PROCESSING ZIRCONIA THROUGH ZIRCON SAND SMELTING WITH NaOH AS A FLUX

PEMBUATAN ZIRKONIA MELALUI METODE PELEBURAN PASIR ZIRKON MENGGUNAKAN NaOH SEBAGAI BAHAN IMBUH

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ABSTRACT

Zirconia had been made through smelting the zircon sand along with NaOH as a flux. The zircon sand as the smelter feed was taken from CV. Kurnia Alam Sejati mine at Palangkaraya, Middle Kalimantan. Major content of the zircon sand was 28.04% ZrO_2 and SiO_2 51.22% with several minor oxides such as 0.54% HfO_2, 2.53% Fe_2O_3, 10.53% TiO_2, 3.27% Al_2O_3 and less than 1% of alkali, alkaline earth and rare earth elements. In order to economizing the process, zircon sand upgrading was conducted prior to zirconia production. The upgrading process was conducted using several comprehensive equipments, consist of shaking table, magnetic separator and high tension separator (HTS).The upgraded sand contained 65.35% of ZrO_2+HfO_2 with 73.25% recovery, which was then used for smelting process at 650°C for 2 hours using NaOH as a flux. The product was then leached with water and sulphuric acid then crystallized to get precipitated zirconium hydroxide. The precipitated product was calcined at 900°C for 1 hour to get the zirconia and analyzed for its content. The zirconia content was 97.27% of ZrO_2+HfO_2 with 65.13% recovery.

Keywords: zirconia, zircon sand, smelting, upgrading process and concentrate

ABSTRAK

Pembuatan zirkonia telah dilakukan dengan melebur pasir zirkon menggunakan NaOH sebagai bahan imbuh. Pasir zirkon yang digunakan sebagai bahan baku zirkonia berasal dari lokasi penambangan pasir zirkon CV. Kurnia Alam Sejati di Palangkaraya, Kalimantan Tengah, dengan kandungan ZrO_2 sebesar 28,04% dan silikat (SiO_2) 51,22%, serta pengotor-pengotor lainnya berupa HfO_2 sebasar 0,54%, Fe_2O_3 sebesar 2,53%, TiO_2 10,53%, Al_2O_3 3,27%, sedangkan pengotor alkali, alkali tanah dan logam tanah jarangnya <1%. Pasir zirkon tersebut belum ekonomis untuk menjadi bahan baku pembuatan zirkonia, maka perlu dilakukan peningkatan kadar terlebih dahulu. Proses peningkatan kadar dilakukan menggunakan serangkaian peralatan yang terdiri atas shaking table, magnetic separator dan HTS. Hasil proses peningkatan diperoleh konsentrat berkadar 65.35% (ZrO_2+HfO_2) dengan perolehan sebesar 73,25%. Konsentrat yang diperoleh kemudian digunakan untuk pembuatan zirkonia. Konsentrat tersebut dicampur dengan NaOH sebagai bahan imbuh, lalu dilebur pada suhu 650°C selama 2 jam. Hasil peleburan selanjutnya dilarutkan dengan air dan asam sulfat. Larutan kaya yang diperoleh dikristalisasi dan dikalsinasi pada suhu 900°C selama 1 (satu) jam untuk mendapatkan zirkonia. Hasil diperoleh adalah zirkonia berkadar 97,27% (ZrO_2+HfO_2) dengan perolehan sebesar 65,13%.

Kata kunci: zirkonia, pasir zirkon, peleburan, peningkatan kadar dan konsentrat

39

INTRODUCTION

Zirconia (ZrO_2) known as baddeleyite is hardly found in nature. Such a material can be processed from zircon sand ($ZrSiO_4$). Zirconia has three crystal structures, namely monoclinic, tetragonal and cubic. Both monoclinic and tetragonal zirconia are unstable at 1000-1100°C due to reversible transformation occurrence at such temperatures and results in volume change of the material. Of the three-zirconia type, cubic zirconia (k-ZrO_2) is the stable one at those temperature. Generally, zirconia has high melting point (2700°C), low thermal conductivity and can be formed into stable phase by adding bivalent or trivalent oxides, such as CaO, MgO and Y_2O_3 (Anonim, 2009; Bobbin, 2008; Anonim, 2010). Based on such properties, zirconia can be applied for optical, fiber and color tv glasses as well as advanced ceramic to be applied in machine/motor component, chemical pump, nozzle, cylinder lining, piston head, valve and fuel cell system and also for controlling fuel and oxygent within the machine. By controlling both fuel and oxygent makes best efficiency on vehicle machine and reduces environment impact (Anonim, 2006 and http://www.zirox.co.in/advanced_materials_division.htm accessed on 15 September 2009 at 13.44).

Making the zirconia can be made through smelting zircon sand and alkali compound as a flux. The use of alkali compound in this process is named as alkali fusion. The very reactive alkali compound to be applied is NaOH. The purpose of zircon sand smelting is to break chemical bond between ZrO_2 and SiO_2 to form alkali zirconium compound (Na_2ZrO_3) and sodium silicate (Na_2SiO_3) at 650°C (Kwela, 2006; Yuhelda et al., 2010). In order to separate quartz, the smelted product should be leached in water and the residue from water leaching was used for further leaching with sulphuric acid to have zirconium sulphate (Rehim, 2005; http://www.alkane.com.au/pdf/asx/archive/20080408.pdf). The zirconia was produced by crystallizing zirconium sulphate and calcining the crystal.

Raw material for alkali fusion process is the zircon sand more than 65% of ZrO_2+HfO_2 in order to economizing the process. However, the natural zircon sand content is only 1-5% of ZrO_2, therefore upgrading process is required. The zircon sand upgrading process has been conducted to separate gangue mineral such as quartz, ilmenite, rutile, xenotim, monazite and others (Saleh and Pramusanto, 2007; Yuhelda et al., 2009).

The objective of this study is to utilize zircon sand for zirconia production. This can increase the added value of the sand. Referring to the export price of upgraded zircon (Rp 14,500/kg) and the price of zircon (Rp. 891,800/kg), such zircon processing is reasonable for increasing the local and national government income.

METHODOLOGY

The zircon sand for zirconia production was characterized in order to evaluate chemical composition, particle size distribution and mineralogy character. Mineral composition was detected by X-ray diffraction instrument and chemical composition was analyzed by XRF instrument. Particle size distribution of sand was conducted by setting several sieves from 60, 100, 150 and 200 meshes and then, generated on ro-tap sieve shaker for 1 hour. The retained and passing materials was measured for its weight.

The zircon sand was then upgraded to separate its mineral association such as quartz, ilmenite, rutile, hematite, magnetite, pyrite, limonite, xenotime and monazite. Upgrading process was accomplished through physical separation process based on densities, magnetism properties and conductivity. The upgrading process was completed using shaking table, magnetic separator and high tension separator (HTS).

Separation of mineral employed shaking table and water stratification media with the flowrate of 12 liters/minute, 3° inclination of the table and 6 mm stroke (Yuhelda et al., 2012; Saleh and Pramusanto, 2007). The product consisted of ZrO_2+HfO_2 as a concentrate and quartz, clay, xenotime, monazite, magnetite, hematite, rutile and ilmenite as tailing products. A few of concentrates were characterized by XRF instrument for analyzing its contents. The rest concentrates were then upgraded using magnetic separator. Some minerals such as magnetite, hematite, limonite, ilmenite and pyrite were separated by magnetic intensity of 10,000-20,000 gauss (Yuhelda et al.,

2012). The non-magnetic product was then characterized by XRF method and then separated using HTS. Before separation, the material had to be dried first one night at 100°C. The feeder speed was set at 25.06 rpm and 100°C while the roll speed at 240 rpm. The HTS product was also examined through XRF analysis.

Further separation with silicate had been accomplished with smelting. The smelting was intended to break the strong bond between ZrO_2 and SiO_2 which can be completed around 2700°C without any flux addition. Interms of acquiring lower temperature for the process, it is required to add NaOH as a flux (Kwela, 2006). Upgraded zircon sand smelting was prepared within a crucible furnace. In order to get ZrO_2+HfO_2 more than 65%, the upgraded sand was mixed with NaOH as a flux for some stoichiometric amounts then stirred and smelted at 650°C (Yuhelda et al., 2010). The smelted product was then cooled, ground and prepared for silica dissolution. The product was also examined by XRD instrument to identify the Na_2ZrO_3 and Na_2SiO_3.

Silica dissolution was generated in water to have zirconium and then leached in 6-M sulphuric acid to produce zirconium sulfate (Yuhelda et al., 2012; Rehim, 2005). The solution was then precipitated by adding aqueous ammonia until white precipitation appeared as zirconium hydroxide. Then it was calcined at 900°C for 1 hour (Kwela, 2006; Yuhelda et al., 2010). The whole process can be seen in Figure 1.

RESULTS AND DISCUSSION

The zirconia production consists of four steps; namely raw material characterization, upgrading process, smelting process and zirconia making. Chemical composition of zircon sand is presented in Table 1. Zircon sand contains 28.04% ZrO_2 and 51.22% SiO_2. As known that pure zircon contains 33.48% SiO_2, therefore some treatment must be completed to fulfill required specification of

smelting process namely more than 65% of ZrO_2+HfO_2. The zircon sand also consists of rare earth elements and radioactive materials that are less than 1 %. The amounts of those elements are not hazardous. It is not necessary to have special treatment for those material separation. According to National Nuclear Energy Agency of Indonesia, secure limitation for radioactive in materials is 500 ppm.

Other characterization is particle size distribution. The size was set to 60, 100, 150 and 200 meshes. The distributions were stated in weight percent. The data was used for calculating each oxide content at each particle size as seen in Table 2. The calculation showed that zircon oxide (ZrO_2) is well distributed at +100 mesh for 88.94% and the calculation grade is 28.27%. The ZrO_2 is not well distributed at -200 mesh. While, quartz (SiO_2) is well distributed in any sizes within almost similar grade, the largest amount can be found at -100+150 mesh. Nevertheless, the gangue minerals such as TiO_2, Fe_2O_3, Al_2O_3, alkali mineral, alkali, rare earth, rare elements also occur in small number (<1%). The calculation result is similar with chemical composition in Table 1. Therefore, chemicals amounts calculation wasdone by using chemical composition analysis result (28.24% of ZrO_2). Those particle size distributions can be used for determining liberation degree of raw material. At coarse size, the liberation is quite good and gain highest liberation at -200 mesh as seen in Table 3, but the liberation has not reached 100% yet. It is because of gangue minerals especially rutile that attached on zirconsilicate, which can be seen in Figure 2.

The conviction of mineral content in the raw material was analyzed by XRD method. Referring to Figure 3, zircon silicate appeared as the major mineral followed by quartz, microcline and ilmenite. The last three minerals were in small intensity as they were present in small amounts that supported by chemical composition as shown in Table 1.

Zircon sand

Preparation/sampling

Upgrading process

Characterization

Chemical composition

Particle size distribution

Mineralogy & Liberation degree

XRD

Shaking table

Magnetic separator

HTS

Concentrate
Zircon sand >65% (ZrO_2+HfO_2)

Smelting — NaOH

H_2O → **Silicate dissolution**

Filtering → Silicate solution

Zirconate

H_2SO_4 → **Leaching**

Filtering → residue

Zirconium sulphate

Crystallisation ← NH_4OH
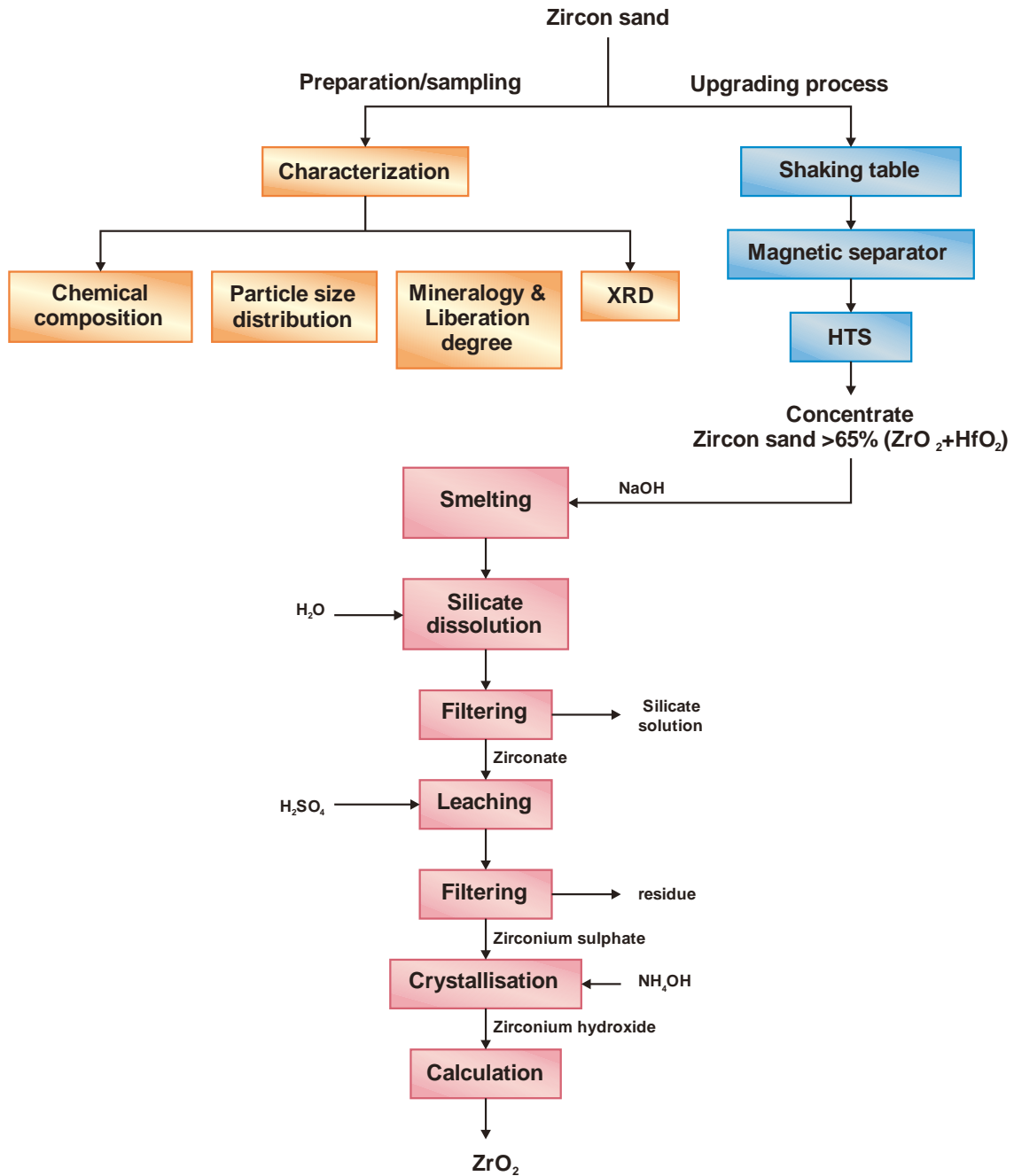
Zirconium hydroxide

Calculation

ZrO_2

Figure 1. A flow chart showing the activities of zirconia making

Previous characterization showed that the upgrading process for zircon sand had to be completed before smelting process. Continuous physical treatment based on three different properties namely densities, magnetic strength and conductivity had been done. The result of all upgrading process can be seen in Table 4. Using HTS, the ZrO_2 increased from 28.04 to 64.01% ZrO_2 or 65.35% (ZrO_2+HfO_2) with recovery of 73.25%. It means that separation process of quartz and ilmenite from zircon sand run well and make the ZrO_2 content increase in final concentrate.

Table 1. Chemical composition of zircon sand

No.	Oxides	Amount (%)	No.	Oxides	Amount (%)
1	ZrO_2	28.04	17	CeO_2	0.020
2	SiO_2	51.22	18	CO_2O_3	0.019
3	TiO_2	10.53	19	Cr_2O_3	1.180
4	Al_2O_3	3.27	20	$Dy2O3$	0.001
5	Fe_2O_3	2.53	21	Y_2O_3	0.051
6	MnO	0.063	22	Gd_2O_3	0.007
7	CaO	0.35	23	ThO_2	0.013
8	MgO	0.0452	24	U_3O_8	0.012
9	CuO	0.045	25	La_2O_3	<0.001
10	K_2O	0.012	26	Lu_2O_3	0.001
11	P_2O_5	0.022	27	Nd_2O_3	0.11
12	SO_3	0.11	28	Pr_6O_{11}	0.0114
13	ZnO	0.064	29	Sm_2O_3	0.007
14	NiO	0.010	30	Yb_2O_3	0.256
15	PbO	0.019	31	SnO_2	0.81
16	HfO_2	0.54	32	LOI	0.41

Table 2. Particle size distribution of zircon sand part 1

Sizes (mesh)	Weight (grams)	% Weight	Content (%)									
			ZrO_2	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	SO_3	K_2O
+60	1029.23	51.4615	30.05	51.07	8.77	4.33	2.64	0.065	0.083	0.39	0.088	0.012
-60+100	749.66	37.4830	28.27	54.61	9.96	1.08	2.13	0,051	0.12	0.34	0.088	0.009
-100+150	121.29	6.0645	28.32	40.89	18.42	1.11	2.64	0,055	0.17	0.34	0.10	0.010
-150+200	87.15	4.3575	34.66	31.23	17.32	0.86	3.92	0,100	0.25	0.24	0.24	0.009
-200	12.30	0.6150	46.18	31.30	5.92	0.55	4.23	0,074	0.17	0.13	0.66	0.027
Calculation grade (%)	1999.63	99.9815	29.29	50.59	10.12	2.76	2.49	0,330	0.19	0.36	0.095	0.010

Table 2. Particle size distribution of zircon sand part 2 (continued)

Sizes (mesh)	Content (%)											
	P_2O_5	HfO_2	CeO_2	CO_2O_3	SnO_2	Y_2O_3	ThO_2	U_3O_8	La_2O_3	ZnO	Cr_2O_3	LOI
+60	O.16	0.59	<0.001	0.017	<0.001	0.051	0.011	0.011	<0.001	0.064	1.18	0.39
-60+100	0.19	0.73	<0.001	0.019	0.40	0.052	0.012	0.012	<0.001	0.023	1.31	0.36
-100+150	0.21	0.72	<0.001	1.67	4.63	0.046	0.016	0.015	<0.001	0.033	1.67	0.38
-150+200	0.26	0.89	<0.001	1.00	8.38	0.056	<0.001	<0.001	<0.001	0.033	1.00	0.37
-200	0.27	1.02	<0.001	0.66	6.73	0.090	<0.001	<0.001	<0.001	0.150	0.66	1.04
+60	O.16	0.59	<0.001	0.017	<0.001	0.051	0.011	0.011	<0.001	0.064	1.18	0.39
Calculation grade (%)	0.40	0.66	<0.001	0.16	0.80	0.051	0.011	0.011	0.001	0.045	1.24	0.375

Table 3.   Liberation degree of zircon sand

Particle size (mesh)	Liberation degree (%)
+60	82.66
-60+100	84.39
-100+150	86.42
-150+200	88.47
-200	91.16

Shaking table method employed density differences of zircon, quartz, ilmenite and rutile. Zircon sand has highest density (4.6-5.8 g/cm^3) among them (Harben, 1995), therefore quartz and ilmenite were separated and went to tailing (Yuhelda, et al., 2008). Process using water flow velocity with velocity of 12 litre/minute for zircon sand (Yuhelda, et al., 2008; Saleh and Pramusanto, 2007) resulted 45.18% of ZrO_2+HfO_2 content in the concentrate. If the velocity of was too fast, it caused the raw material went to middling or tailing product.
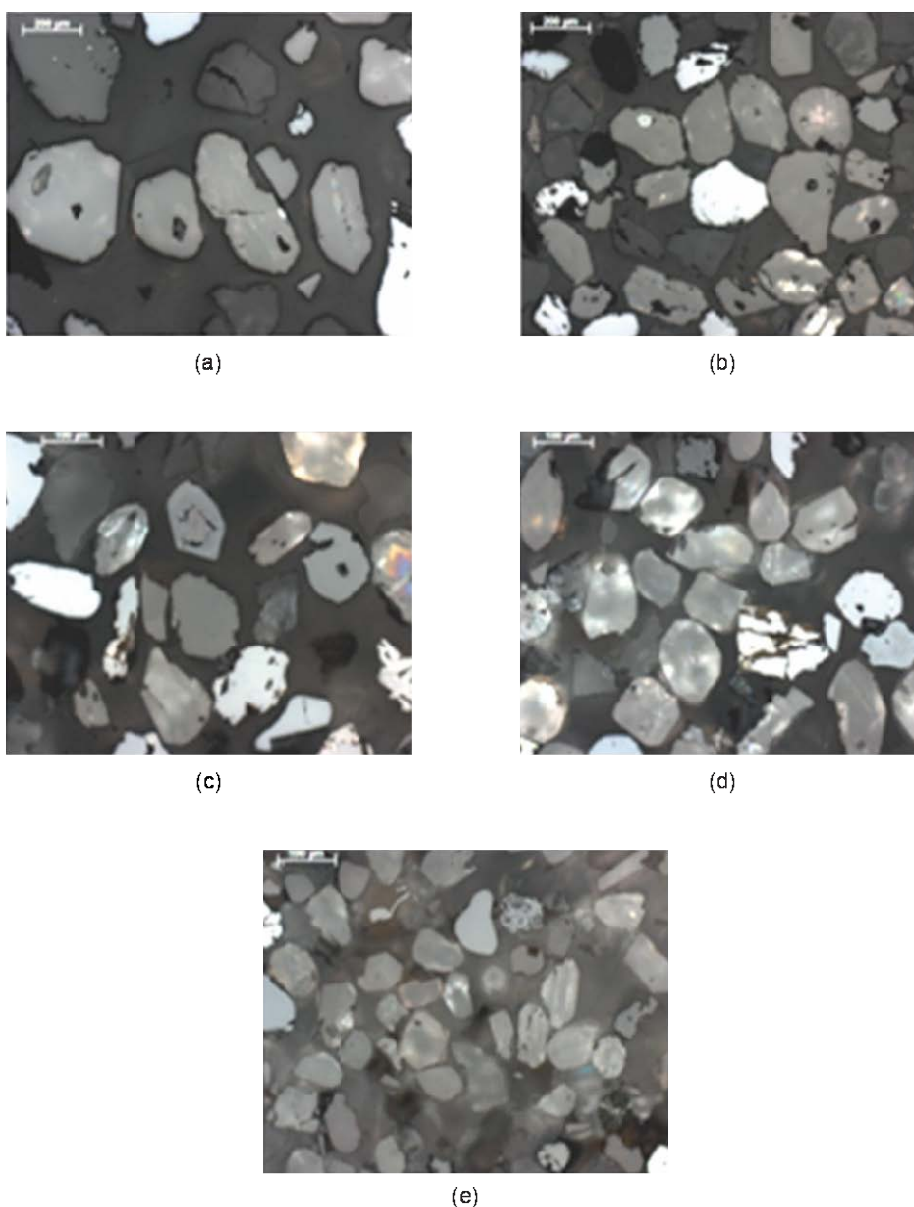

(a)

(b)

(c)

(d)

(e)

Figure 2. Photomicrograph of zircon sand polished section (a) +60 mesh, (b) -60+100 mesh, (c) -100+150 mesh, -150+200 mesh dan -200 mesh
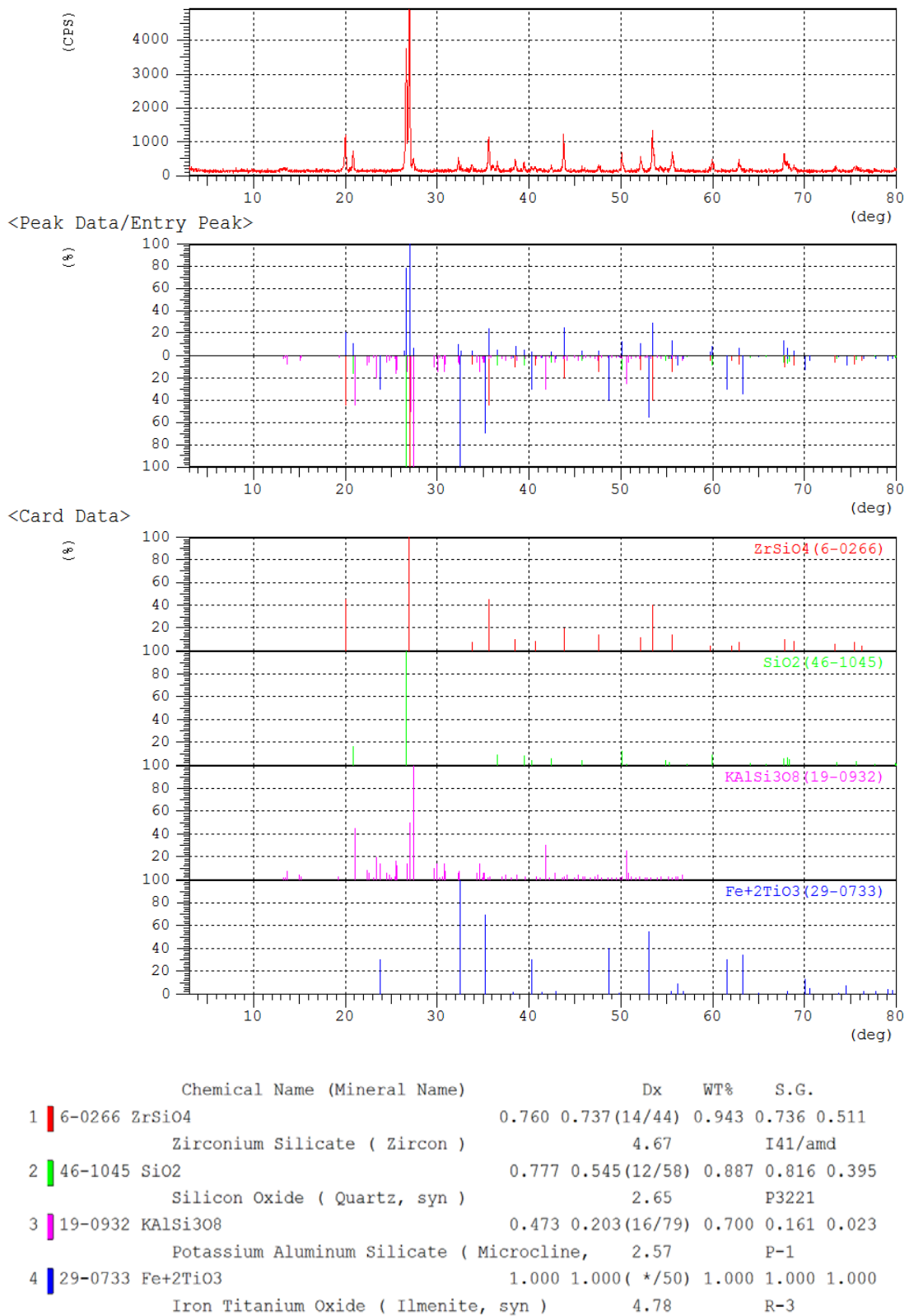
Figure 3. Result of X-Ray diffraction result for zircon sand

Table 4. Result of zircon sand upgrading process

Equipment	Sample Weight (kg)	Concentrate Weight (Kg)	Recovery (%)	Content (%)						
				ZrO$_2$	SiO$_2$	Fe$_2$O$_3$	TiO$_2$	Al$_2$O$_3$	HfO$_2$	LOI
Shaking table	102.170	58.760	57.51	44.21	49.59	2.12	1.89	0.75	0.97	0.06
Magnetic separation	56.280	47.838	85.00	61.72	33.62	1.09	0.89	0.80	2.18	0,01
High Tension separation	55.00	41.39	73.25	64.01	32.22	0.11	1.15	0.05	1.34	0.07

Concentrate from stratification process served as the feed for magnetic separation process using magnetic intensity of 12.000 gauss. The result shows that the iron content decreases from 2.12 to 1.09% and increased the zircon content from 44.21% to 61.72% with 85% recovery in the concentrate because of ilmenite and mangnetic minerals have been separated at the process (Yuhelda, et al, 2009). Then the upgrading process was continued with conductivity-based property. Zircon as a conductive material was separated from non conductive one such as rutile. The product contained 65.35% of ZrO$_2$+HfO$_2$ that was ready for smelting process. The smelting process was held at 650°C for 2 hours using upgraded zircon sand as the feed. Such material was mixed with NaOH as a flux. Smelted product was then analyzed through XRD and the result can be seen in Figure 4. It is showed that smelted product consisted of two major minerals namely sodium zirconate and sodium silicate. It is indicated that smelting process had broken off the chemical bond of zircon silicate as reported by Kwela (2006). The sodium zirconate intensity was stronger than that of sodium silicate because of SiO$_2$ content was smaller than ZrO$_2$ content. The reaction of smelting process is as follows:

$$ZrSiO_4 + 4NaOH \xrightarrow{650°C} Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$
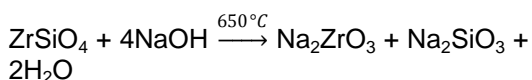
Separating sodium zirconate and sodium silicate was performed through disolving the silicates in water. The residue was then leached with 6-M sulphuric acid to produce zirconium sulphate solution. The solution was then added with aqueous ammonia to precipitate zirconium hidroxide and continued to be calcined at 900°C for 1 hour. The produced zirconia from calcination was examined its chemical composition. The result can be seen in Table 5.

Table 5. Zirconia composition

Oxides	Content (%)
ZrO$_2$	95.67
HfO$_2$	1.60
SiO$_2$	1.04
Fe$_2$O$_3$	0.15
Al$_2$O$_3$	0.11
TiO$_2$	0.90

The produced zirconia had high purity (95.67%) with 65.35% recovery and major gangue SiO$_2$ (1.04%) which is free silica that can not dissolve in hot water (90°C). Meanwhile, others gangue such as Fe$_2$O$_3$, Al$_2$O$_3$ dan TiO$_2$ content are less than 1 % each, therefore, they were not detected in XRD result as seen in Figure 4. Strong intensity of ZrO$_2$ can be seen at the peaks of diagram (Figure 5).
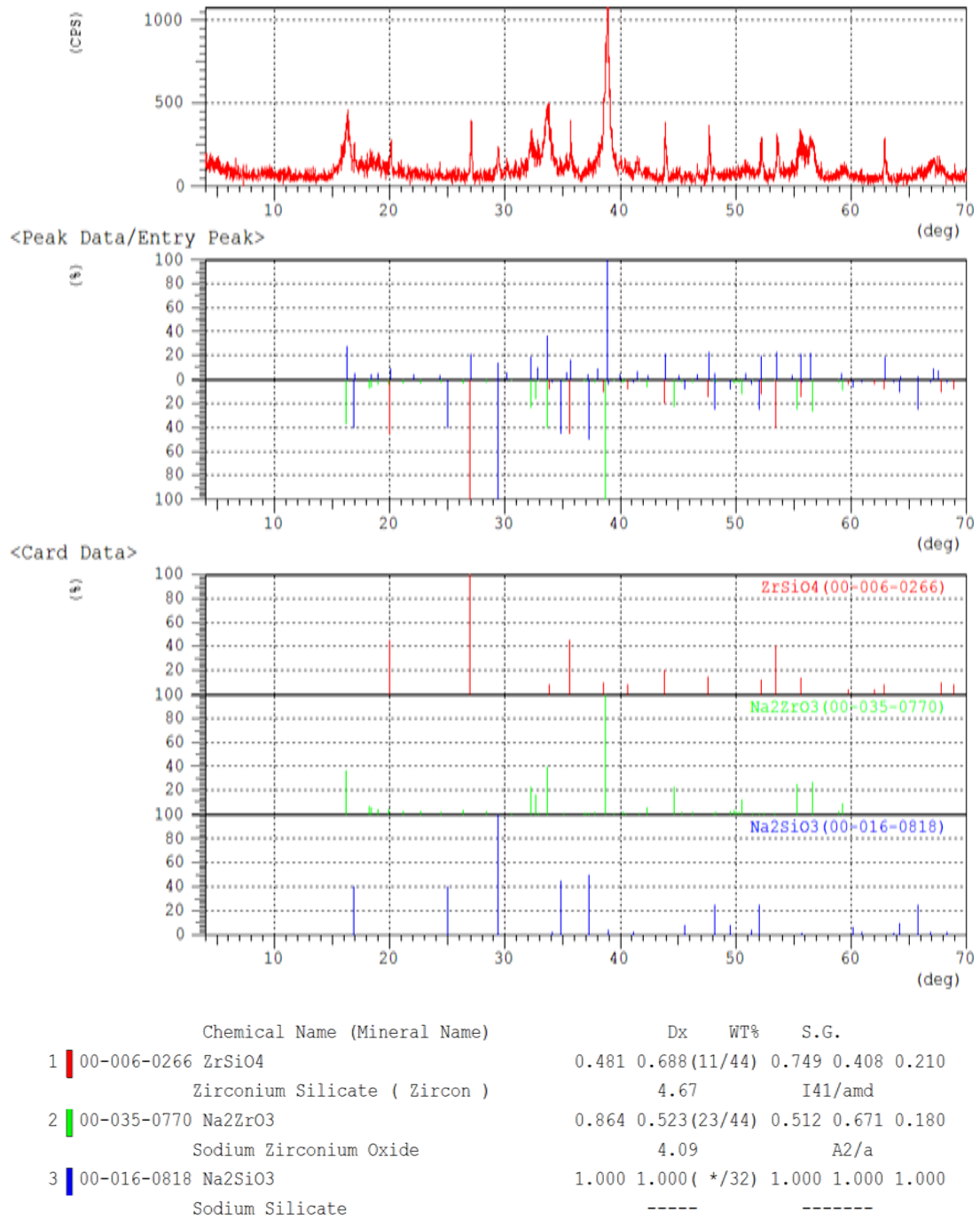
	Chemical Name (Mineral Name)	Dx	WT%	S.G.		
1	00-006-0266 ZrSiO4	0.481	0.688(11/44)	0.749	0.408	0.210
	Zirconium Silicate (Zircon)		4.67	I41/amd		
2	00-035-0770 Na2ZrO3	0.864	0.523(23/44)	0.512	0.671	0.180
	Sodium Zirconium Oxide		4.09	A2/a		
3	00-016-0818 Na2SiO3	1.000	1.000(*/32)	1.000	1.000	1.000
	Sodium Silicate		-----	-------		

Figure 4. Result of x-ray diffraction on smelted zircon sand

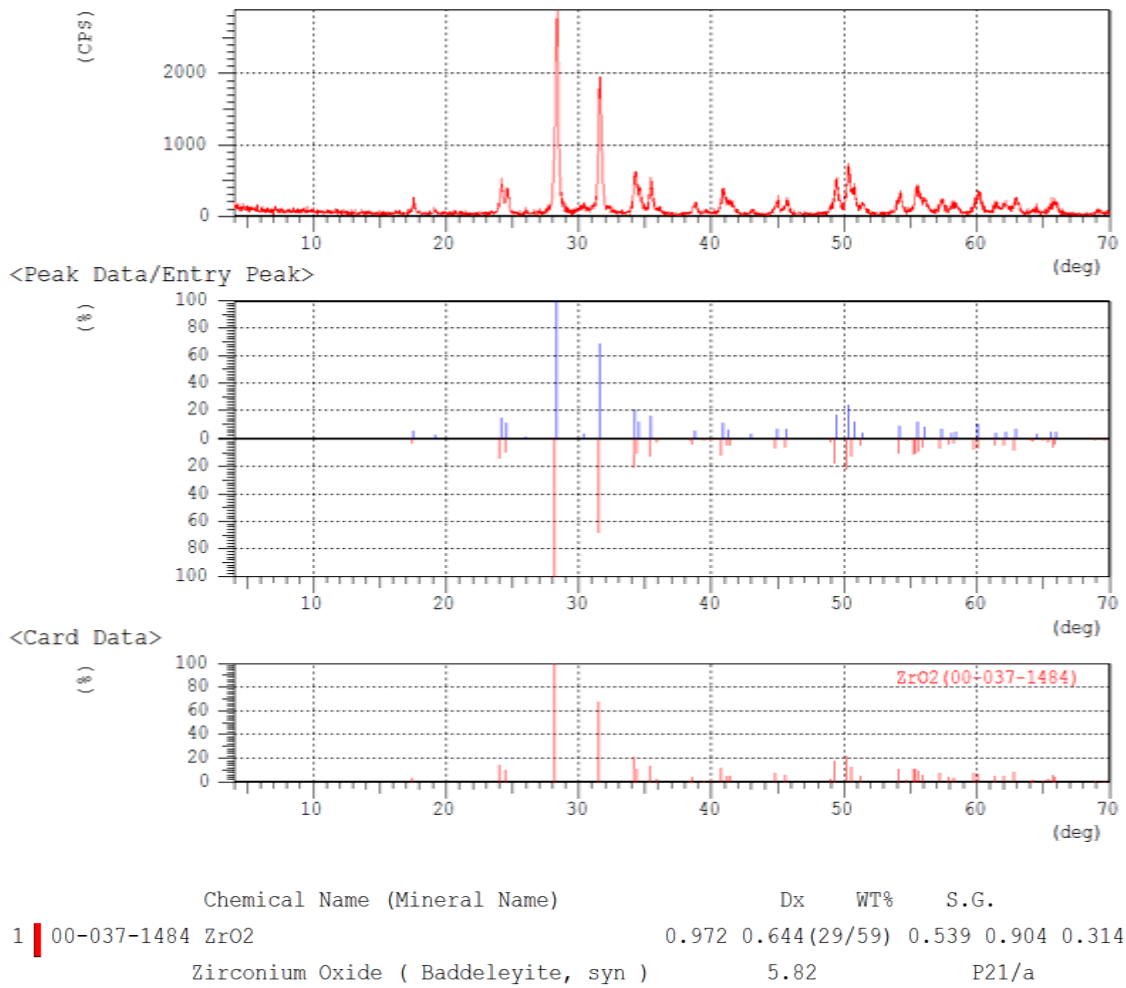| Chemical Name (Mineral Name)	Dx	WT%	S.G.
1 ▌00-037-1484 ZrO2	0.972	0.644(29/59)	0.539 0.904 0.314
Zirconium Oxide (Baddeleyite, syn)	5.82		P21/a

Figure 5. X-ray diffraction of the product

CONCLUSION

Palangkaraya zircon sands consisted of 28.04% ZrO_2. It is well distributed within a +100 mesh for 88.94% with liberation of 84.39%. Upgraded zircon sand resulted from simultaneous concentration equipment increased ZrO_2 content from 28.4 to 64.01% as $ZrO_2 + HfO_2$ with 73.25% recovery, and reduce the gangue minerals such as SiO_2 and others.

The addition of NaOH in smelting process has proved to be effective in breaking the strong bond between ZrO_2 and SiO_2 of zircon sand at 650°C . The smelted zircon sand identified by XRD showed sodium zirconate and sodium silicate. Further process of sodium zirconate succeedly result zirconia. The zirconia contained ZrO_2 95.67% ZrO_2 and 1,60% HfO_2, or ($ZrO_2 + HfO_2$) 97.27% with 65.13% recovery.

ACKNOWLEDGEMENTS

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