

Upgrading the Zirconium Content in the Egyptian Zircon Concentrate Using Alkaline Molten Salt and Leaching Processes

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Abstract—Zircon is one of the heavy minerals in black sand; Zirconia, Zirconium, and hafnium can be extracted from zircon minerals. Zirconium is a corrosion-resistant metal that is used in high-performance pumps and valves and nuclear reactors to provide the cladding. Zirconium oxide (zirconia "ZrO₂") is a material with very high resistance to crack propagation. It also used in structural applications in engineering, such as in the manufacture of cutting tools, gas sensors, refractories, and prevention of crack propagation. Also, zirconia has very high thermal expansion and is, therefore, often the material of choice for joining ceramic and steel. In this paper, the upgrading process of zircon concentrate separated from the Egyptian black sand deposits was carried out using leaching and fusion process. Chemical composition was analyzed before and after leaching using XRF. The powder morphology was examined using SEM and EDX. The optimum leaching parameters were HCl as leaching agent with 6 M concentration, 80 °C, 1-6 solid-liquid ratio, and 2 hrs leaching time. Results showed that zirconium content was upgraded from 43% to 77% by leaching before calcination. A further upgrade to 88% was developed by calcination at 650 °C for 2 hrs. The zirconium content was upgraded from 43% to 91% by the fusion of ZrSiO₄ concentrate with the molten salt (NaOH-KOH; 50-50 mol%) under the conditions of 1:1 KOH-NaOH/ZrSiO₄ mass ratio and 600 °C temperature for 0.5 hr.

Index Terms— Egypt, Black Sand, Zircon, Zirconium, Upgrading, Leaching, Alkali Fusion.

1 INTRODUCTION

The Egyptian black sands placer deposits located in the Mediterranean Coastal Plain contain many mineral species since they have been derived from igneous and metamorphic rocks. [1]. It is well known that black sand deposits contain various heavy economic minerals such as Magnetite, Ilmenite, Monazite, Zircon, Monazite, and rutile [2]. One of these essential minerals is zircon (ZrSiO₄), which is usually associated with small amounts of hafnium (1-3 wt. %), a chemically similar element (both elements belong to Group 4 of the Periodic Table) [3]. Zircon has low thermal expansion and good resistance to abrasion and generally used in the foundry industry as well as for manufacturing acid-resistant and fire-resistant glassware [1], [4], [5], [6], [7].

Zirconia, which is one of the Zirconium chemicals, has remarkable properties such as low thermal conductivity, flexural strength, resistance to crack propagation, improved fracture toughness, and excellent biocompatibility [8], [9]. Zirconia, due to its impressive characteristics, has attracted particular attention in multi-industrial and scientific applications such as the ceramic industry and biomedical applications. Zirconia can be used in hip and knee prostheses, hip joint heads, tem-

porary supports, tibial plates, dental crowns [10], [11], [12]. Moreover, zirconia toughened alumina ceramic foams can be used in potential bone graft applications [13]. Also, thin films of zirconia have beneficial ceramics properties that offer various possibilities for technological applications such as optical coating, thermal barrier, catalysis, or catalytic supports [14].

Furthermore, zircon is the primary source for the commercial production of zirconium, its compounds, and alloys [1]. Zirconium is a vital element, as it has a unique combination of properties. Zirconium has good strength at elevated temperatures, corrosion-resistant and does not form highly radioactive isotopes. Therefore, it can be used in nuclear fuel rods cladding, reactor-core structures, chemical piping in corrosive environments, heat exchangers, and many biomedical alloys [15].

Many processes can be used to extract zirconia or zirconium from zircon, for example, thermal dissociation, decomposition by fusion, acidic leaching, and many other methods, which may be explained elsewhere [16], [17], [18], [19]. However, the percent of zirconium or Zr-content plays a crucial role in the process of extraction. It affects the efficiency and recovery of the extraction process significantly.

Therefore, it is highly required to improve the Zr-content to improve the process of extraction. Hence, the present work aims to upgrade the zircon concentrate separated from the Egyptian black sand deposits using wet processes such as leaching and fusion in the light of the economic and environmental impact. Quantification of the optimum leaching parameters was developed. The effect of calcination and fusion processes on the upgrading process was evaluated.

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2 EXPERIMENTAL PROCEDURE

2.1 Materials

The material used in this study is zircon concentrate separated from Egyptian black sand deposits provided by the Nuclear Materials Authority, Cairo, Egypt. As received sample from zircon concentrate has been analyzed using XRF. The main elements associated with zircon and their percentages shown in Table 1

TABLE 1
XRF ANALYSIS OF THE ZIRCON CONCENTRATES

Element	% Content
Cu	5
Zr	42.3%
Zn	< 2
Sr	< 2
Pb	< 2

2.2 Leaching Method

Firstly, the sample was analyzed to identify the various elements associated with zircon and their percentages (mineralogy) for the aim of choosing a suitable method to upgrade zircon. The XRF analysis of the studied concentrate shows that the Zr-content in the zircon concentrate is equal to 42.3%. Moreover, there are some traces from other elements such as Ba, Cr, and Y....etc.

Zircon was conditioned with 17.5 M of NaOH solution 70% as concentration for 3hrs at 120 °C and S/L=1:5, and this step was constant in all procedures as the initial step. The second step includes these procedures (leaching, washing, filtration, and calcination). The optimum leaching parameters such as time, temperature, acid molarity, and S/L were determined during this procedure.

Fig. 1 summarizes all treatment processes. The molarity was quantified at (4, 5, 6, 7, 8 M), the time varied from (0.5 to 3 hrs with an 0.5 hr intervals, the temperature changed from (25 to 180 °C), and the S/L Ratio was evaluated at (1:4, 1:5, 1:6, 1:7, 1:8). After this, the samples were produced are analyzed to study the upgrading of zirconia (ZrO_2) from zircon concentrate.

2.3 Fusion with Sodium and Potassium Hydroxide Method

Aqueous hydroxide (NaOH and KOH) 50 wt% solution was prepared to be used as the decomposition agent of zircon sand. The zircon sand was mixed with (NaOH-KOH; 50-50 mol%) under the conditions of 1:1 KOH-NaOH/ $ZrSiO_4$ mass ratio, as shown in Fig. 2. The mixture was carefully charged into an iron crucible and set in a crucible furnace. The alkaline fusion reaction was conducted following thermal treatment: heating with rate 20 °C/min up to 100 °C, holding at this temperature for 1 hr, and then heating with rate 20 °C/min up to 200 °C, holding for 1 hr, and finally, the temperature was increased to 600 °C for 2 hrs. Caustic frit is formed, a mixture of

sodium or potassium zirconate and silicate. This frit was washed with water, removing the soluble sodium silicate and hydrolyzing the zirconate to impure hydrous zirconium oxide. The water-leached frit was treated in 6M HCl at 120°C for obtaining an impure zirconyl chloride solution. Undecomposed zircon remains in the insoluble residue and is separated from the zirconyl chloride solution by filtration.

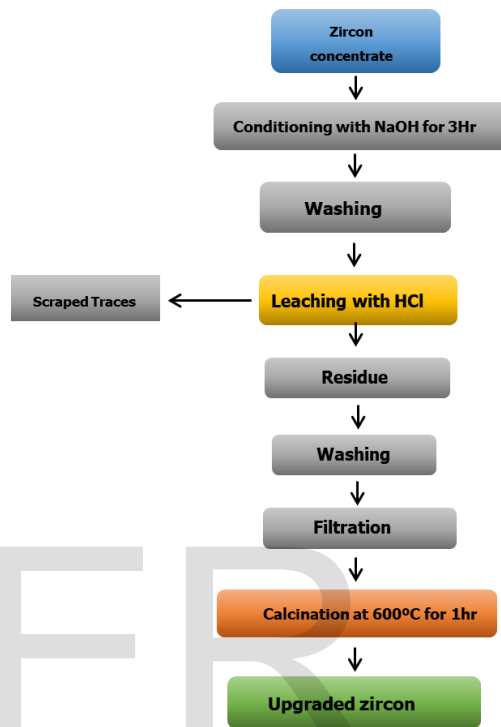


Fig. 1 Flow chart of the leaching process for upgrade zirconium content.

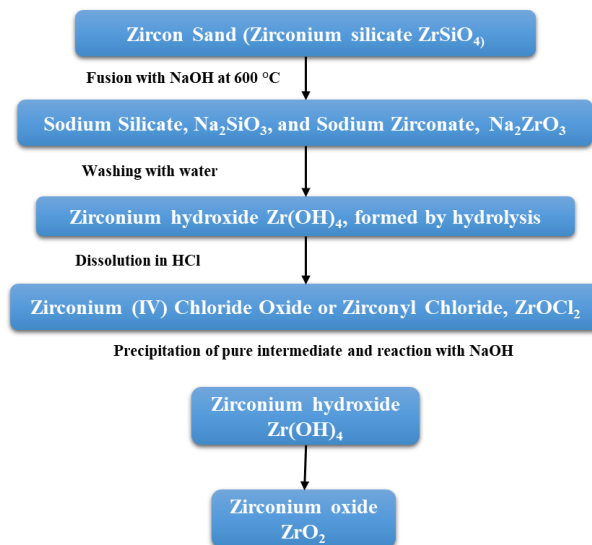


Fig. 2 Flow chart summarizes fusion with metal hydroxide method

2.4 Characterization

The chemical composition of the as-received and produced

samples were characterized using X-ray fluorescence (XRF) and Energy-dispersive X-ray spectroscopy (EDX). Powder morphology and the effect of calcination were evaluated using a Scanning Electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Leaching Method

I - Effect of HCl concentration

Various hydrochloric acid concentrations ranged from 4 to 8 M have been applied to study the effect of HCl concentration on the leaching process. Equation (1) describes the reaction of zircon paste with HCl:



Fig. 3 shows that the Zr-content has significantly increased from $\approx 43.3\%$ to reach $\approx 60\%$ at 5M. Moreover, Zr-content increases to 75%, with the increase of the HCl concentration to 6M. However, a further rise in the HCl concentration (7 and 8 M) show no significant effect upon the Zr-content (Almost the same). Therefore, 6M HCl is considered as the best HCl concentration in this study.

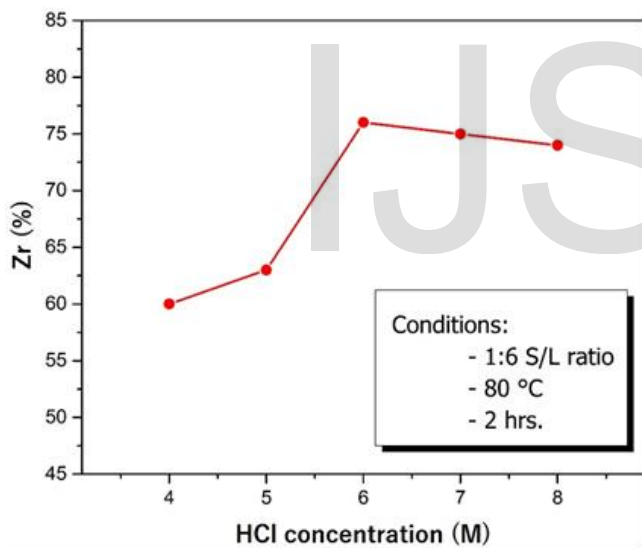


Fig. 3 Shows the effect of HCl concentration

II - Effect of S/L Ratio

The effect of S/L ratios 1:4, 1:5, 1:6, 1:7, and 1:8 between zircon and 6 M HCl on the leaching of zircon was studied. The results are presented in Fig. 4. As shown in this figure, the Zr-content increases from 42.3% to 50% at a 1:4 S/L ratio. Moreover, at 1:6 S/L ratios, Zr-content increased to reach 75% then started to decrease by increase the S/L ratio to 1:7 and further increase at 1:8 S/L ratio. It seems that the higher dissolution affecting ZrO_2 appears at the range of 1:6 to 1:8 S/L ratio. Therefore, the 1:6 solid to liquid ratio is considered as the best condition under the circumstances of this study.

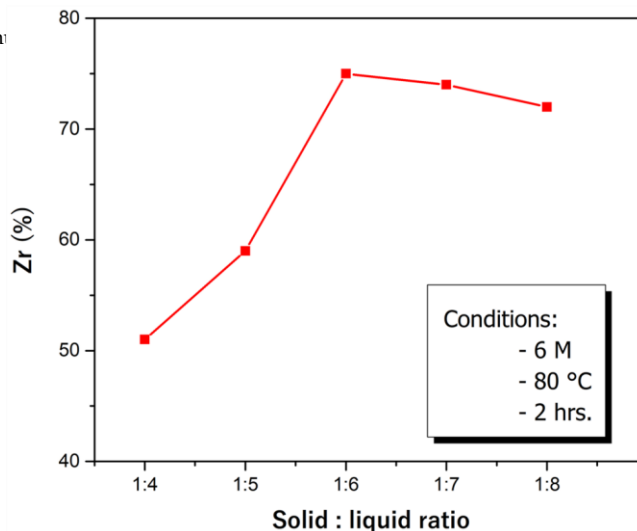


Fig. 4 shows the effect of S/L Ratio

III - Effect of temperature

The effect of temperature on the upgrading process was investigated at various temperatures ranged from room temperature to 180 °C, as shown in Fig. 5. As shown in this figure, the temperature undoubtedly affects the upgrading process, the higher the leaching temperature, the higher the Zr-content. It was noticed that below 60 °C, there is no significant effect of temperature upon upgrading performance. However, Zr-content is sharply increased with increasing the temperature up to 75 °C, then slightly increase up to 80% at 120 °C. Further increase in the temperature led to a gradual decrease in the Zr-content to reach 76 and 72% at the solution temperature of 140 and 160 °C, respectively. These results indicate that the overcoming of bonds between different components was preferred at a higher temperature, and the best temperature condition is 120 °C. However, due to the slight difference in Zr-content between 120 and 80 °C, and cost and environmental considerations, 80 °C is selected as the best temperature condition in the current study.

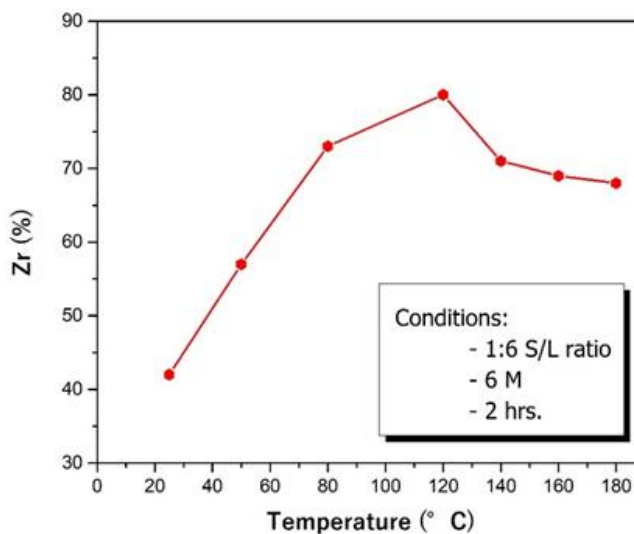


Fig. 5 shows the effect of temperature.

IV - Effect of leaching time

The effect of leaching was studied in the time range from 0.5 to 3 hours with 0.5 hr intervals while fixing the other parame-

ters at their optimized values. Fig. 6 shows that Zr-content increases with increasing the time until it reaches about 75% at 2 hrs. However, it slightly decreases by increasing time to 2.5 and 3 hrs. Consequently, 2 hr considered the best condition in the current study.

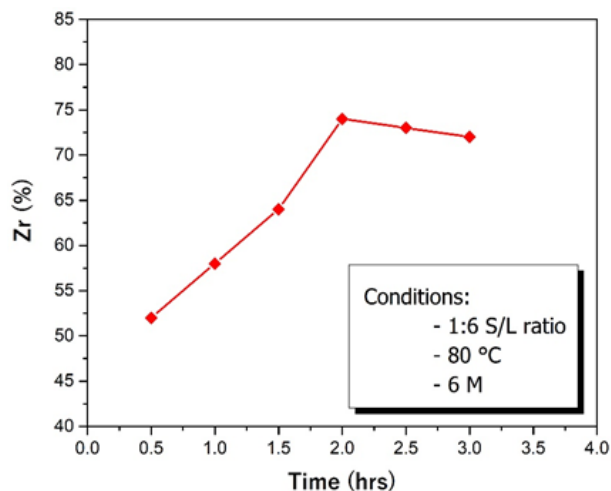


Fig. 6 shows the effect of temperature

After applying the leaching process by using the optimum conditions concluded from each step, as discussed earlier, Energy-dispersive X-ray spectroscopy (EDX) investigation was performed on selected samples. The EDX spectrums shown in Fig. 7(a), reveal the existence of Si, Zr, and small traces of Ti in the investigated sample. Moreover, the results of EDX analysis confirms the upgrading from 42.3% to 80% Zr-content before calcination. On the other hand, the scanning electron microscope images shown in Fig. 7(b) explain that powder size is ranging from 50 μm to 110 μm.

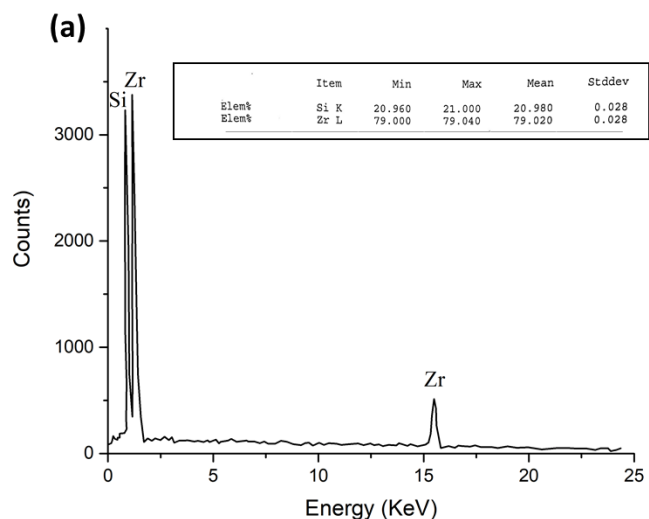


Fig. 7 (a) EDX spectrum of the upgraded sample

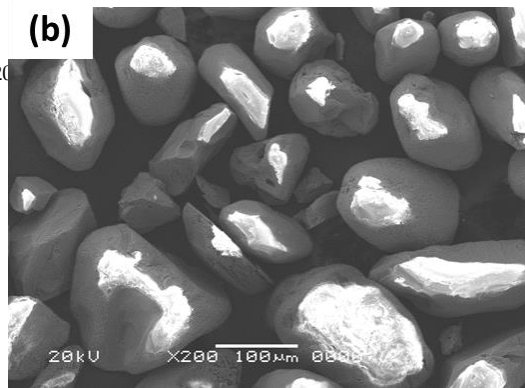


Fig. 7 (b) SEM images of zircon concentrate

V - Effect of calcination

Calcination was performed at 650 °C for 2 hrs after the leaching process. The samples were analyzed using XRF. The results of XRF showed that there is a significant increase in the Zr-content of the analyzed samples to ≈ 88%. The EDX analysis confirms the upgrading of Zr-content after calcination, as shown in Fig 8.

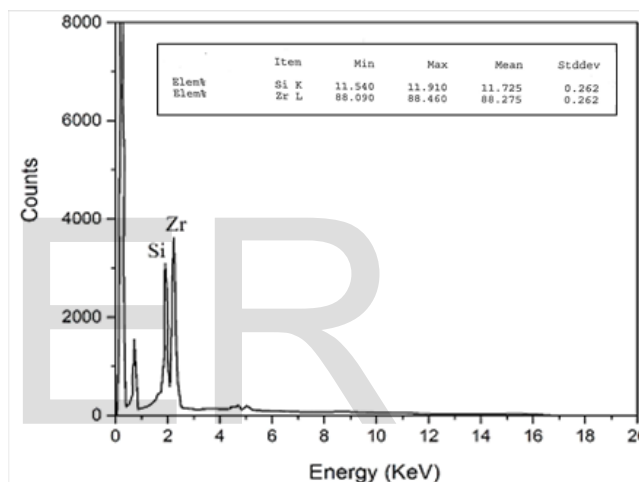


Fig. 8 EDX spectrum of the upgraded sample after calcination

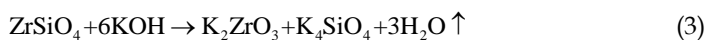
3.2 Alkali Fusion

The fusion of the zircon concentrate with sodium hydroxide is a common practice used in leaching [2], [10], [11]. However, as far as the authors know, using potassium hydroxide is quite limited.

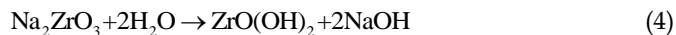
According to the state diagram of the KOH-NaOH system, the melting temperature of NaOH and KOH are equal to 321 and 404 °C, respectively. At the same time, the eutectic composition containing 50 mol % KOH, melts at 170 °C [12]. Which firmly allows obtaining a low-temperature fusion alkali process [13]. Therefore, in the current study, a mixture of 50% mol of NaOH-KOH was used in the fusion process under the conditions mentioned before (see the experimental part).

The produced fused mass is composed of a mixture of sodium and potassium zirconate, water-soluble and insoluble sodium silicates, unreacted sodium hydroxide, unreacted zircon, and metal impurities. The main chemical reactions that occur between sodium and potassium hydroxide and zircon during the alkali fusion process are shown in equation (2) and (3) [14]





Separation of metal zirconate from metal silicate is based on the leaching of the fused mass with water. While metal meta-silicate and unreacted sodium hydroxide are soluble in water, the insoluble residue with other insoluble compounds, as shown in equation (4) and (5). [15]



This frit was washed with water, removing the soluble metal silicate and hydrolyzing the zirconate to impure hydrous zirconium oxide. Impure hydrous zirconium oxide treated in 6M HCl at 120°C for obtaining an impure zirconyl chloride solution. Undecomposed zircon remains in the insoluble residue and is separated from the zirconyl chloride solution by filtration.

After that, the washed frit was dried in a muffle furnace, followed by leaching under the generated optimum conditions, which are HCl as leaching agent with 6 M concentration, 80°C, 1-6 solid-liquid ratio, and 2 hrs leaching time.

The product was analyzed by EDX to evaluate the Zr-content. As shown in Fig. 9 (a), Zr-content increased to reach 91% in comparison to 88% appeared in leaching without the fusion process. It means that the separation process of quartz and silicate from zircon sand runs well and makes the ZrO₂ content increase in final concentrate. Although there is a slight increase in the Zr-content in comparison to the leaching method, this increase still below the expected one; this attributed to the agglomerated irregular grain observed in the SEM micrographs shown in Fig. 9 (b). This agglomeration causes the surface area to be decreased drastically. Hence, the performance of the leaching process decreased. Generally, it is strongly believed that applying mechanical milling after fusion and before applying the leaching process will result in enhanced leaching performance due to the increase in the surface area conducted by milling,

4 CONCLUSION

The zirconium content in the Egyptian black sand was successfully upgraded by leaching method, the best leaching parameters obtained in this work are: 6M HCl as the acid concentrate, S/L equal to 1:6, the temperature is 80°C and time is 2hrs. Zirconium content was upgraded from 43% to 80% by applying the best concluding leaching parameters. The calcination process notably increased the zirconium content from 80% to 88%. The addition of the mixture of NaOH and KOH in the fusion process has proved to be effective in breaking the strong bond between ZrO₂ and SiO₂ of zircon sand at 600°C. The upgrading of zircon content increased from 43 to 91% by fusion process followed by leaching, and this percentage is expected to increase significantly with the increase in the surface area developed by mechanical milling after fusion.

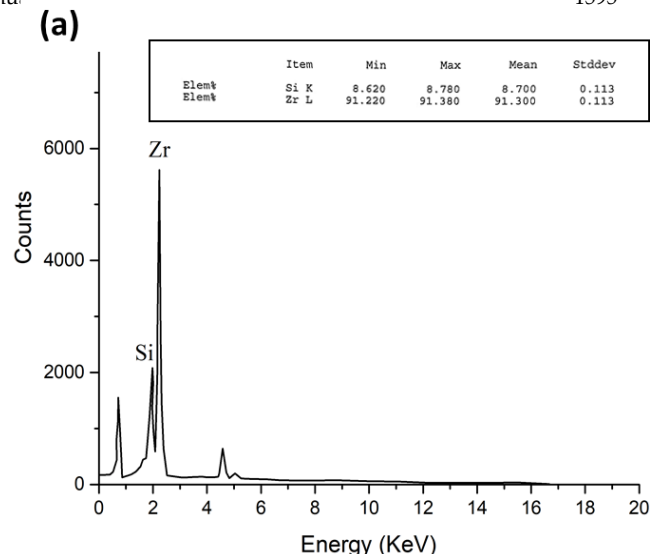


Fig. 9 (a) EDX spectrum for zircon concentrate after fusion

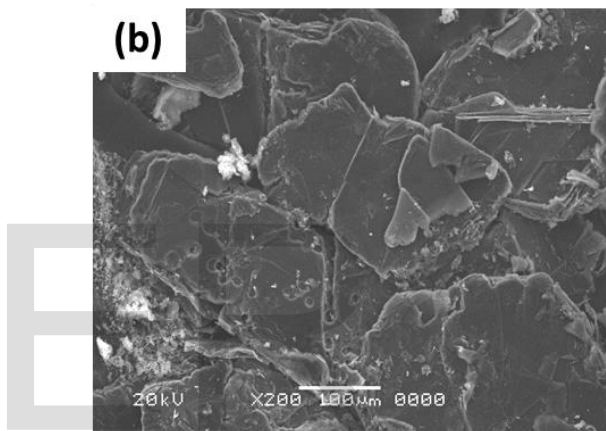


Fig. 9 (b) SEM micrograph showing the agglomerated frit after fusion with NaOH-KOH mixture

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