio of coke to zircon, chlorine concentration, and temperature play crucial roles in the chlorination process. Reducing the size of coke and zircon particles usually speeds up the reaction. The ratio of coke to zircon impacts the reaction in a more complex way. Higher chlorine concentrations tend to accelerate the reaction, though this seems more linked to its influence on diffusion rather than on reaction kinetics directly. The rate of reaction also rises with temperature, although the specific effects are complicated by how temperature influences diffusion.

The technology for chlorinating zircon has been well-established and utilized on a large scale for decades, but available information is largely found in patents and academic research, both of which are often vague, incomplete, and contradictory, thus failing to provide adequate guidance for designing a commercial-scale chlorinator [42].

### 2.1.3 Zircon Acid Leaching

Purification of zircon using acid is capable of removing surface coatings and some lattice impurities, mineral acids such as  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  are mostly used. In the dry acid process developed by Westralian Sands Ltd, Capel, as detailed by Liu[43], zircon containing 0.172% iron was treated using  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ . The procedure involved adding 40 g of concentrated  $\text{H}_2\text{SO}_4$ , diluted to a 50% solution in water to 2 kg of zircon contained in a glass flask. This flask was then placed in an oil bath at 120°C for

60 minutes and rotated around to mix the acid and zircon thoroughly. After the treatment, the zircon was washed to remove any residual acid and subsequently roasted in an open dish at 500°C for 30 minutes. Chemical analysis of the cooled, purified zircon showed a reduced iron content of 0.034%. The process was later modified by pre-roasting the zircon at 600°C for 30 minutes before the acid cleaning process, using both  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  in separate trials. The acid digestions were carried out in a glass flask, placed in a water bath at 100°C for 60 minutes. The specific acid used was added as a 50% solution, with  $\text{HCl}$  at 5% or  $\text{H}_2\text{SO}_4$  at 2% by mass of the zircon. The results indicated minimal improvement: the  $\text{HCl}$  leaching resulted in zircon with an iron content of 0.034%, whereas the  $\text{H}_2\text{SO}_4$  leaching left the iron content slightly higher at 0.036%.

In a patent application filed by Philipet al[44] for removing iron oxide from the surface of zircon, impure zircon was first heated to temperatures ranging from 200°C to 450°C for up to 30 minutes without using any chemical agents. The treated zircon was then subjected to a weak acid leaching, washing and attritioning steps to remove the iron oxide coatings. This thermal treatment is thought to enhance the exposure of iron hydroxides on the zircon surface, improving the efficiency of the subsequent leaching process. For achieving a whiter appearance of the zircon, the optimal heating range was found between 370°C and 420°C. A heat treatment temperature exceeding 450°C is not recommended, as it not only failed to improve the removal of coatings but also caused the remaining iron oxides on the zircon to become more intensely coloured.

The feasibility of using Bangladesh zircon as a raw material for opacifiers was studied by Naher and Haseeb [45]. The zircon sand was processed through both dry and wet ball milling in an alumina-lined mill, with alumina used as the grinding media. It was observed that wet milling was significantly more effective than dry milling, achieving particle sizes around 8  $\mu\text{m}$ . For purification, the milled zircon underwent a leaching process in a specially designed apparatus. This setup included a conical leaching flask with a 1000  $\text{cm}^3$  capacity, equipped with dual condensers in series and a magnetic stirrer hot plate. The temperature within the flask was monitored with a thermometer and controlled via the hot plate's thermostatic controller. The concentration of  $\text{H}_2\text{SO}_4$  used ranged from 10 to 80  $\text{ml/L}$ , and the leaching duration varied from 2 to 20 hours. The leaching was performed at a consistent temperature of 180°C and a stirring speed of 100 rpm. Following the treatment, the mixture was cooled, allowing the zircon to settle before it was washed with distilled water. The zircon was then dried first in a water bath and subsequently in an oven at 110°C. The optimal conditions for producing purified zircon in the study were identified as using 80%  $\text{H}_2\text{SO}_4$  concentration and a leaching time of 10 hours. However, it is important to note that no analysis was conducted on the zircon opacifier produced to determine whether it met market standards in terms of purity.

A South African zircon containing 0.20%  $\text{Fe}_2\text{O}_3$  and 0.53%  $\text{Al}_2\text{O}_3$  was processed for use as an opacifier in a study by Snyders, et al.[46]. The process began with the zircon being milled in a conventional ball mill until 95% of the particles sizes were < 45  $\mu\text{m}$ . Subsequently, the milled

zircon was mixed with selected, albeit unspecified, mineralizers using a Y-cone tumbler mixer. The mixture was then calcined in an air furnace to produce a raw calcined product. Following calcination, the product underwent a washing process to remove excess mineralizers as well as other impurities. The washed calcined product was then subjected to further size reduction through wet milling, achieving an average particle size of 0.8 – 1.2  $\mu\text{m}$ . To prevent contamination during this milling process, yttria-stabilized zirconia milling media was utilized. An XRF analysis of the resultant zircon product showed significant reductions in impurity levels:  $\text{Fe}_2\text{O}_3$  content was reduced to 0.04%, and  $\text{Al}_2\text{O}_3$  content to 0.12%. It was found that the treated zircon product exhibited improved milling characteristics compared to the untreated zircon. Notably, the milling time required for the treated zircon to reach an average particle size of about 5.6  $\mu\text{m}$  was 8.5 hours, significantly less than the 15 hours required for the untreated material. This reduction in milling time is particularly significant considering the high costs associated with electric power and grinding media, which are major expense factors in opacifier production. Although the study did not specify the types of mineralizers used nor the calcining temperature, the improved efficiency in milling the treated zircon highlights the potential cost benefits of the treatment process in industrial applications.

#### 2.1.4 Removal of Radionuclides

Removal of radionuclides such as uranium and thorium from highly altered zircon can be quite challenging, especially when zircon is the product desired. It is known that alkali fusion decomposes zircon and some applications make use of zircon and not zirconia. Acid leaching on the other hand maintains the structure of zircon but can only effectively remove surface impurities only leaving some lattice impurities (in some cases the radionuclides). Methods have thus been studied to remove both surface and lattice impurities without significantly changing the structure of the zircon sand.

It was showed that vigorous leaching of a zircon concentrate consecutively with boiling NaOH, boiling  $\text{H}_2\text{SO}_4$  and  $\text{NH}_4\text{F}$  and concentrated HCl lowered the uranium levels from 595 to 510 parts per million (ppm) and the thorium levels from 750 to 375 ppm [47].

Murray Basin zircon concentrate containing 475 ppm U and 482 ppm Th was treated using NaOH fusion. The zircon was heated with sodium hydroxide at 600°C for 1 hour and then leached with water to remove silica and excess alkali and to hydrolyse the zirconate to hydrated zirconia. The product was leached again with concentrated HCl at 90°C for 1 hour, and the zirconyl chloride that precipitated on cooling was converted to zirconia by heating at 700°C for 1 hour. A product was obtained that contained 99.1%  $\text{ZrO}_2 + \text{HfO}_2$ , 60 ppm U and <10 ppm Th with significantly lower activity levels than those present in the zircon concentrate [48].

Mechanical activation in ammonium carbonate was used to remove radionuclides from zircon but retain the zircon structure [49]. The mineral was reacted with ammonium carbonate  $[(\text{NH}_4)_2\text{CO}_3]$ , while milling in a high

energy stirred mill. The milling increased the amount of amorphous zircon in the sample assisting the leaching of the radionuclides by the carbonate. From a feed with 205 ppm U and 115 ppm Th, a product with 95 ppm U and 80 ppm Th was obtained after milling for 5 hours. This reaction time could be reduced by grinding the zircon before the milling. A subsequent leach with HCl removed a little more thorium (to 45 ppm Th), but the uranium assay was higher at 110 ppm. Furthermore, some zircon dissolved in the acid leach. The final product was characterised by a narrow particle size, high surface area, density and hardness and was considered suitable for application as a pigment or filler in rubber and plastics.

In the pure zircon process reported in Aral et al. [50], treatment of a fine grained zircon sample containing 1059 ppm U + Th was achieved. The pure zircon process conditions yielded a product with 414 – 485 ppm U + Th. This product was achieved by grinding the zircon concentrate with initial particles size of about 80  $\mu\text{m}$  to particle size of around 20  $\mu\text{m}$ . The ground zircon was calcined with 15 wt-% calcium borate,  $\text{Ca}_3(\text{BO}_3)_2$ , (colemanite) at 1200°C for 4 hours, cooled and leached with 0.5 or 1.0M HCl at 80°C for 30 minutes. The structure of the zircon was retained with only the presence of a negligible amount of zirconia from some decomposition of the zircon in the product. Impurities such as Al, Fe, Ti and P were also decreased by the process. The leach products were white and had a particle size similar to the initial zircon, thus making the products suitable for glaze and other applications. This method though has shown to be effective in removing surface and lattice impurities; the high temperature involved is a major drawback.

### 3. Challenges of zircon chemical beneficiation

As with any process the chemical beneficiation of zircon sand is faced with a number of challenges. The drawbacks of alkali fusion for instance include; high NaOH consumption, significant water and energy usage. While ongoing research aims to find more sustainable alternatives, none have yet met industrial standards without sacrificing efficiency and scalability [51]. Although chlorination serves as the predominant industrial approach for zirconium metal extraction from zircon, it presents notable environmental concerns. As noted by Mukhachev [33], the process results in substantial quantities of waste containing chlorine, leading to costly disposal procedures. During the processing of zircon especially by acid leaching, low to high levels of uranium and thorium can be found in waste effluent. Great cost is also incurred to ensure their safe disposal. Other issues include the use of harsh chemicals and their cost, the high cost of milling zircon before beneficiation and scaling up processes from the laboratory to commercial scale while maintaining efficiency and quality.

Generally the challenge for whichever chemical beneficiation method is adopted remains the need to balance production efficiency with environmental sustainability and resource conservation without sacrificing efficiency and scalability.

#### 4. Advancements and Future Directions

Electricity-driven intensified processes, i.e., microwave, ultrasound, hi-gee (rotating) reactors, etc., are innovative technologies that carry the potential to decrease energy consumption and cost, avoid or use less harmful chemicals, and enhance process economics and output in hydrometallurgical processes [52]. In particular, ultrasonic and microwave-assisted separation processes of various inorganic compounds and metals from the matrix using extracting agents have been explored and found to be more efficient than regular techniques as seen in some studies [53 - 60]. Consequently, finding new applications of these techniques in the beneficiation processes of zircon sand could be highly advantageous.

The use of organic acids in the hydrometallurgy has gained more attention in recent years due to environmental concerns in the use of inorganic acids. The use of organic acids have been investigated [61 - 66] and have shown remarkable promise in their ability to replace or compliment inorganic acids in leaching out impurities from various materials. Studies geared towards the utilization of organic acids alone or in conjunction with other organic/inorganic acids in the treatment of zircon sand should be pursued to take advantages of their potential benefits.

#### 5. Conclusion

Enhancing the purity of zircon sand for industrial applications is a critical process, with chemical beneficiation playing a vital role. This review examines the various methods and processes involved in zircon chemical beneficiation. Physical beneficiation methods serve as preliminary steps, effectively concentrating zircon by removing lighter minerals and other impurities. However, some surface and lattice impurities often necessitate the use of chemical beneficiation techniques. Among these, alkali fusion, particularly with NaOH, has proven effective in breaking down the zircon structure, facilitating the removal of silica and other contaminants. Chlorination is another efficient method for producing zirconium tetrachloride directly from zircon sand. Acid leaching, using mineral acids like  $H_2SO_4$  and HCl, is also a popular technique for surface impurity removal. The choice of method depends on the specific impurities present and the intended application of the zircon product. Continued research and optimization of these processes are essential for improving efficiency, reducing costs, and minimizing environmental impact.

#### References

- [1]. Dunan, C. F., (2019). Technical Handbook on Zirconium and Zirconium Compounds. Zircon Industry Association, Mayfair, London.
- [2]. Ejiofor, J. U., Okorie, B. A. and Reddy, R. G., (1997). Powder Processing and Properties of Zircon-Reinforced Al-13.5Si-2.5Mg Alloy Composites. *Journal of Materials Engineering and Performance*, 6, 326-334.
- [3]. Okoli, B. I., Agboola, O. A., Onwualu, A. P., Bello, A., Sholiyi, O. S., Anye, V. C. and Yusuf, O. T., (2023). Characterization of Nigerian Zircon Sand and its Suitability for Different Industrial Applications, *Minerals*, 13(6), 1-26.
- [4]. Samin, S., Poernomo H., Rozana K. and Suyanti, S., (2000). *The Processing and Validation of Zircon Sand Concentrate Process into Zircon Opacifier*. Proceeding of International Conference on Science and Applied Science, Surakarta, Indonesia, 1-11.
- [5]. Tahlil, L. and Wahyudi T., (2016). A Characteristic Study of Popay Zircon Sand used for Ceramics, Refractory and Foundry Raw Materials. *Indonesian Mining Journal*, 19(1), 1-17.
- [6]. Othmer, D. F. and Kirk, R. E., (2001). Encyclopedia of Chemical Technology, 4th ed., vol.25. Wiley-Interscience Publishers, Hoboken, New Jersey
- [7]. Musyarofah, M., Lestari, N. D., Nurlaila, R., Muwwaqor, N. F., Triwikantoro T. and Pratapa S., (2019). Synthesis of High-Purity Zircon, Zirconia, and Silica Nanopowders from Local Zircon Sand. *Ceramics International*, 45(6), 6639-6647.
- [8]. Abajo, C., Jiménez-morales, A. and Manuel, J., (2015). New Processing Route for  $ZrSiO_4$  by Powder Injection Moulding using an Eco-Friendly Binder System. *Boletín de la Sociedad Española de Cerámica y Vidrio*, 54(3), 93-100.
- [9]. Jain, P. L., (2009). Principles of Foundry Technology, 5th ed. McGraw-Hill Education Private Limited, New Delhi.
- [10]. Sai, T. V., Vinod, T. and Sowmya, G., (2017). A Critical Review on Casting Types and Defects. *International Journal of Scientific Research in Science, Engineering and Technology*, 3(2), 463-468.
- [11]. Bundy, J. and Viswanathan, S. (2009). Characterization of Zircon-Based Slurries for Investment Casting. *International Journal of Metal Casting*, 3(1), 27-37.
- [12]. Asuquo, L. O., Bassey, E. N. and Ihom, A. P., (2013). Characteristics of Zircon Sand and the Effect on Foundry Casting. *Journal of Mechanics and Industry Research*, 1(1), 27-32.
- [13]. Bansode, S. N., Phalle, V. M. and Mantha, S. S., (2020). Influence of Slurry Composition on Mould Properties and Shrinkage of Investment Casting. *Transactions of the Indian Institute of Metals*, 73(3), 763-773.
- [14]. Pirkle, F. L. and Podmeyer, D. A., (1998). Zircon: Origin and Uses. Society for Mining, Metallurgy, and Exploration, Englewood.
- [15]. Pownceby, M. I., Sparrow, G. I., Aral, H., Smith, L. K. and Bruckard, W. J., (2015). Recovery and Processing of Zircon from Murray Basin Mineral Sand Deposits. *Mineral Processing and Extractive Metallurgy*, 124(4), 240-253.
- [16]. Rejith, R. G. and Sundararajan, M., (2017). Combined Magnetic, Electrostatic, and Gravity Separation Techniques for Recovering Strategic Heavy Minerals from Beach Sands. *Marine Georesources and Geotechnology*, 36(1), 1-8.
- [17]. Nouri, S., Hoseinian, F. S., Rezai, B. and Saberyan, K., (2019). New pretreatment method for high-tension electrical separation of zircon from



- quartz. *Transactions of Nonferrous Metals Society of China*, 29(8), 1737–1743.
- [18]. Hoşten, Ç., (2001). Micro-Floatability of Rutile and Zircon with Soap and Amine Type Collectors. *Physicochemical Problems of Mineral Processing*, 35, 161–170.
- [19]. Gul, A., (2004). Flotation Behaviours Of Microlite And Zircon. *Minerals Engineering*, 17, 561–563.
- [20]. Gul, A. (2006). Separation of Microlite from Zircon by Flotation. *Canadian Metallurgical Quarterly*, 45(1), 111–117.
- [21]. Lubbe, S., Munsami, R. and Fourie, D. (2012). Beneficiation of Zircon Sand in South Africa. *The Journal of the Southern African Institute of Mining and Metallurgy*, 7, 583–588.
- [22]. Manhique, A., Kwela, Z. and Focke, W. W. (2003). De Wet Process for the Beneficiation of Zircon: Optimization of the Alkali Fusion Step. *Industrial & Engineering Chemistry Research*, 42(4), 777–783.
- [23]. Biswas, R. K., Habib, M. A., Karmakar, A. K. and Islam, M. R. (2010). A Novel Method For Processing of Bangladeshi Zircon: Part I: Baking, and Fusion with NaOH. *Hydrometallurgy*, 103, 124–129.
- [24]. Da Silva, R. J. F., Dutra, A. J. B. and Afonso, J. C. (2012). Alkali Fusion Followed by a Two-Step Leaching of a Brazilian Zircon Concentrate. *Hydrometallurgy*, 117–118, 93–100.
- [25]. Song, J., Fan, J. F., Liu, J. C., Liu, R., Qu, J. K. and Qi, T., (2015). A Two-Step Zircon Decomposition Method to Produce Zirconium Oxychloride: Alkali Fusion and Water Leaching, *Rare Metals*, 39(4), 448–454.
- [26]. Yuhelda, Y., Amalia, D. and Nugraha, E. P. (2017). Processing Zirconia through Zircon Sand Smelting with NaOH as a Flux. *Indonesian Mining Journal*, 19(1), 39–49.
- [27]. Poernomo, H., Sajima, P. and Pusporini, N. D. (2020). Synthesis of Zirconium Oxychloride and Zirconia Low TENORM by Zircon Sand from Landak West Kalimantan. *Journal of Physics: Conference Series*, 1436, 1-12.
- [28]. Cyriac, B., (2023). Zirconia: Synthesis and Characterization, in Basheer Al-Naib, U. M. (Ed.), *Zirconia - New Advances, Structure, Fabrication and Applications*, IntechOpen, London, 1-32.
- [29]. El-Barawy, K. A., El Tawil, S. Z. and Francis, A. A., (2000). Alkali fusion of zircon sand. *Mineral Processing and Extractive Metallurgy*, 109(1), 49–56.
- [30]. Abdelkader, A. M., Daher, A. and El-Kashef, E., (2008). Novel decomposition method for Zircon. *Journal of Alloys and Compounds*, 460, 577–580.
- [31]. Yustanti, E., Ode, F. A. F. and Sulistiyono, E. (2020). Primary Study of KOH Alkali Fusion – Nitric Acid Leaching Process in Extraction of West Kalimantan Zircon Concentrate. *Materials Science and Engineering*, 763, 1-6.
- [32]. Abdullah, M., Triwikantoro, T., Umamah, C. and Andi, H. J., (2021). The Effect of pH and Calcination Temperature on the  $ZrO_2$  Phase Formation from Natural Zircon Sand of Kereng Pangi. *Jurnal Fisika dan Aplikasinya*, 13(2), 39–48.
- [33]. Mukhachev, A., Shevchenko, V. and Yelatontsev, D. (2023). Zircon Processing in Sodium Carbonate Melt. *Institute of Physics Conference Series: Earth and Environmental Science*, 1156, 1–7.
- [34]. Liu, J., Song, J., Qi, T., Zhang, C. and Qu, J., (2016). Controlling the Formation of  $Na_2ZrSiO_5$  in Alkali Fusion Process for Zirconium Oxychloride Production. *Advanced Powder Technology*, 27(1), 1–8.
- [35]. Ayranci, B., (1989). A Rapid Decomposition Method for Analyzing Zirconia. *Bulletin of the Mineral Research and Exploration*, 109, 75–79.
- [36]. Mashaal, H. (2023). Preparation of Insoluble Zirconate from Egyptian Zircon via Alkali Fusion Process to Enhancement Al Alloy Performance. *Egyptian Journal of Chemistry*, 66(3), 53–57.
- [37]. Subuki, I., (2022). Influence on Ratio of  $NaOH/ZrSiO_4$  in Alkali Fusion for Amang Zircon Sand. *ASM Science Journal*, 17, 1–10.
- [38]. Pusporini, N. D., Suyanti, S. Amiliana, R. A. and Poernomo, H. (2020). Processing and Refining of Tin Tailing Mining. *Journal of Physics: Conference Series*, 1436, 1–11.
- [39]. Yamagata C., Andrade, J. B., Ussui, V., De Lima, N. B. and Paschoal, J. O. A. (2008). *High Purity Zirconia and Silica Powders via Wet Process: Alkali Fusion of Zircon Sand*. Proceeding of 6th International Latin-American Conference on Powder Technology, Búzios, Rio de Janeiro, Brazil.
- [40]. Rahmawati, F., Permadani, I., Soepriyanto, S., Syarif, D. G. and Heraldy, E. (2014). *Double Steps Leaching and Filtration in Caustic Fusion Method to Produce Zirconia from Local Zircon Concentrate*. Proceeding of 7th International Conference on Physics and its Applications, Solo, Indonesia, 99–102.
- [41]. Bidaye, A. C., Gupta, C. K. and Venkatachalam, S. (1999). Studies on the Chlorination of Zircon: Part I. Static Bed Investigations. *Metallurgical and Materials Transactions B*, 30(2), 205–213.
- [42]. Donald, V., (2011). Zirconium Chlorination Behavior: A Literature Review, in EPD Congress Hoboken: John Wiley & Sons, Incorporated, Hoboken, New Jersey, 511–519.
- [43]. Brennan, L. J., Field, R. V., George, T. J and Marshall, R. E. (1984). Chemical beneficiation of zircon concentrates in Western Australia. *International Journal of Mineral Processing*, 13(4)251–258.
- [44]. Philip, M. K., Kent, G. S. and Douglas Ward, D. S. (1995). Zircon Treatment, European Patent Application, No. 95301429.7. Munich, Germany. European Patent Office.
- [45]. Naher, S. and Haseeb, A. S. M. A. (2008). Production and Purification of Zircon Opacifier from zircon found in the coastal area of Bangladesh.



- Journal of Materials Processing Technology*, 205, 203–206.
- [46]. Snyders, E., Potgieter, J. H. and Nel, J. T. (2005). The Upgrading of an Inferior Grade Zircon to Superior Opacifier for Sanitary Ware and Glazes. *The Journal of the South African Institute of Mining and Metallurgy*, 105, 459–464.
- [47]. Aral, H. (2000). Impurities in a Murray Basin zircon sand. Proc. The Australasian Institute of Mining and Metallurgy, Minprex, Melbourne, Australia, September, 373–379.
- [48]. Aral, H., (2000). The Fate of Radionuclides during Processing of Zircon to Zirconia. Proc. Resources Week, Adelaide, SA, Australia, 101–105.
- [49]. Aral, H. (2000). A Novel Process for Radioactive Impurity Removal from Zircon Sand. Proc. 21st International Mineral Processing Congress, Amsterdam, A6-60–A6-66.
- [50]. Aral, H., Sparrow, G. J., McDonald, K. and Norgate, T. E. (2007). Pure Zircon Process For Removing Radionuclides from Zircon Concentrates. *Transactions of the Institute of Mining and Metallurgy*, 116(3), 145–151.
- [51]. Zhang, J., Wang, L. and Jiang, D. (2012). Decomposition Process of Zircon Sand Concentrate with CaO-NaOH. *Rare Metals*, 31(4), 410–414.
- [52]. Saidi, A., El Khawaja, R. and Boffito, D. C. (2024). A Review of Traditional and Intensified Hydrometallurgy Techniques to Remove Chromium and Vanadium from Solid Industrial Waste, *American Chemical Society Engineering Au*, 4(1), 49–70.
- [53]. Chen, Y., Zhou, J., Zhang, L., Peng, J., Li, S., Yin, S., Yang, K. and Lin, Y. (2018). Microwave-Assisted and Regular Leaching of Germanium from the Germanium-rich Lignite Ash. *Green Processing and Synthesis*, 7(6) 538–545.
- [54]. Mizuno, N., Kosai, S. and Yamasue, E. (2021). Microwave-Based Extractive Metallurgy to Obtain Pure Metals: A Review. *Cleaner Engineering and Technology*, 5(17), Article 100306.
- [55]. Xi, F., Li, S., Ma, W., Chen, Z., Wei, K. and J. Wu, J. (2021). A Review of Hydrometallurgy Techniques for the Removal of Impurities from Metallurgical-Grade Silicon. *Hydrometallurgy*, 201, 1 - 18.
- [56]. Du, F., Li, J., Li, X. and Zhang, Z. (2011). Improvement of Iron Removal from Silica Sand using Ultrasound-Assisted Oxalic Acid. *Ultrasonics Sonochemistry*, 18(1), 389–393.
- [57]. Javad, S.M. and Barani, K. (2012). Microwave applications heating in mineral processing, in Cao, W. (Ed), *The Development and Application of Microwave Heating*, InTech, 79-104.
- [58]. Xiao, J., Yuan, J., Tian, Z., Yang, K., Yao, Z., Yu, B. and Zhan, L. I., (2018). Comparison of Ultrasound-Assisted and Traditional Caustic Leaching of Spent Cathode Carbon (SCC) from Aluminum Electrolysis. *Ultrasonics Sonochemistry*, 40, 21–29.
- [59]. Rahimi, G., Rastegar, S. O., Chianeh, F. R. and Gu, T. (2020). Ultrasound-Assisted Leaching of Vanadium from Fly Ash using Lemon Juice Organic Acids. *Royal Society of Chemistry Advances*, 10(3), 1685–1696.
- [60]. Bao, S., Chen, B., Zhang, Y., Ren, L., Xin, C., Ding, W., Yang, S. and Zhang, W. (2023). A Comprehensive Review on the Ultrasound-Enhanced Leaching Recovery of Valuable Metals: Applications, Mechanisms and Prospects. *Ultrasonics Sonochemistry*, 98, 1–23.
- [61]. Jumari, A., Yudha, C. S., Nizam, M., Dyartanti, E. R., Suranto, and Purwanto, A. (2022). An Environmentally Friendly Hydrometallurgy Process for the Recovery and Reuse of Metals from Spent Lithium-Ion Batteries, using Organic Acid. *Open Engineering*, 12(1), 485–494.
- [62]. Lazo, D. E., Dyer, L. G., Alorro, R. D. and Browner, R. (2017). Treatment of Monazite by Organic Acids I: Solution Conversion of Rare Earths. *Hydrometallurgy*, 174, 202–209.
- [63]. Vapur, H., Top, S. and Demirci, S. (2017). Purification of Feldspar from Colored Impurities using Organic Acids. *Physicochemical Problems of Mineral Processing*, 53(1), 150–160.
- [64]. Urias, P. M., Dos Reis Menêzes, L. H., Cardoso, V. L., Resende, M. M. and De Souza Ferreira J. Leaching with Mixed Organic Acids and Sulfuric Acid to Recover Cobalt and Lithium from Lithium Ion Batteries. *Environmental Technology*, 42(25), 4027–4037.
- [65]. Omid, M. H., Nuri, O. S. and Tavakoli, H. (2018). Optimization of Ilmenite Dissolution by Synergistic Effect of Oxalic Acid and Hydrochloric Acid for Preparing Synthetic Rutile. *International Journal of Nonferrous Metallurgy*, 7(3), 25–38.
- [66]. Hussaini, S., Tita, A. M., Kursunoglu, S., Kaya, M. and Chu, P. (2024). Leaching of Nickel and Cobalt from a Mixed Nickel-Cobalt Hydroxide Precipitate using Organic Acids. *Minerals*, 14(3), 1-12.