

Article

Zirconia Enrichment of Zircon from Arikya, Nasarawa State, Nigeria, by Magnetic and Gravity Separation Processes for Use as Reinforcing Agent in Composite Formulation

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Abstract: Acceptable zircon for composite formulation in the aerospace industry requires that the mineral contains a minimum of 65% zirconia (ZrO_2). Despite having vast deposits of zircon, Nigeria's aerospace industry has historically relied primarily on imported mild steel tubes for solid rocket motor cases (SRMCs) construction, resulting in three major challenges: low strength-to-weight ratio, pressure, and temperature containment. In this study, the Arikya zircon deposit located in northern Nigeria was investigated with the aim of upgrading low-grade zircon ore using magnetic and gravity separation processes for use in composite formulation for SRMCs. The dry high-intensity magnetic separator (DHIMS) produced a ZrO_2 grade of 52.48%, recovery of 57.99%, and an enrichment ratio of 0.78 with a separation efficiency of 0.56, while the air-floating separator (AFS) generated the highest of 65.52% ZrO_2 grade with 70.81% recovery and enrichment ratio of 1.25 with a separation efficiency of 0.25. The ZrO_2 content increased from 40.77 to 65.52% after beneficiation. Iron oxide and titanium dioxide contaminants at 0.73 and 0.83% were reduced to 0.66 and 0.54%, respectively, while the specific gravity increased from 4.4 to 4.6 g/cm³. The ZrO_2 content and specific gravity were improved to the minimum standard specified for zirconia-reinforced composite application and competed effectively with industrially/globally accepted zircon. These results demonstrated the efficacy of combining DHIMS and AFS to upgrade the low-grade zircon ore from Arikya, Nasarawa State.

Keywords: magnetic methods; zircon upgrade; zirconia-reinforced composite; heavy mineral; mineral processing; material characterization; gravity methods; separation efficiency; material applications

1. Introduction

Nigeria is endowed with abundant natural resources such as raw minerals [1,2]. The nationalization policy of the early 1970s caused foreign company owners to leave the Nigerian mining industry, which caused a sharp decline in mineral production. After petroleum was discovered in 1958 and the global energy crisis of the 1970s, the Federal Government of Nigeria (FGN) finally turned its focus from the solid mineral sector to the petroleum sector, which resulted in very poor activities in the mining sector [3]. Unfortunately, these raw minerals have been neglected and underutilized despite having a wide range of industrial applications. Zircon is one example of such a mineral that has not been adequately explored. The FGN, in a bid to diversify the economy away from the petroleum sector, subsequently

recognized these potentials and eventually established legislation banning the export of deep-mining raw minerals and mandating that they be processed domestically first in the country. These legislative measures are intended to promote both domestic and foreign investment in the country's local mineral resources [2,4]. The government's ongoing promotion of the diversification of the mineral sector has interested numerous domestic and foreign mining entities in the exploration of Nigerian mineral deposits [5]. Although the Nigerian zircon reserve estimate has not yet been identified, its potential is significant [6].

Zircon (ZrSiO_4) has a zirconia (zirconium oxide, ZrO_2) theoretical composition of 67.2%, 32.8% silica, and a small percentage of hafnia (hafnium oxide, HfO_2), generally between 0.4 and 2%. It has a specific gravity of between 4.2 and 4.86 g/cm^3 , and in terms of electrical and magnetic properties, zircon is non-conducting and non-magnetic [7–10]. Zircon can be processed to produce zirconium chemical compounds like zirconia or zirconium metal [11]. Zirconia is produced through different techniques, including reacting zircon ore with caustic soda and the sol-gel process. Zirconia has a high melting point ($2700 \text{ }^\circ\text{C}$) and low thermal conductivity [12,13]. These properties are essential when considering their use in the aerospace industry. Different cast materials (metals, polymers, and natural fibers) reinforced with particulates of zircon acting as reinforcing agents are being studied for various applications, especially in the aerospace industry where the material's lightweight and the ability to withstand high temperatures and harsh environments are the basic considerations. In the aerospace industry, materials that can function in oxidizing or corrosive atmospheres at temperatures higher than $2000 \text{ }^\circ\text{C}$ and sometimes, for a long lifetime are needed for nozzles, rocket and hypersonic vehicle components, re-entry vehicles, engine components, and leading-edge applications [14]. Zirconia-reinforced composite is one example of such material [14–16]. Other applications of zircon and its concentrate include the fabrication of ceramic membranes, the development of passive energy-saving systems, fuel cells and batteries, nanomaterials, optical materials, electronics, and solid-state devices.

Zircon of low grade needs to be upgraded to have the minimum purity, composition, and specific gravity needed for aerospace and other industrial applications [6]. The combined content of zirconia and hafnia is a standard way to determine the purity of zircon. Typically, zirconia content (expressed as $\text{ZrO}_2 + \text{HfO}_2$), iron oxide (Fe_2O_3), aluminum oxide (Al_2O_3), titanium dioxide (TiO_2), and, occasionally, radioactivity (U+Th) are used to describe zircon specifications. Additionally, standard guaranteed ranges are given as follows: $\text{ZrO}_2 + \text{HfO}_2$: minimum 65%, Fe_2O_3 : maximum range from as low as 0.04 to 0.25%, TiO_2 : maximum range from 0.10 to 0.30% [10,17]. A high percentage of zircon implies that the mineral has a high ZrO_2 content [18]. For zircon to be used efficiently, interfering impurities or contaminants must be removed because they can affect performance, reduce its value, and limit its industrial applications. The differences in specific gravity, magnetic, and conductive characteristics of heavy mineral species are frequently used to enhance the mineral [19–21]. The separation processes for zircon upgrade have extensively been explored and reported in the literature [19,21–28]. Nevertheless, these findings do not contain much information on specific procedures for the appraisal of separation processes of zircon upgrade in Nigeria with a focus on the performance of the processes and provide a corresponding comparison of the locally obtained vis a vis the industrially/global accepted zircon. The preceding study on zircon from Nigeria has focused on the minerals' characterization, location database, suitability for different industrial applications, and geological age. Specifically, the beneficiation of the Arikya zircon deposit to meet the minimum industrial/global standard, performance, and separation efficiency have not been addressed, reported, and documented.

Over the years, Nigeria's Space Agency has been constructing SRMCs (nozzle and motor components) using imported mild steel tubes [29]. This has led to several challenges, which include the cost of importing the mild steel and the overall cost of construction, launching, and performance of the sounding rockets. The issues associated with using mild steel other than composite for SRMCs include low strength-to-weight ratio, pressure, and temperature containment. These challenges have a significant influence on the lift-off mass of rockets and, by extension, reduce the targeted altitude. The SRMCs constructed with

mild steel do fail during static tests and sometimes when the rocket is in flight. This could be a result of the material not being able to withstand the generated pressure and heat from propellant combustion. In the fourth quarter of 2019 alone, the FGN spent billions of Naira valued at over 1 million United States dollars on the importation of mild steel tubes [30]. These monies could have been channeled into other meaningful developmental projects. The scientific information presented in this study is an effort to discourage the wastage of resources through foreign exchange and over-dependence on importation, but rather looking inwards on the local materials or minerals that can outperform its counterpart, in this context, zirconia (synthesized from zircon) when used as a composite reinforcing agent for the construction of SRMCs as against using mild steel.

This study aimed to determine the feasibility of magnetic and gravity separation processes for upgrading the quality of the local zircon ore from the Arikya deposit by increasing the ZrO_2 content to compete favorably with zircon products on the global market. The manuscript, in a nutshell, seeks to provide the value addition and prospects of upgraded zircon from Nigeria to developing aerospace industries/agencies in Africa, as well as to serve as a reference for the development of similar low-grade zircon deposits. For Nigeria, the findings from this study will encourage an increase in the utilization of local content; export of the beneficiated zircon to significantly impact the economy, increase foreign exchange, and lower dependence on oil; and reduction in the wastage of resources through the importation of materials or minerals that can be sourced and processed locally.

2. Materials and Methods

2.1. Feed Material

The unprocessed Arikya zircon sample reported in our previous work [6] was collected and crushed using a jaw crusher (Retsch GmbH, Haan, Germany, Jaw crusher BB 50 rostfrei-rostoffrei); operating conditions: 0.0002 m gap width, and a speed of 89.0118 m/s, and a representative weight of 100 g was used for the study. The chemical composition analysis of energy dispersive X-ray fluorescence (EDXRF) of the unprocessed zircon, as shown in Figure 1, indicated that the sample mainly contains zirconia, ZrO_2 (40.77%); quartz, SiO_2 (17.61%); apatite, P_2O_5 (10.48%); tantalum pentoxide, Ta_2O_5 (7.00%); cerium (IV) oxide, CeO_2 (4.54%); potassium oxide, K_2O (4.00%); and other heavy minerals (15.60%), making it a relatively low-grade zircon mineral.

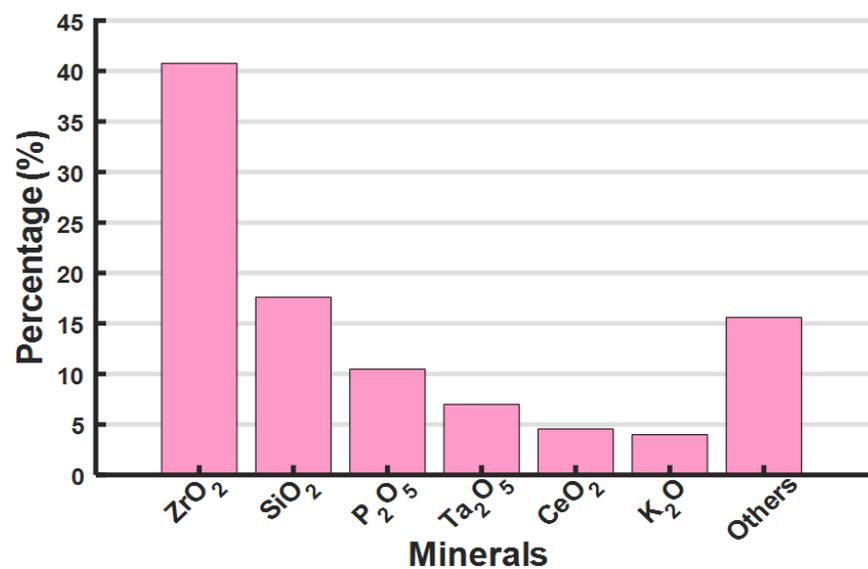


Figure 1. Oxide chemistry of feed sample (unprocessed Arikya zircon).

2.2. Study Area

Arikyā, depicted in Figure 2, is a town located in the Lafia local government area (L.G.A.) in Nasarawa State of Nigeria. Lafia is the capital of Nasarawa State and the largest town. According to the 2006 census, it has a population of 330,712 inhabitants [31]. Lafia experiences two different seasons, the dry and rainy seasons, with an average temperature of 30 °C. The L.G.A. has a tropical savannah climate, with an estimated average humidity of 40% and an estimated average wind speed of 11 km/h [32,33]. Arikyā lies between latitude 8°29'17.99" N and longitude 8°30'59.99" E.

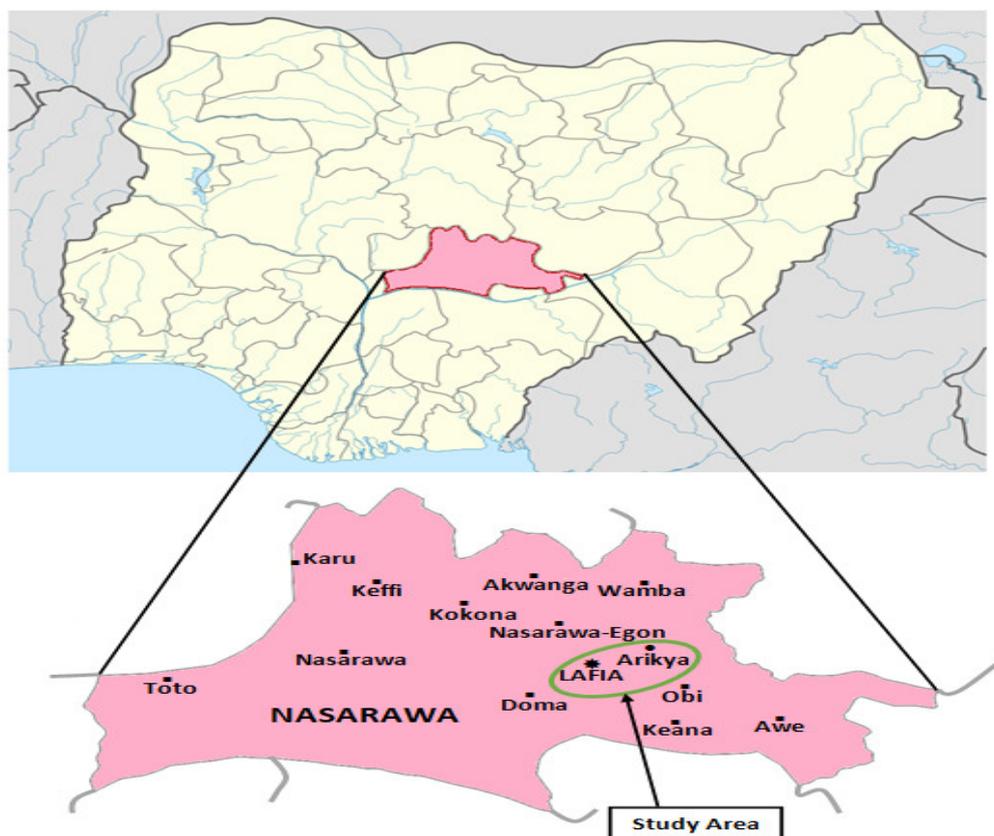


Figure 2. The geographic location of the study area. The star indicate Lafia L.G.A., Nasarawa State, Nigeria and circled in green to show the study area (Arikyā town in Lafia L.G.A.).

2.3. Experimental Methods

To achieve the beneficiation and characterization operations, the flowsheet presented in Figure 3 was utilized. The upgrading of the unprocessed Arikyā zircon was carried out in this order: magnetic, followed by gravity separation processes. After the separation, the processed zircon (concentrate fraction/final product) was characterized. After each separation, the fractions (magnetic, non-magnetic, concentrate, and tailings) were handpicked and weighed using a digital weighing balance (NewClassic MF, MS8001S/01, Mettler Toledo, Greifensee, Switzerland), and a small portion of each was packed in zip-lock polymer bags, labeled for identification, and kept for characterization (see Figure 3). To prepare the portions for characterization, they were crushed and sieved with an Endecotts sieve (Octagon 200, Endecotts Limited, London, UK) to obtain a particle size that is <50 μm.

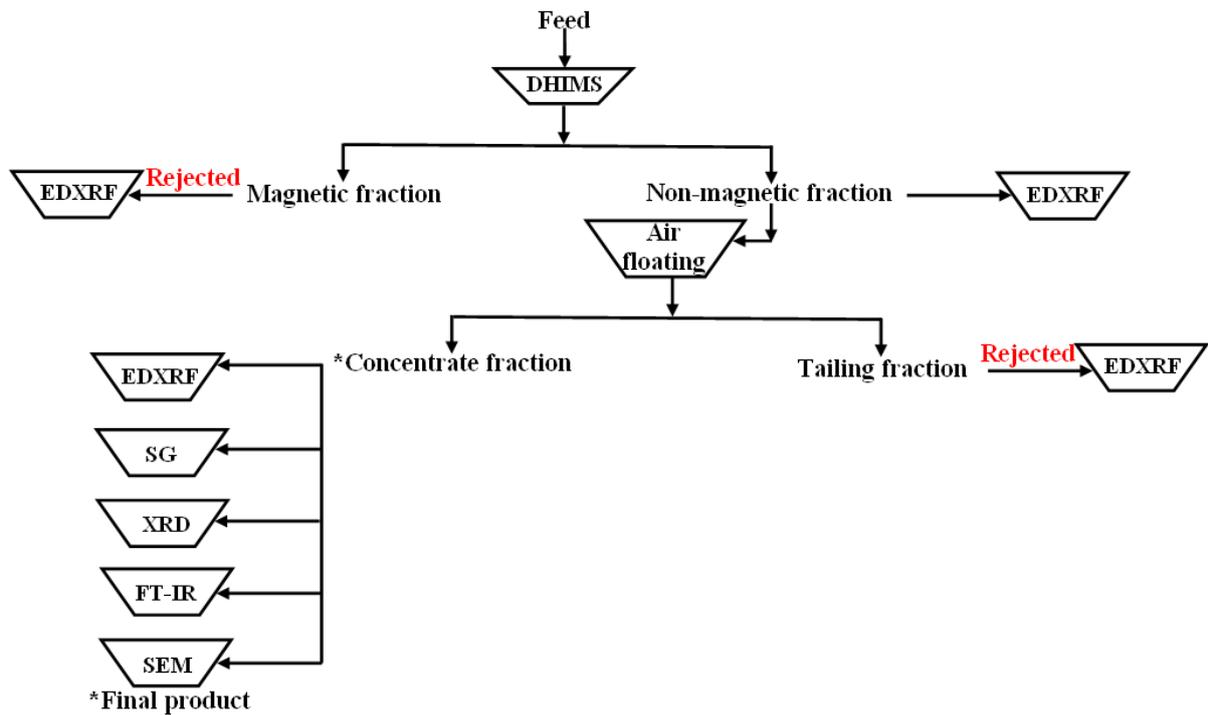


Figure 3. Flowsheet for the beneficiation and characterization operations. The 'Rejected' in red indicated for magnetic and tailing fractions were because zircon is non-magnetic and mineral processing separates minerals into two or more products, with the valuable minerals in the concentrate fraction and the gangue in the tailing fraction. The asterisk denotes the concentrate fraction (final product) after the beneficiation.

2.3.1. Beneficiation Testwork

Regardless of the process employed, the goal of mineral processing is always the same: to separate the minerals into two or more products, with the valuable minerals in the concentrates, the gangue in the tailings, and the "composite" particles in the middlings. The testwork aimed to upgrade the unprocessed Arikya zircon by increasing the zirconia (ZrO₂) content, which was around 40.77%, to an industrial/global grade of 65.00%.

Magnetic Separation

The feed (100 g) was fed to a dry high-intensity magnetic separator (DHIMS) (Rapid Magnetic Separator 4-3-15 OG, Birmingham, UK) shown in Figure 4 to recover magnetic and non-magnetic fractions at a standard feed rate of 50 kg/h.

A magnetic induction of 1.8 T was applied, with the shutter slightly opened to allow an even gradual dispersion of the feed onto the magnetic belt. The separator is made up of three magnetic discs for the lifting and pinning processes of the products, two of which are for magnetic minerals and the other for non-magnetic minerals. The magnetic minerals were lifted by the magnetic discs as they passed through the conveyor belt and discharged through discs 1 and 2 into the collection tray, while the non-magnetic minerals were pinned to the conveyor belt and collected via disc 3 into the collection tray. To enhance zirconia recovery, the produced non-magnetic fraction was re-circulated back to the magnetic circuit twice (total pass = 3). The magnetic and non-magnetic fractions were weighed, and the non-magnetic fraction was subjected to gravity separation.



Figure 4. Rapid magnetic separator (source: National Metallurgical Development Centre (NMDC), Jos, Nigeria).

Gravity Separation

To enrich the grade of the zircon concentrate, the non-magnetic fraction was fed into the hopper and the deck of a pneumatic air-floating separator (AFS) (Kip Kelly, MY-1151, Winnipeg, MB, Canada) shown in Figure 5 at a feed rate of 50 kg/h with the deck slanting at an angle of 180° and the air inlet opening at 2 cm to yield the concentrate, middling, and tailings fractions. The resulting middlings were re-circled back to the gravity circuit to produce concentrate and tailings. To enhance zirconia recovery, the produced concentrate fraction was re-circulated back to the gravity circuit twice (total pass = 3).

The metallurgical process assessment of any concentration operation can be expressed in terms of the recovery (R) achievable for any given value of concentrate grade (G) and the enrichment ratio (ER).



Figure 5. Pneumatic air-floating separator (source: National Metallurgical Development Centre (NMDC), Jos, Nigeria).

Recovery in the case of concentration of metallic ore is the total metal contained in the ore that is recovered from the concentrate. The percentage recovery R can be calculated using weights and grades, given by Equation (1) [34]:

$$R (\%) = \frac{C_c}{F_f} \times 100 \quad (1)$$

where C and F are the weights of concentrate and feed, and c and f are the grades of elements (ZrO_2 , SiO_2 , and Fe_2O_3) in concentrate and feed, respectively.

The grade, or assay, typically refers to the content of the material's marketable end product. Several metals are sold in their oxide form; consequently, the grade can be expressed in terms of the marketable oxide content.

The enrichment ratio ER is the ratio of the grades of minerals in concentrate c to the grades of elements in feed f . This is expressed by Equation (2) [35]:

$$ER = \frac{c}{f} \quad (2)$$

2.4. Characterization of Arikya Zircon Beneficiated Fractions

2.4.1. Chemical Analysis

The chemical analyses of the magnetic, non-magnetic, concentrate, and tailings fractions (see Section 2.3) from the two separation processes were carried out using energy dispersive X-ray fluorescence (EDXRF). A weight of 2 g was obtained for each portion and placed into the sample holder in a vacuum for 10 min before being transferred to the XRF (ARL QUANT'X EDXRF analyzer 9952120, Thermo Fisher Scientific, Basel, Switzerland).

2.4.2. Specific Gravity

The specific gravity of the concentrate fraction was determined by the pycnometer method, following the American Standard Testing Method ASTM D 854-00 [36]. A portion of the concentrate fraction was poured inside the pycnometer, mixed with distilled water, and swirled with a glass rod (soaked for 10 min at an operating temperature of 25 °C). The specific gravity SG was calculated using Equation (3) [37]:

$$SG \text{ (g/cm}^3\text{)} = \frac{m_2 - m_1}{(m_4 - m_1) - (m_3 - m_2)} \quad (3)$$

where m_1 is the weight of the pycnometer, m_2 is the weight of the pycnometer + sample, m_3 is the weight of the pycnometer + sample + water, and m_4 is the weight of the pycnometer + water.

2.4.3. Mineralogical Evaluation

The mineral or crystalline phase of the concentrate fraction was identified using an X-ray diffractometer (ARL'XTRA, Thermo Fisher Scientific, Basel, Switzerland) with a revolving anode at 45 kV and 40 mA and illuminated using a Cu anode material (scan speed was 2°/s from 4.99 to 77.99° with a step size of 0.026261° and dwell time of 29.07 s).

2.4.4. Functional Groups

The functional groups of the concentrate fraction were identified using an FT-IR spectrophotometer (Nicolet iS50 FT-IR, Thermo Fisher Scientific, Waltham, MA, USA). A 1:10 particle-to-potassium bromide (KBr) ratio was observed for the mixture. A small portion of the fraction was thoroughly mixed with the KBr using a pestle and mortar and pulverized before it was transferred into the pellet-forming die. The spectra of the produced pellet were examined in the frequency range of 500–4000 cm^{-1} .

2.4.5. Morphology

The shape of the concentrate fraction was identified using a Phenom ProX desktop SEM (ProX 800-07334 MVE01570775 PhenomWorld, Thermo Fisher Scientific, Basel, Switzerland).

3. Results and Discussion

3.1. Beneficiation Studies

The material balance, grade, and recovery are shown in Table 1. As shown in Table 1a, the magnetic separator produced magnetic and non-magnetic fractions according to the

magnetic properties of minerals, and it was observed that the highest ZrO₂ grade was in the non-magnetic fraction. The air-floating separator produced concentrate and tailings fractions according to the specific gravity properties of minerals. The concentrate fraction, which is the final product (processed zircon), has a zirconia grade of 65.52% with 70.81% recovery, as shown in Table 1b. It was observed that in the concentrate fraction, the grade and recovery of ZrO₂ were higher than those obtained in the magnetic, non-magnetic, and tailings fractions. The reduction in the grade of zirconia observed in the later fractions can be attributed to entrapped contaminants.

Table 1. Beneficiation studies on the unprocessed Arikya zircon sample to upgrade the zirconia content.

(a) Feed							
Fraction	Weight (g)	ZrO ₂	Grade (%)		Fe ₂ O ₃	Recovery (%)	
			ZrO ₂	SiO ₂		ZrO ₂	SiO ₂
Feed	<i>F</i> 100	40.77	<i>f</i> 17.61	0.73	-	-	-
Magnetic fraction	<i>T</i> 59.95	1.27	<i>t</i> 3.47	0.71	57.99	49.66	31.47
Non-magnetic fraction	<i>C</i> 45.05	52.48	<i>c</i> 19.41	0.51	-	-	-
(b) Non-Magnetic Fraction							
Feed (non-magnetic fraction)			-	-			
Concentrate fraction	<i>C</i> 25.55	65.52	<i>c</i> 20.48	0.66	70.81	59.84	73.39
Tailings fraction	<i>T</i> 17.00	41.34	<i>t</i> 26.88	0.78			

3.2. Dry High-Intensity Magnetic Separator

The DHIMS generated a total of 59.95 g magnetic and 45.05 g non-magnetic fractions. The grade and recovery of zirconia in the Arikya zircon from the magnetic separation process are shown in Figure 6. In the magnetic fraction, the grades of ZrO₂, SiO₂, and Fe₂O₃ were 1.27%, 3.47%, and 0.71%, respectively (Table 1a), which corroborates the recoveries of these elements (Figure 6). Significantly, with an increase in the recoveries of

ZrO₂ and SiO₂ (denoted by numbers 3 and 2 in red—Figure 6, respectively), their grades increased to 52.48% and 19.41% in the non-magnetic fraction. The enrichment ratios of ZrO₂, SiO₂, and Fe₂O₃ are in this order: 1.10 (SiO₂) > 0.78 (ZrO₂) > 0.69 (Fe₂O₃) in the magnetic separations.

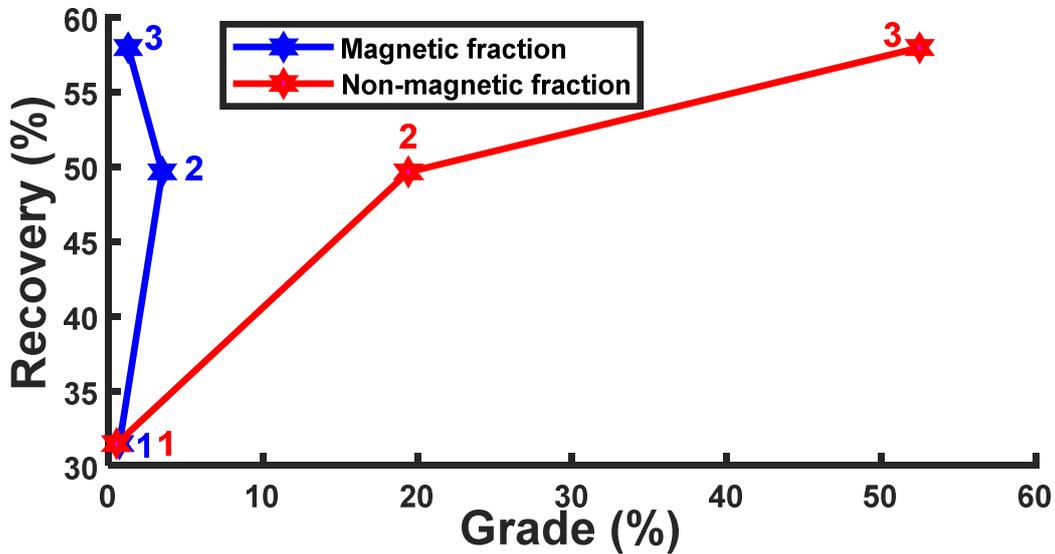


Figure 6. The gangue recoveries of Fe₂O₃ and SiO₂ from the unprocessed Arikya zircon in magnetic fraction and ZrO₂ in non-magnetic fraction. The numbers denote 1—Fe₂O₃, 2—SiO₂, and 3—ZrO₂.

There have been numerous attempts to define the metallurgical efficiency of separation. The most widely used is the Newton efficiency η_n defined in Equation (4) by [38,39]:

$$\eta_n = R_v + R_g - 1 \tag{4}$$

where R_v and R_g are recoveries of valuable (ZrO₂) and gangue (SiO₂ or Fe₂O₃) elements into the concentrate and tailings, expressed by Equations (5) and (6), respectively:

$$R_v (\%) = \frac{Cc_z}{Ff_z} = \frac{c_z(f_z - t_z)}{f_z(c_z - t_z)} \times 100 \tag{5}$$

$$R_g (\%) = \frac{T(1 - t_z)}{F(1 - f_z)} = \frac{(c_z - f_z)(1 - t_z)}{(c_z - t_z)(1 - f_z)} \times 100 \tag{6}$$

where F is the weight of feed, C is the weight of ZrO₂ in concentrate, T is the weight of gangue element in tailings (SiO₂ or Fe₂O₃), and c_z , f_z , and t_z are the grades of ZrO₂ in concentrate, feed, and tailings, respectively.

The computed separation efficiency of ZrO₂ from gangue minerals in the magnetic and non-magnetic fractions is 0.56. Notwithstanding that the enrichment ratio for ZrO₂ is low (0.78), the separation efficiency result showed that ZrO₂ upgrading and recovery in the non-magnetic fraction of magnetic separation is more efficient when compared to the value obtained in the gravity separation, although the latter yielded higher ZrO₂ grade in the concentrate fraction.

3.3. Air-Floating Separator

The recovery of zirconia in the Arikya zircon from the gravity separation process is shown in Figure 7. In the concentrate fraction, the grades of ZrO₂, SiO₂, and Fe₂O₃ were 65.52%, 20.48%, and 0.66%, respectively (Table 1b), which corroborates the recoveries of these elements (Figure 7).

Significantly, with an increase in the recoveries of ZrO₂ and SiO₂ (denoted by numbers 2 and 3 in magenta—Figure 7), their grades increased to 65.52% and 20.48% in the

concentrate fraction. The enrichment ratios of ZrO_2 , SiO_2 , and Fe_2O_3 are in this order: $1.29 (Fe_2O_3) > 1.25 (ZrO_2) > 1.06 (SiO_2)$ in the gravity separations. Although the Fe_2O_3 enrichment ratio is high, the gangue mineral was not effectively separated from the processed zircon sample, as indicated in Table 1b. This could be a result of the constant magnetic induction used in the magnetic separation.

The computed separation efficiency of ZrO_2 from gangue minerals in the concentrate and tailings fractions is 0.25. Although the grade of ZrO_2 obtained from the gravity separation is high (Table 1b), this result showed that the efficiency of the operation is remarkably low; this could be a result of not considering the effect of particle sizes in the separation operations.

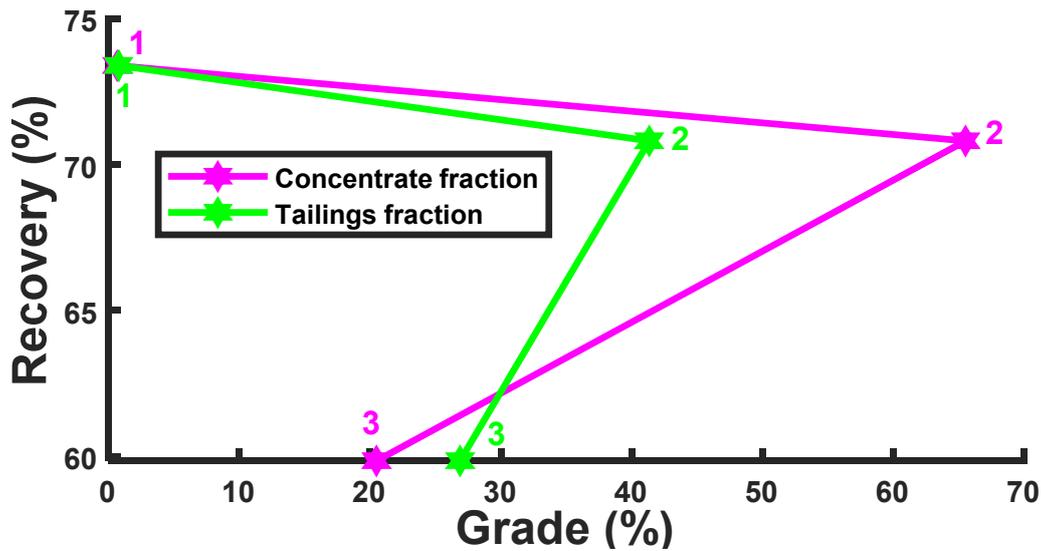


Figure 7. The recoveries of ZrO_2 from the unprocessed Arikya zircon in concentrate fraction and SiO_2 and Fe_2O_3 gangue in tailings fraction. The numbers denote 1— Fe_2O_3 , 2— ZrO_2 , and 3— SiO_2 .

3.4. Characterization of Generated Products

3.4.1. Chemical Analysis of Magnetic Separation Products

The DHIMS generated magnetic and non-magnetic fractions (minerals), and the complete chemical analysis is given in Table 2a,b. The magnetic fraction in Table 2a shows that it contained mainly rare earth elements (REEs) as they are ferromagnetic. The wt.% of these elements increased from low values to higher values (CeO_2 initially at 4.54 wt.% in the unprocessed zircon increased to 23.47 wt.% and La_2O_3 from 3.51 to 13.78 wt.%).

Table 2. (a) Oxide chemistry components in the magnetic fraction and (b) Oxide chemistry components in the non-magnetic fraction.

(a)								
Element/Oxide Content (%)	Fe_2O_3 0.71	SiO_2 3.47	Al_2O_3 1.44	MgO 0.80	P_2O_5 10.08	SO_3 0.15	TiO_2 0.91	MnO 0.00
Element/Oxide Content (%)	CaO 0.52	K_2O 0.00	CuO 0.00	ZnO 0.01	Cr_2O_3 0.00	V_2O_5 0.14	As_2O_3 0.00	PbO 0.13
Element/Oxide Content (%)	Rb_2O 0.00	Ga_2O_3 0.00	NiO 0.00	Cl 0.01	ZrO_2 1.27	Ta_2O_5 0.10	Br 0.00	SrO 0.47
Element/Oxide Content (%)	Nb_2O_5 0.47	Bi_2O_3 0.09	Sb_2O_3 0.64	Co_3O_4 0.00	CdO 0.00	HfO_2 0.00	Ag_2O 0.00	CeO_2 23.47
Element/Oxide Content (%)	BaO 1.00	Au 0.00	WO_3 0.03	MoO_3 0.00	La_2O_3 13.78	ThO_2 1.88	Sn_2O 0.92	

Table 2. Cont.

(b)								
Element/Oxide Content (%)	Fe ₂ O ₃ 0.51	SiO ₂ 19.41	Al ₂ O ₃ 2.86	MgO 0.00	P ₂ O ₅ 3.60	SO ₃ 0.00	TiO ₂ 0.67	MnO 0.00
Element/Oxide Content (%)	CaO 0.58	K ₂ O 0.00	CuO 0.00	ZnO 0.00	Cr ₂ O ₃ 0.00	V ₂ O ₅ 0.02	As ₂ O ₃ 0.32	PbO 0.09
Element/Oxide Content (%)	Rb ₂ O 0.00	Ga ₂ O ₃ 0.00	NiO 0.00	Cl 0.00	ZrO ₂ 52.48	Ta ₂ O ₅ 0.09	Br 0.00	SrO 0.74
Element/Oxide Content (%)	Nb ₂ O ₅ 0.39	Bi ₂ O ₃ 0.29	Sb ₂ O ₃ 0.62	Co ₃ O ₄ 0.30	CdO 0.15	HfO ₂ 0.28	Ag ₂ O 0.00	CeO ₂ 1.11
Element/Oxide Content (%)	BaO 1.00	Au 0.00	WO ₃ 0.00	MoO ₃ 0.33	La ₂ O ₃ 1.59	ThO ₂ 0.42	Sn ₂ O 6.44	

The non-magnetic fraction indicated in Table 2b shows that it contains 52.48 wt.% ZrO₂, 3.60 wt.% P₂O₅, 2.86 wt.% Al₂O₃, 19.41 wt.% SiO₂, 1.59 wt.% La₂O₃, 1.11 wt.% CeO₂, and other heavy metals.

3.4.2. Chemical Analysis of Gravity Separation Products

The non-magnetic fraction of 45.05 g generated a 25.55 g concentrate fraction and 17.00 g tailings fraction, and Table 3a,b show the complete chemical analysis.

Table 3. (a) Oxide chemistry components in the concentrate fraction and (b) Oxide chemistry components in the tailings fraction.

(a)								
Element/Oxide Content (%)	Fe ₂ O ₃ 0.66	SiO ₂ 20.48	Al ₂ O ₃ 2.66	MgO 0.40	P ₂ O ₅ 3.45	SO ₃ 0.00	TiO ₂ 0.54	MnO 0.00
Element/Oxide Content (%)	CaO 0.47	K ₂ O 0.00	CuO 0.02	ZnO 0.00	Cr ₂ O ₃ 0.00	V ₂ O ₅ 0.01	As ₂ O ₃ 0.37	PbO 0.07
Element/Oxide Content (%)	Rb ₂ O 0.00	Ga ₂ O ₃ 0.00	NiO 0.01	Cl 0.00	ZrO ₂ 65.52	Ta ₂ O ₅ 0.12	Br 0.00	SrO 0.79
Element/Oxide Content (%)	Nb ₂ O ₅ 0.55	Bi ₂ O ₃ 0.27	Sb ₂ O ₃ 0.95	Co ₃ O ₄ 0.30	CdO 0.15	HfO ₂ 0.29	Ag ₂ O 0.00	CeO ₂ 1.36
Element/Oxide Content (%)	BaO 1.00	Au 0.00	WO ₃ 0.00	MoO ₃ 0.33	La ₂ O ₃ 0.98	ThO ₂ 0.49	Sn ₂ O 5.55	
(b)								
Element/Oxide Content (%)	Fe ₂ O ₃ 0.78	SiO ₂ 26.88	Al ₂ O ₃ 5.98	MgO 0.09	P ₂ O ₅ 11.19	SO ₃ 0.00	TiO ₂ 1.79	MnO 0.03
Element/Oxide Content (%)	CaO 0.69	K ₂ O 0.00	CuO 0.02	ZnO 0.00	Cr ₂ O ₃ 0.00	V ₂ O ₅ 0.02	As ₂ O ₃ 0.33	PbO 0.08
Element/Oxide Content (%)	Rb ₂ O 0.00	Ga ₂ O ₃ 0.00	NiO 0.01	Cl 0.00	ZrO ₂ 41.34	Ta ₂ O ₅ 0.09	Br 0.00	SrO 0.69
Element/Oxide Content (%)	Nb ₂ O ₅ 0.67	Bi ₂ O ₃ 0.24	Sb ₂ O ₃ 0.79	Co ₃ O ₄ 0.30	CdO 0.14	HfO ₂ 0.29	Ag ₂ O 0.00	CeO ₂ 0.43
Element/Oxide Content (%)	BaO 1.00	Au 0.00	WO ₃ 0.01	MoO ₃ 0.20	La ₂ O ₃ 0.00	ThO ₂ 0.29	Sn ₂ O 3.55	

The data in Table 3a and Figure 8A reveal that the processed zircon in the concentrate fraction averages 65.52% ZrO₂. This compares favorably with the 65% ZrO₂ content for standard guaranteed zircon used as a reinforcing agent in the composite formulation. Hafnium oxide (HfO₂) was detected, and it has a value of 0.29%; triuranium octoxide (U₃O₈) was not detected, or it was below the detection limits (bdl).

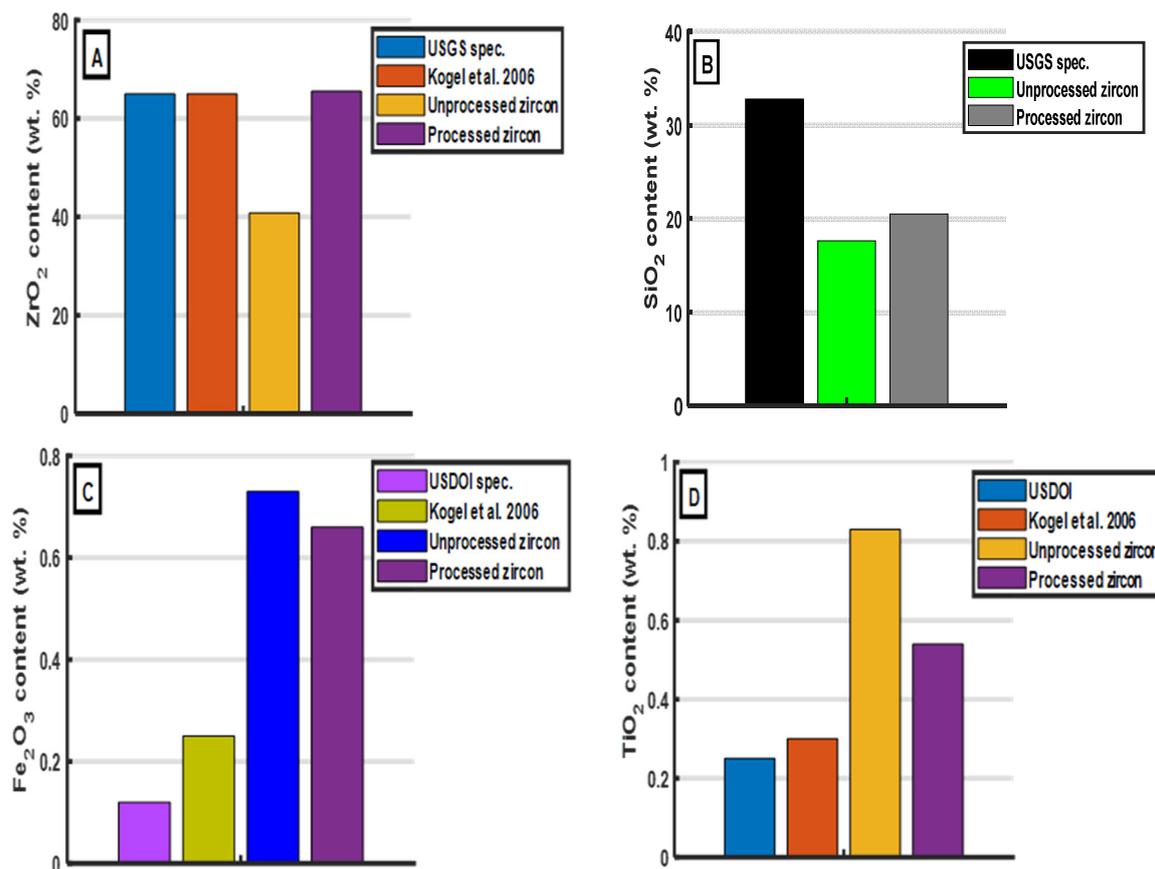


Figure 8. Comparison studies of the unprocessed and processed Arikyia zircon from Lafia L.G.A., Nasarawa State, Nigeria, and comparison studies with the industrially/globally/standard grade accepted specifications grade reported in the literature (A) ZrO₂, (B) SiO₂, (C) Fe₂O₃, and (D) TiO₂ contents, Kogel et al., 2006, [17].

The presence of calcium, niobium, thorium, iron, and rare earth elements (REEs) reduces ZrO₂ content [40]. Zircon often contains liquid inclusions as well as other minerals, such as cassiterite, monazite, aluminum silicates, xenotime, magnetite, rutile, spinel, feldspar, mica, silica, and especially apatite [8]. The major contaminants in the processed zircon include 20.48 wt.% quartz (SiO₂), 5.55 wt.% cassiterite (SnO₂), 3.45 wt.% apatite (P₂O₅), 2.66 wt.% aluminum oxide (Al₂O₃), 1.36 wt.% Cerium (IV) oxide (CeO₂), and 1.00 wt.% barium oxide (BaO). Minor amounts of 0.47 wt.% calcium oxide (CaO), 0.55 wt.% niobium oxide (Nb₂O₅), 0.49 wt.% thorium dioxide (ThO₂), 0.66 wt.% iron oxide (Fe₂O₃), and 0.54 wt.% titanium dioxide (TiO₂), also constitute impurities in the processed zircon (concentrate fraction). These impurity components could be mineral species that precipitate in the pores and cracks of the grains, or they could be inclusion phases that exist within the zircon crystal structure. The level of titanium mineral contamination, typically leucoxene or rutile, which occurs in separate grains, mostly determines the quantity of TiO₂ content. The high P₂O₅ value points to the presence of trace amounts of a Y-rich phase (i.e., xenotime-rich monazite), while the TiO₂ values indicated the incorporation of small titanates. Additionally, the high Al₂O₃ concentrations are commonly an indication of kyanite or sillimanite contamination linked to aluminosilicate gangue minerals, either in the form of isolated grains or in conjunction with clay coatings or pore filler materials [10].

The generated products in the tailings fraction are presented in Table 3b. It is observed that the fraction contains 41.34 wt.% ZrO₂, 26.88 wt.% SiO₂, 11.19 wt.% P₂O₅, 5.98 wt.% Al₂O₃, and other heavy metals.

The weight percentages of ZrO₂, Fe₂O₃, and TiO₂ of unprocessed or crude zircon, locally processed zircon (concentrate fraction), and other zircon reported in the literature,

which are the industrially/globally/standard grade accepted specifications for zircon were compared as presented in Table 4 and Figure 8. The obtained weight percentages of Fe_2O_3 and TiO_2 (Figure 8C,D) are not within the United States Geological Survey Agency (USGS) and United States Department of Interior (USDOI) specified standards for zircon. These gangue minerals can be reduced to the minimum range using lower magnetic intensity for magnetic separation and electrostatic separation.

Table 4. Elemental evaluation of Arikya zircon.

Composition	Percentage (%)		
	USGS and USDOI Specifications [7,17]	Unprocessed [6]	Arikya Zircon Processed
ZrO ₂	Minimum 65.00	40.77	65.52
HfO ₂	0.40 to 2.00	n.d or bdl *	0.29
SiO ₂	32.80	17.61	20.48
Fe ₂ O ₃	0.12	0.73	0.66
TiO ₂	0.25	0.83	0.54

n.d*: not detected and bdl: below the detection limits.

3.4.3. Specific Gravity

The unprocessed zircon used in this study has a specific gravity of 4.4. The specific gravity of the unprocessed zircon was successfully increased by the beneficiation process from 4.4 to 4.6 g/cm³. The specific gravities of unprocessed or crude zircon, locally processed zircon, and other zircon reported in the literature, which are the industrially/globally accepted specifications for zircon as a reinforcing agent, were compared as presented in Figure 9.

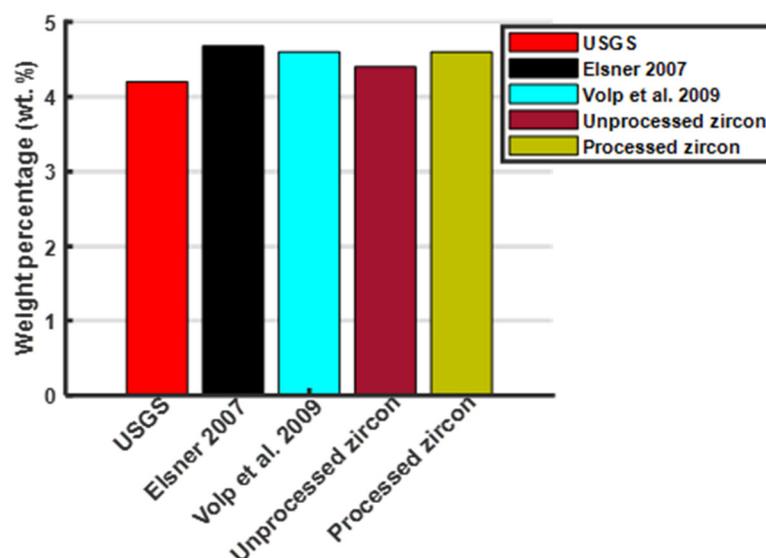


Figure 9. Specific gravities of the unprocessed and processed from Arikya zircon site, Nasarawa State, Nigeria, and comparison studies with the industrially/globally accepted specifications for specific gravity reported in the literature, Elsner 2007, [8], Volp et al., 2009, [9].

A decrease in the specific gravity can occur if some light or low-density minerals, which are impurities in the zircon ore (such as quartz and clay), are being carried away as tailings or trapped in the valuable minerals, thereby lowering the specific gravity of the processed zircon.

3.4.4. Mineralogical Evaluation

The XRD patterns of the unprocessed and locally processed zircon were compared, as shown in Figure 10. The unprocessed zircon (Figure 10a) used in this study has a zircon

($Zr_4Si_4O_{16}$) mineral phase with traces of rodolicoite ($Fe_3P_3O_{12}$), while the processed zircon (Figure 10b) contained a zircon mineral phase with the chemical formula of $ZrSiO_4$ with traces of quartz (SiO_2) and aluminum silicates (orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$)) as gangue minerals, which is corroborated by the EDXRF results (Table 3a).

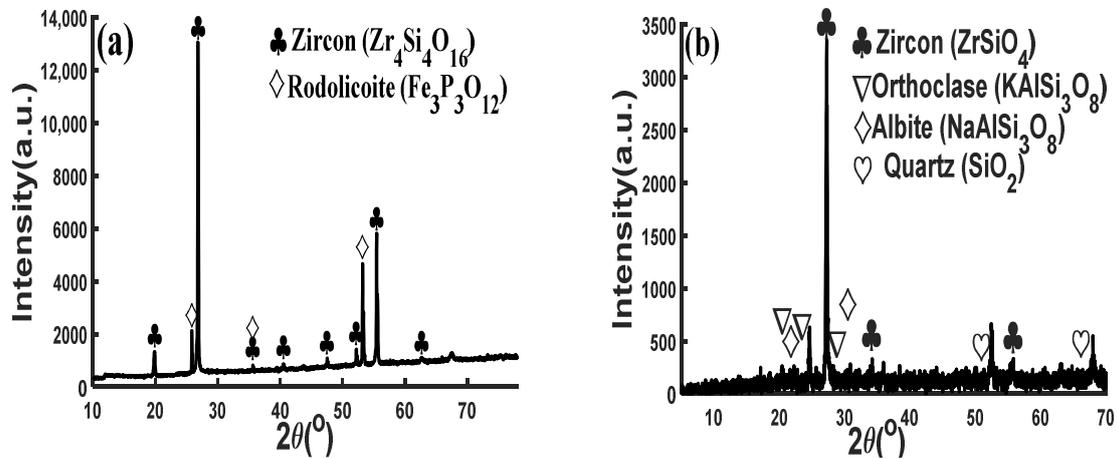


Figure 10. XRD of the (a) unprocessed and (b) processed Arikya zircon.

The XRD pattern of the processed Arikya zircon in Figure 10b reveals the presence of tetragonal (at 27.23° , 3.27 \AA , height of 2193 (a.u) and size of 381 \AA) and monoclinic zircon phases (at 32.61° and 52.12°). The sharp peak observed at 27.23° corresponds to the (200) plane, which is an indication of the suitable crystalline nature of the processed zircon. It can be visualized that the processed zircon has the chemical formula of the industrially/globally accepted zircon, and the dissociation of zirconium (Zr_4) from the unprocessed Arikya zircon to Zr in the processed zircon is an indication of the success of the beneficiation operation. Additionally, the oxygen atom initially at O_{16} was successfully dissociated into the processed zircon and the accompanying elements. It was observed that rodolicoite ($Fe_3P_3O_{12}$) in the unprocessed zircon was successfully removed during the magnetic separation as a result of the iron content.

3.4.5. Functional Groups and Morphology

The FT-IR spectra of the unprocessed and processed zircon in absorbance mode are presented in Figure 11. In both samples (Figure 11a,b), the broad band at $900\text{--}1000 \text{ cm}^{-1}$ can be assigned to the Zr-O bond. The band observed at 1587.80 cm^{-1} (Figure 11b) for the processed zircon and the unique band between 1600 and 1640 cm^{-1} , centered at 1629.48 cm^{-1} (Figure 11a) for the unprocessed zircon can be attributed to the absorption of nonbridging -OH groups and the bending mode region is due to the O-H bending vibration of -OH group of water molecule [41,42] due to the presence of water inside the sample or magnesium-rich chlorite. The intensity of the band is not high, and it shifted to a lower wave number (1587.80 cm^{-1}) in the spectrum of the processed zircon (Figure 11b). This suggests a structural difference in the two samples (unprocessed and processed), as the unprocessed sample was redried before the beneficiation operation. The bands at 2355.70 cm^{-1} (Figure 11b) and 2359.86 cm^{-1} (Figure 11a) refer to the characteristic stretching vibration of the hydroxyl zirconium (Zr-OH) bond [43]. The prominent absorption bands between 3200 and 3800 cm^{-1} (Figure 11a,b) correspond to the stretching vibration -OH group of water molecules from the atmosphere, which was retained by the KBr pellet. The band is not significant in the processed zircon as a result of the redrying carried out on the sample before the beneficiation operation. The different variations in where the bands were observed for the unprocessed and processed zircon show the extent of the purification. Additionally, it can be deduced that the elimination of water molecules from the processed zircon sample is the cause of the absorption band's intensity decreasing (Figure 11b).

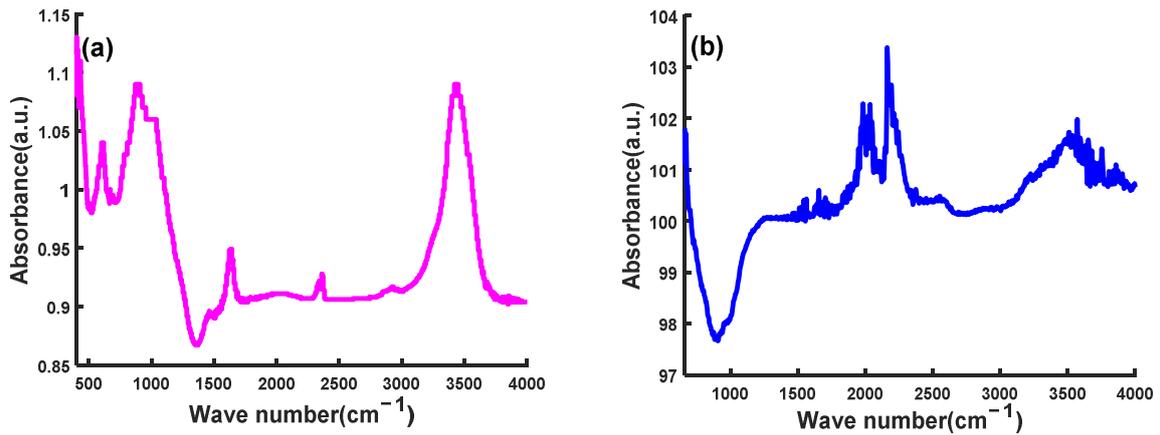


Figure 11. FT-IR spectra for the (a) unprocessed and (b) processed Arikya zircon.

The morphologies of the unprocessed and processed Arikya zircon are shown in Figure 12. The unprocessed zircon used for this study is wedge shaped, as indicated in Figure 12a, while the processed zircon has an angular blocky shape (Figure 12b). The processed zircon (Figure 12b) showed a composition of Zr as 61.50% and Si as 20.86%, and this gave 82.36% of the Zr-Si empirical composition.

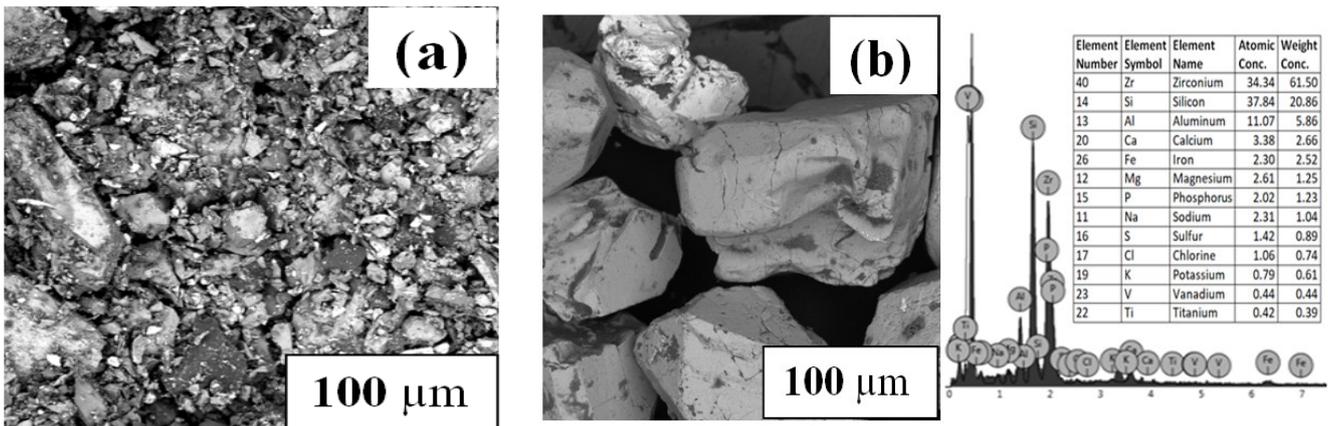


Figure 12. (a) SEM image of unprocessed—showing wedge and (b) SEM-EDX of processed—angular blocky.

The morphologies of both samples (unprocessed and processed Arikya zircon) are an indication of the presence of zircon, as the mineral usually has prismatic and pyramidal morphology. The factors that influence crystal shapes are mainly the crystal composition and crystallization temperature.

4. Conclusions

The possibility of using magnetic and gravity separation processes to increase the zirconia (ZrO₂) content of unprocessed Arikya zircon collected from Nasarawa State, Nigeria, was taken into consideration in this study. Two fractions each were generated from the magnetic and gravity separation processes. The DHIMS generated a ZrO₂ grade of 1.27% and 52.48% in the magnetic and non-magnetic fractions, respectively, with 57.99% recovery and enrichment ratio of 0.78, while the highest ZrO₂ grade of 65.52% with a 70.81% recovery and enrichment ratio of 1.25 in the AFS in the concentrate fraction, while 41.34% was obtained in the tailings fraction. The ZrO₂ content previously at 40.77% in the unprocessed zircon was successfully increased in the concentrate fraction of the gravity separation to 65.52% ZrO₂ grade after the beneficiation. The minimum guaranteed standard range is 65%, as recommended by the USGS. The grade of ZrO₂ obtained would have been

higher but lost to the magnetic and tailings fractions, which are mostly as entrapped minerals that include titanium dioxide; silicates, predominantly quartz; and aluminosilicates, mostly feldspars and clays generated as contaminants. Primary contaminants initially at 0.73% iron oxide (Fe_2O_3) and 0.83% titanium dioxide (TiO_2) in the unprocessed zircon were reduced to 0.66 and 0.54%, respectively, after the beneficiation operation. The specific gravity previously at 4.4 was successfully increased to 4.6 g/cm^3 ; 4.2 is the minimum USGS standard. The significant improvements in the ZrO_2 content and specific gravity in the processed Arikya zircon sample can be attributed to the different separation processes utilized to upgrade the crude Arikya sample. The unprocessed Arikya zircon mineral was upgraded to the minimum purity, composition, and specific gravity that is within the USGS guaranteed ranges and is thus suitable for use as a reinforcing agent in composite formulation for SRMCs construction in the aerospace industry and compares favorably with the industrially/globally accepted zircon. This study has highlighted and elaborated on some vital information that space engineers, scientists, researchers, and other industrial users need about upgrades, utilization, and the prospects of locally processed zircon. Using flotation and electrostatic separation to further upgrade the zircon concentrates from the gravity separation and studying the effect of feed rate, particle sizes, and magnetic induction is recommended.

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