Controlling the formation of $\text{Na}_2\text{ZrSiO}_5$ in alkali fusion process for zirconium oxychloride production

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Abstract

In the alkali fusion process for the production of zirconium oxychloride, the formation of the water-insoluble by-product, $\text{Na}_2\text{ZrSiO}_5$, largely affects NaOH recovery and results in the formation of silicon slags. Thus, controlling $\text{Na}_2\text{ZrSiO}_5$ formation is necessary. In this paper, we studied the effects of roasting temperature, NaOH/zircon mole ratio, and particle size of zircon sand on $\text{Na}_2\text{ZrSiO}_5$ formation. The optimum reaction parameters, when the roasting time was 1 h, were as follows: $\geq 95 \mu\text{m}$ average particle size of zircon sand, 6:1 NaOH/zircon mole ratio, and 750 °C roasting temperature. To avoid an uneven roasting temperature during alkali fusion, the use of a rotary kiln reactor is recommended. The amount of $\text{Na}_2\text{ZrSiO}_5$ was significantly decreased under these optimum conditions, and the content of Na_2O was reduced from 7.049% to only 2.21% after three water-leaching cycles.

Keywords: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ production; zircon sand; $\text{Na}_2\text{ZrSiO}_5$; alkali roasting

1. Introduction

Zircon sand (ZrSiO_4) is the source of many zirconium compounds for industrial use, such as zirconium phosphate, basic sulfate, oxychloride and oxynitride, tetrahalides, and pure or doped zirconium oxide [1]. Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), an important basic chemical product, is widely used in ceramic, chemical, electronic, military, and other industries, and it is the main raw material for zirconium-based chemicals [2-4]. According to statistical data, China has been the largest $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ producing country and exporter in the world since 2007, with an annual output of 200 000 tons [5]. In the process of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ production, the first step is the sintering reaction, where the structure of zircon is broken to achieve the preparatory separation of zirconium and silicon. A series of chemical treatments give intermediate products. However, due to the high thermal and chemical stability of ZrSiO_4 , owing to the high coordination of bisdisphenoid ZrO_8 in a tetragonal structure with SiO_4 tetrahedra, aggressive reaction conditions and reagents are needed to decompose the zircon crystal lattice or dissociate the zircon into zirconia and silica [6-8]. Alkali treatment has been one of the effective methods to decompose silicate minerals. The sintering of zircon with sodium carbonate (Na_2CO_3) at 900–1200 °C, or with sodium hydroxide (NaOH) at 650–750 °C is very well known [9, 10]. Researchers [1, 11] have studied the usage of mixed alkalis, such as, CaO-NaOH or KOH-NaOH to decompose zircon. Zircon decomposition in NaOH solution has also been reported [12, 13]. Some methods do not use alkalis to decompose zircon. For instance, pyrolysis can break down the zircon into zirconia and silica at temperatures above 1750 °C [8], and potassium hexafluorosilicate has been used to decompose zircon at approximately 700 °C [14]. Zircon can also be decomposed when sintered with alkaline earth metal oxides such as CaO or MgO-CaO [15, 16], and can be decomposed by

reacting with dolomite at about 1400 °C to produce calcium zirconate and calcium silicate [17].
 Nicholas [18], ground zircon with MgO for up to 100 h, in a procedure that resulted in a
 solid-state reaction leaching ZrO₂. ZrC can be formed by carbonization in an electric furnace
 (2000–2200 °C), followed by chlorination at 350–450 °C [19]. The chlorination method refers to
 the chlorination of zircon sand with coal in a blast furnace at 900–1000 °C [20].

NaOH fusion of zircon, which is widely used in industries and is the key method for producing
 ZrOCl₂·8H₂O at present, is highly efficient when compared with other methods and can be used
 for large-scale production of zirconium oxychloride. The procedure for NaOH fusion technology
 to produce ZrOCl₂·8H₂O involves several processes, namely: alkali fusion, washing, transition,
 acid leaching, flocculation, and crystallization [2]. Alkali fusion is a very crucial step because pure
 ZrOCl₂·8H₂O can be obtained by treating the fused products. The main reactions that take place
 between ZrSiO₄ and NaOH during alkali fusion are as follows:

Most of the water-soluble Na₂SiO₃, Na₄SiO₄, and unreacted NaOH dissolve in water, whereas the
 insoluble Na₂ZrO₃ 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 before evaporation. However, Na₂ZrSiO₅ is water insoluble and does not hydrolyze in water.
 It reacts with HCl in the transition process, leading to Na⁺ wastage. Undoubtedly, this fact places
 the burden of silicon removal on the flocculation process, resulting in the formation of silicon
 slags in industrial production, which should be minimized. The by-product, Na₂ZrSiO₅, generated

1 during $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ production remains an issue. According to Ran Liu's report, the Na_2O
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3 content in water leaching products, from Jiangxi Jing'an Hi-technology Co., Ltd., was 7.049%
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6 after three level countercurrent water leaching processes [2]. This meant that some water-insoluble,
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9 non-ideal components were formed during the sintering process. Arao Manhique et al. had
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11 presented an equilibrium phase diagram of fused products processed for 336 h with optimized
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13 fusion conditions namely, a 2:1 NaOH/zircon mole ratio, 850 °C temperature, and 2 h roasting
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15 time [10]. Under these conditions, the production system gave the least alkali salt waste. In
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17 experiments, however, we found that the particle size of zircon sand, together with other factors,
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20 also had a great influence on the fused products under different fusion conditions. In this paper,
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23 we explore the effects of the NaOH/Zircon mole ratio, roasting temperature, and particle size of
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25 zircon sand on $\text{Na}_2\text{ZrSiO}_5$ formation. We also investigated why the roasting temperature,
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28 NaOH/zircon mole ratio, and particle size of zircon sand affect the components of the fused
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31 products. In this study, our aim was to obtain essential information on the control of the formation
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34 of non-ideal components during alkali fusion. This could be beneficial to the entire production
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44 **2. Experimental procedures**

45 *2.1 Materials*

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47 Zircon sand concentrate, offered by Jiangxi Jing'an Hi-technology Co., Ltd. was used. It has an
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50 average grain size $d(50)$ of 140.3 μm . Its chemical composition was captured using X-Ray
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53 Fluorescence (XRF) (Table 1). As shown in Table 1, the zircon sand concentrate contains mainly
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56 ZrO_2 and SiO_2 with small amounts of TiO_2 and Fe_2O_3 . X-ray diffraction (XRD) of the zircon sand
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concentrate indicates that the main crystalline phase is ZrSiO_4 (Fig. 1). Analytical grade HCl and solid NaOH were used in all the experiments. The deionized water used was super-purified using a water super-purification system (Milli-Q, Millipore, USA). The zircon sand was dried prior to being ground for a number of times by ball milling, then wet-sieved to obtain different narrow size fractions, which were expressed as average diameters $d(50)$ of sizes A-D. The size distributions of the different particle sizes of zircon sand are shown in Fig. 2.

2.2 General procedure

The experiments were performed in a muffle furnace using 30 mL nickel crucibles. The roasting temperature of the heating furnace was controlled by a programmable temperature controller with a precision of $\pm 1^\circ\text{C}$. The zircon sand, which has already been described, and NaOH were homogeneously mixed in the nickel crucibles and charged in the muffle furnace to start the fusion process under static conditions, once the temperature reached the pre-set value. Several experimental parameters were varied to obtain information about the behavior of the fusion process. Four particle size fractions of zircon sand were used, the NaOH/zircon mole ratios ranged from 1:1 to 8:1, and the roasting temperatures ranged from 650–950 $^\circ\text{C}$. The roasting time was 1 h for all the experiments. The fused products were leached with 50 $^\circ\text{C}$ deionized water ($L/S = 4:1$) using mechanical stirring at 300 rev/min for 30 min to remove soluble sodium silicate and excess NaOH [2]. Three washing cycles were needed to remove as much soluble sodium and silicon as possible as sodium silicate and excess NaOH, while sodium zirconate was hydrolyzed to hydrated zirconia [21].

The concentration of Na₂O in the filtrate was analyzed using inductively coupled plasma atomic emission spectra (ICP-OES). The water-leached products were mixed with diluted HCl solution (water/HCl = 1:1) in a plastic beaker and placed in a water bath at 65 °C, with mechanical stirring at 300 rev/min, for half an hour. The dissolution reactions took place as follows:

The slurries were filtered, and the concentration of ZrO₂ in the filtrate was measured using ICP-OES. The NaOH recycling rate and ZrO₂ leaching rate could be calculated using the following formulae:

$$R_{\text{NaOH}} = [m(\text{Na}_2\text{O}) / 2m(\text{NaOH})] \times 100\% \quad (7)$$

$$L_{\text{ZrO}_2} = [m(\text{ZrO}_2) / m(\text{ZrSiO}_4)] \times 100\% \quad (8)$$

where R_{NaOH} is the recycling rate of NaOH, L_{ZrO_2} is the ZrO₂ leaching rate, $m(\text{Na}_2\text{O})$ is the mass of Na₂O in the filtrate after washing with water, $m(\text{ZrO}_2)$ is the mass of ZrO₂ in the filtrate after HCl leaching, $m(\text{NaOH})$ is the total mass of NaOH used during sintering, and $m(\text{ZrSiO}_4)$ is the total mass of ZrSiO₄ used during sintering.

2.3 Characterization

The different particle sizes of zircon sand were measured using a laser particle analyzer (Mastersizer 2000, Malvern, Britain). The phases in the raw material and fused products were characterized by XRD, using CuKα radiation (λ = 0.15418 nm) step-scan mode with a step size of

0.02° 2 θ and a counting time of 0.25 s per step (X'Pert PRO MPD, PANalytical, Netherlands).

The chemical composition of the zircon sand was analyzed using XRF (AXIOS-MAX, PANalytical, Netherlands), while the concentrations of Na₂O and ZrO₂ in solution were analyzed using ICP-OES (Optima 5300DV, PerkinElmer, USA).

3. Results and discussion

3.1 Studies on zircon sand fusion

3.1.1 Effects of roasting temperature and NaOH/zircon mole ratio

The effects of the roasting temperature and NaOH/zircon mole ratio on Na₂ZrSiO₅ formation were examined for temperatures ranging between 650–950 °C using size B zircon sand with NaOH/zircon mole ratios of 1:1, 2:1, 4:1, 6:1, and 8:1. The roasting time was 1 h, the same time used commercially, and could reach a high zircon sand decomposition rate [22]. The XRD patterns of the products sintered with different NaOH/zircon mole ratios at a roasting temperature range of 650–950 °C are shown in Fig. 3.

The effects of the roasting temperature and NaOH/zircon mole ratio on the NaOH recycling rate are presented in Fig. 4. The results show that the recycling rate of NaOH slightly decreased with an increase in the NaOH/zircon mole ratio (4:1, 6:1 and 8:1) at a temperature range of 650–750 °C, and decreased with increasing roasting temperatures. However, the strongest diffraction peak of Na₂ZrSiO₅ (JCPDS 39-0210) at 2 θ = 34.276° was not observed in all the spectra under these conditions (Fig. 3). This indicated that Na₂ZrSiO₅ was not formed. The decreased recycling rate can be attributed to the increase in the amount of sodium metasilicate (Na₂SiO₃) or sodium orthosilicate (Na₄SiO₄) with increased NaOH/zircon mole ratios and roasting temperatures. The

1 recycling rate of NaOH was affected when some of the Na_2SiO_3 and Na_4SiO_4 hydrolyzed to
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3 H_2SiO_3 . This absorbed a small number of Na^+ when the alkalinity was reduced after water
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6 leaching for three cycles [23].
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9 In the temperature range between 850–950 °C, the recycling rate of NaOH was low when the
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11 NaOH/zircon mole ratio was below 4:1. This occurs because of the water insolubility of
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13 $\text{Na}_2\text{ZrSiO}_5$ which forms under these conditions. The diffraction peaks of $\text{Na}_2\text{ZrSiO}_5$ at this
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15 temperature range, for NaOH/zircon mole ratios of 1:1 and 2:1 can be observed in Fig. 3. The
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17 effects of roasting temperature and NaOH/zircon mole ratios on the ZrO_2 leaching rate are
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19 presented in Fig. 5. The ZrO_2 leaching rate increased with an increase in roasting temperatures and
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21 NaOH/zircon mole ratios. When the mole ratio was 2:1, the leaching rate was below 30% at both
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23 650 and 750 °C but it rapidly increased to about 60% at 850 and 950 °C. This rapid increase is the
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25 result of $\text{Na}_2\text{ZrSiO}_5$ generated from reaction (1). For this reaction, one mole of ZrO_2 can be
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27 leached out using 2 mol NaOH, whereas 4 and 6 moles of NaOH are needed for reactions (2) and
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29 (3), respectively. Therefore, under the same NaOH/zircon mole ratio, $\text{Na}_2\text{ZrSiO}_5$ formation favors
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31 the leaching out of ZrO_2 . The decreased recycling rates of NaOH at 850 and 950 °C for 2:1
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33 NaOH/zircon mole ratios also support this.
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44 A ZrO_2 leaching rate of 98% could be reached in a roasting time of 1 h by using size B zircon
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46 sand at a roasting temperature of 750 °C and a 6:1 NaOH/zircon mole ratio. The NaOH recycling
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48 rate was also high, indicating that the process formed little or no $\text{Na}_2\text{ZrSiO}_5$. Therefore, the
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50 recommended conditions to reduce $\text{Na}_2\text{ZrSiO}_5$ formation are roasting temperatures of 750 °C and
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3.1.2 *Effect of particle size of zircon sand*

The study of the effect of different particle sizes of zircon on the ZrO_2 leaching rate was carried out at 750 °C with a 6:1 NaOH/zircon mole ratio, and 1 h roasting time. According to literature, a decrease in particle size will increase the ZrO_2 leaching rate, ascribed to the increased contact area between the reactants, and hence their reactivity [24]. Thus, to increase the rate of reaction, size A ($d(50) = 2.5 \mu\text{m}$) zircon sand should be chosen as the reactant. However, in industrial production, a fast reaction rate and a reduction in by-products are required. The fused products obtained by roasting at different temperatures, different NaOH/zircon mole ratios, and different zircon sand size fractions, were characterized by XRD. The results are shown in Table 2, along with the details of the zirconium-containing compounds. From the table, we can see the relatively large effects that the zircon sand particle size has on the fused products under low NaOH/zircon mole ratios and roasting temperatures >750 °C. Industrial sintering reactions between zircon and NaOH usually take place in sintering pots [25], with the bottom of the pots reaching temperatures that are much higher than the reaction temperature. The system would also lack NaOH locally as the reactions progress. Therefore, we performed the experiments using a high roasting temperature of 850 °C and NaOH/zircon mole ratios of 2:1 and 4:1 to study the effect of zircon sand particle size on the fused products. The XRD patterns of the fused products, which were obtained from molten NaOH that reacted with different particle sizes of zircon sand (sizes A-D in Fig. 2) at 850 °C with a 2:1 NaOH/zircon mole ratio and 1 h roasting time, are shown in Fig. 6. The intensity of the $\text{Na}_2\text{ZrSiO}_5$ peak at $2\theta = 14.698^\circ$ gradually weakened with an increase in zircon sand particle size. Rietveld quantitative phase analysis was carried out using the X' Pert High Score Plus v3.0e software package by PANalytical [26] based on the XRD patterns in Fig. 6. The aim was to

semi-quantitatively determine the amount of $\text{Na}_2\text{ZrSiO}_5$ generated using different sizes of zircon sand as the reactant. The results are shown in Fig. 7.

The effects of zircon sand particle size on the recycling rate of NaOH and ZrO_2 leaching rate under these conditions are presented in Fig. 8 and 9, respectively. When size A zircon sand was used as the reactant, the recycling rates of NaOH were low, whereas the ZrO_2 leaching rates were high. With an increase in zircon sand particle size, there was an increase in the recycling rate of NaOH and a decrease in the ZrO_2 leaching rate difference between two adjacent particle distributions (R_1 , R_2 , and R_3 shown in Fig. 9). This can be attributed to the decrease of $\text{Na}_2\text{ZrSiO}_5$ in the fused products. Combining the data presented in Fig. 8 and 9 with the results of Rietveld quantitative analysis of $\text{Na}_2\text{ZrSiO}_5$ in Fig. 7, the production of $\text{Na}_2\text{ZrSiO}_5$ can be assumed to be reduced when a larger size of zircon sand was used as the reactant. Interestingly, we found that when size A zircon sand was used, the NaOH recycling rate was higher for a 2:1 NaOH/zircon mole ratio than for a ratio of 4:1. This is in contrast with the results in Fig. 4, which were obtained from experiments where size B zircon sand was used instead. These results could indicate that the particle size of zircon sand has a bigger impact on $\text{Na}_2\text{ZrSiO}_5$ formation than the NaOH/zircon mole ratio when the roasting temperature is 850 °C.

In particular, the sintering process should not only require a fast reaction rate, but also a reduction in $\text{Na}_2\text{ZrSiO}_5$ production. The results in Fig. 7 show that the $\text{Na}_2\text{ZrSiO}_5$ mass fractions in the fused products, obtained from the reaction of molten NaOH with size C and D zircon sand, did not vary much. Thus, size C zircon sand ($d(50) = 95.2 \mu\text{m}$) is recommended in alkali fusion.

3.1.3 Water leaching

The fused products, obtained under optimum conditions using a rotary kiln reactor, were leached with water for three cycles to remove the soluble sodium silicate. The content of Na_2O was analyzed using ICP-OES. The Na_2O content, after leaching the product for three 30 min cycles at a temperature of 50 °C and an L/S ratio of 4:1, was 2.21%. This was a much smaller value than that currently found at Jiangxi Jing'an Hi-technology Co., Ltd.

3.2 Mechanism analysis

3.2.1 Thermodynamic analysis of the effects of roasting temperature and NaOH/zircon mole ratio

Phase diagrams give information about the thermodynamic stabilities of different phases in a reaction system. Based on the phase diagram of $\text{Na}_2\text{O-SiO}_2\text{-ZrO}_2$ [10, 27], at 800–1250 °C, Na-Zr-Si-O phases such as $\text{Na}_2\text{ZrSiO}_5$, $\text{Na}_2\text{ZrSi}_2\text{O}_7$, $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$, etc., are only thermodynamically stable when ratios of NaOH/ ZrSiO_4 are 2:1 or less. However, when the roasting temperature range is 600–800 °C, Na-Zr-Si-O phases are thermodynamically unstable at any NaOH/zircon mole ratio. Moreover, at a temperature range of 600–1250 °C and mole ratios $\geq$ 4:1, Na-Zr-Si-O phases are not thermodynamically stable. The analysis above further supports the experimental conclusions.

3.2.2 Kinetics analysis of the effect of particle size of zircon sand

A kinetic study of the alkali fusion reaction was performed in order to investigate the mechanism of the effect of the particle size of zircon sand on $\text{Na}_2\text{ZrSiO}_5$ formation. Decomposition of zircon sand in a molten NaOH system is a typical liquid-solid reaction, which

can be analyzed with the shrinking core model [28, 29]. Under different process controls, the kinetics equations can be simplified as follows:

Chemical reaction controlled process

(9)

Diffusion through the residual layer process

(10)

Where X is the ZrO_2 leaching rate at time t (min), and k_1 ($m \cdot min^{-1}$) and k_2 ($m \cdot min^{-1}$) are the apparent rate constants.

The experiments were carried out in an NaOH system, with an NaOH/zircon mole ratio of 6:1 and a fusion time of 1 h, using size A (treated by ball milling for several hours) and size D (untreated) zircon sand. Based on ZrO_2 , the leaching rate at time t , given in Fig. 10, was calculated from eq. (9) and (10), respectively. As shown in Fig. 11, eq. (9) gives better linear tendencies (from 0 to 40 min) at each reaction temperature for both sizes of zircon sand. Plots of

$1 - (1 - X)^{1/3}$ vs. time shown in Fig. 12 indicate that the ZrO_2 leaching rate at

650–950 °C gives a good correlation with the chemical reaction controlled kinetics equation.

Therefore, decomposition of zircon sand in the molten NaOH system is a chemical reaction

controlled process in the temperature range of 650–950 °C when using size A or D zircon sand.

The apparent rate constants can be obtained from Fig. 12. The specific apparent activation energy can then be calculated based on the Arrhenius equation in Fig. 13. The apparent activation energy, when using size D zircon sand, is 50.3 kJ/mol, while for size A it is 41.1 kJ/mol. Thus, it is likely that the particles in the size A zircon sand gained some mechanically induced disorder after ball milling, which reduced the activation energy of the chemical reaction process. In addition, we can therefore speculate that the apparent activation energy increases when the zircon sand size increases from A-D, respectively.

At the early stage of this alkali fusion, the zircon sand first reacts with molten NaOH on the particle surface, refer to eq. (3), to generate Na_2ZrO_3 and Na_4SiO_4 [30]. The alkali fusion reaction has a lower apparent activation energy when using smaller particle size zircon sand as a reactant, thus favoring the following reaction:

On the other hand, Eq. (11) could not easily take place when using larger particle sized zircon sand because of the higher activation energies. This would explain why the formation of $\text{Na}_2\text{ZrSiO}_5$ is controlled by using larger particle sized zircon sand.

4. Conclusion

Reaction parameters were investigated to control and reduce $\text{Na}_2\text{ZrSiO}_5$ formation in the sintering process during $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ production. The use of a rotary kiln reactor is recommended. The main conclusions are as follows:

- (1) The roasting temperature, NaOH/zircon mole ratio, and particle size of zircon sand all

1 have effects on $\text{Na}_2\text{ZrSiO}_5$ formation. The optimum reaction parameters are a roasting
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3 temperature of 750 °C, an NaOH/zircon mole ratio of 6:1, and zircon sand average
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5 particle size $\geq 95 \mu\text{m}$.
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9 (2) The amount of $\text{Na}_2\text{ZrSiO}_5$ is significantly reduced under these optimum conditions, and
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11 the content of Na_2O decreased to only 2.21% after three cycles of water leaching the
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13 products. This is much less than the 7.049% content currently found at Jiangxi Jing'an
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15 Hi-technology Co., Ltd.
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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10(a)

Figure 10(b)

Figure 11

Figure 12(a)

Figure 12(b)

Figure 13

Fig. 1 XRD pattern of zircon sand.

Fig. 2 Size distributions of zircon sand obtained from ball milling at different times expressed as average diameters $d(50)$ (Sizes: A, 2.5 μm ; B, 56.5 μm ; C, 95.2 μm ; and D, 140.3 μm).

Fig. 3 XRD patterns of fused products obtained from molten NaOH that reacted with size B zircon sand at 650–950 $^{\circ}\text{C}$ with an NaOH/zircon mole ratio range of 1:1–8:1.

Fig. 4 Effects of roasting temperature and NaOH/zircon mole ratios on the recycling rates of NaOH.

Fig. 5 Effects of roasting temperature and NaOH/zircon mole ratios on ZrO_2 leaching rates.

Fig. 6 XRD patterns of fused products obtained when molten NaOH reacted with different particle sizes of zircon sand (sizes A–D in Fig. 2) at 850 $^{\circ}\text{C}$ with an NaOH/zircon mole ratio of 2:1.

Fig. 7 $\text{Na}_2\text{ZrSiO}_5$ and Na_2ZrO_3 mass fractions of fused products obtained when molten NaOH reacted with different particle sizes of zircon sand (A–D in Fig. 2) at 850 $^{\circ}\text{C}$ with an NaOH/zircon mole ratio of 2:1.

Fig. 8 Effect of particle sizes (A–D in Fig. 2) of zircon sand on the recycling rates of NaOH at 850 $^{\circ}\text{C}$ with NaOH/zircon mole ratios of 2:1 and 4:1.

Fig. 9 Effect of particle sizes (A–D in Fig. 2) of zircon sand on ZrO_2 leaching rates at 850 $^{\circ}\text{C}$ with NaOH/zircon mole ratios of 2:1 and 4:1.

Fig. 10(a) ZrO_2 leaching rates at time t using size A zircon sand at a temperature range of 650–950 $^{\circ}\text{C}$.

Fig. 10(b) ZrO_2 leaching rates at time t using size D zircon sand at a temperature range of 650–950 $^{\circ}\text{C}$.

Fig. 11 Plots of $1 - (1 - X)^{1/3}$ and $1 - 3(1 - X)^{2/3} + 2(1 - X)$ vs. time at 650 $^{\circ}\text{C}$ using size A and

size D zircon sand as reactants, respectively.

Fig. 12(a) Plots of $1 - (1 - X)^{1/3}$ vs. time using size A zircon sand.

Fig. 12(b) Plots of $1 - 3(1 - X)^{2/3} + 2(1 - X)$ vs. time using size D zircon sand.

Fig. 13 Activation energy plot of the decomposition process of zircon sand using size A and size D zircon sand as reactants, respectively.

Table 1

Composition	ZrO ₂ +HfO ₂	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	RE oxides
Content (wt. %)	66.81	32.56	0.12	0.11	0.34	0.06

Table 2

Size A			Size B		Size C		Size D	
Roasting	NaOH/zircon	Phase	NaOH/zircon	Phase	NaOH/zircon	Phase	NaOH/zircon	Phase
temp.°C	mole ratio		mole ratio		mole ratio		mole ratio	
650	1:1	ZS	1:1	ZS	1:1	ZS	1:1	ZS
	2:1	ZS, NZ	2:1	ZS, NZ	2:1	ZS, NZ	2:1	ZS, NZ
	4:1	ZS, NZ	4:1	ZS, NZ	4:1	ZS, NZ	4:1	ZS, NZ
	6:1	NZ, ZS	6:1	NZ, ZS	6:1	NZ, ZS	6:1	NZ, ZS
	8:1	NZ, ZS	8:1	NZ, ZS	8:1	NZ, ZS	8:1	NZ, ZS
750	1:1	ZS, NZS, NZ	1:1	ZS, NZ	1:1	ZS, NZ	1:1	ZS, NZ
	2:1	ZS, NZS, NZ	2:1	ZS, NZ	2:1	ZS, NZ	2:1	ZS, NZ
	4:1	NZ, ZS	4:1	NZ, ZS	4:1	ZS, NZ	4:1	ZS, NZ
	6:1	NZ	6:1	NZ	6:1	NZ	6:1	NZ
	8:1	NZ	8:1	NZ	8:1	NZ	8:1	NZ
850	1:1	ZS, NZS	1:1	ZS, NZS, NZ	1:1	ZS, NZ	1:1	ZS, NZ
	2:1	ZS, NZS, NZ	2:1	ZS, NZ, NZS	2:1	ZS, NZ, NZS	2:1	ZS, NZ, NZS
	4:1	NZS, NZ, ZS	4:1	NZ, ZS	4:1	NZ, ZS	4:1	NZ, ZS
	6:1	NZ	6:1	NZ	6:1	NZ	6:1	NZ
	8:1	NZ	8:1	NZ	8:1	NZ	8:1	NZ
950	1:1	ZS, NZS	1:1	ZS, NZS, NZ	1:1	ZS, NZS	1:1	ZS, NZS
	2:1	ZS, NZS, NZ	2:1	ZS, NZS, NZ	2:1	ZS, NZS, NZ	2:1	ZS, NZS, NZ
	4:1	NZS, NZ	4:1	NZ, ZS	4:1	NZ, ZS	4:1	NZ, ZS

6:1	NZ	6:1	NZ	6:1	NZ	6:1	NZ
8:1	NZ	8:1	NZ	8:1	NZ	8:1	NZ

Note: “ZS” refers to ZrSiO_4 , “NZ” refers to Na_2ZrO_3 and “NZS” refers to $\text{Na}_2\text{ZrSiO}_5$.

Table 1 Average chemical compositions of zircon concentrate.

Table 2 Phase compositions of fused products obtained from molten NaOH that reacted with zircon sand of sizes A–D, in Fig. 2, at roasting temperatures of 650–950 °C and NaOH/zircon mole ratios of 1:1–8:1 at a roasting time of 1 h.

Intensity/a.u.