

High Purity Zirconia and Silica Powders via Wet Process: Alkali Fusion of Zircon Sand

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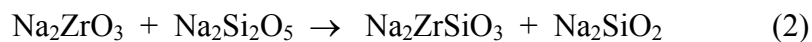
Abstract. Zircon sand was reacted with liquid caustic soda (50% NaOH) in open vessel at 600 °C for 2h. The effect of NaOH/ZrSiO₄ reactant ratio on the yield of zirconia recovery was verified. Samples of fusion products water washed were characterized by X-ray diffraction (XRD) to identify the main compounds formed. Silica powders were obtained via acid catalyzed reaction and zirconia powders were resulted from crystallization of zirconium oxychloride. Both zirconia and silica powders were analyzed by XRF (X-ray fluorescence) and BET method. Laser Quasi Elastic Light Scattering (QLS) technique was used for agglomerate size distribution determination. High purity and fine zirconia and silica powders were obtained. The specific surface area of zirconia calcined at 550 °C reached ~ 70m²g⁻¹. Silica powder calcined at 800 °C presented a high specific surface area ~ 500 m²g⁻¹.

Introduction

Zirconia, ZrO₂, has attracted considerable attention as a high technology material for industrial applications because of its mechanical, thermal, electrical, chemical and optical properties. The main mineral precursor of zirconia production is zircon (ZrSiO₄). It is a natural combination of zirconium oxide (ZrO₂) and silica (SiO₂), which occurs as accessory mineral in silica rich igneous rocks such as granite, pegmatite and nepheline syenite. It is also found concentrated with other heavy minerals e.g., rutile, in river and beach sands. Zircon is of the most important among the heavy minerals occurring in the beach sand along the coast of Brazil [1,2]. It is commonly obtained as a byproduct in mining and processing of heavy minerals sands such as rutile and ilmenite. [2]. For extraction of zirconia from zircon a variety of techniques have been proposed in the literature [3], including alkali digestion, chloration, reductive smelting and extraction with basic oxides. Work has been published on alkali fusion of zircon [4, 5, 6] to recover ZrO₂, but any paper has concerned with the wet-chemical treatments to recovery silica to avoid troubles in the waste disposal of solid or liquid by-products. This work proposes not only the extraction of zirconia, but also the recovery of silica content of the solid residue (sodium zirconyl silicate) and liquid effluent (sodium silicate) both resulted from water leaching of zircon caustic fritted. The frit obtained in the alkali fusion of zircon sand was washed with water to remove the water-soluble sodium silicate. In the insoluble residue contain most of zirconium in form of sodium zirconate, water- insoluble silica and a small amount of hydroxides of the most common impurities. While intentionally introduced cations (Y³⁺, Mg²⁺, Ca²⁺, rare earth cations) provide special properties to final product in many cases (transformation toughened ceramics, cation impurities from the raw material, e. g. zircon sand, are often undesirable. The present work has processed Brazilian zircon sand by alkali fusion to obtain pure zirconia and pure silica as byproduct. Although it is difficult to express the alkaline fusion reaction by any single equation, it has been proposed the following reaction plays a main role in the fritting of zircon sand with NaOH [7]:



However, silica insoluble in water but acid soluble is observed in the frit, signifying that other minor reactions take place simultaneously. It was suggested the formation of sodium zirconium silicate during fritting, which may be expressed by the following equations [4]:



The effect of NaOH/ZrSiO₄ reactant ratio on the alkali fusion of zircon to recover ZrO₂ was studied in this work. The present authors are engaged in examine the recuperation of silica as a byproduct. The recovery of silica is very attractive due to its importance in various fields of science and technology, such as catalysis [8], ceramics [9], biological labels [10], optical resonance [11] etc. The properties of these nanoparticles such as high surface area are high desirable for catalytic support because of high surface area provides more active sites for gas/solid interactions. Moreover, the morphology of nanosized amorphous silica powders is great interest since many of mechanical, electrical, and other properties of the existing materials can be improved or modified by this silica addition. The characterization of these properties or morphologies can lead to new potential uses. For example, high porous silica powders with high surface area can also be used as insulating for microelectronic packaging since silica has relatively low dielectric constant among inorganic oxides. This paper presents a route to obtain pure silica powder with extremely high specific surface area, by wet chemical processing of the effluents provided from the alkali fusion of zircon technique for ZrO₂ extraction. The recovery of silica is environment friend because it avoids troubles in the waste disposal of solid or liquid by-products. The recovered silica is significant because of it may be used as supplier in important silica based materials, given widespread importance of SiO₂ nanoparticles in several industrial applications.

Experimental Procedure

Aqueous caustic soda (NaOH) 50 wt% solution was prepared to using as the decomposition agent of zircon sand. The prepared solution and Brazilian zircon sand were mixed in wt/wt ratio of 1.0; 1.2 and 1.5 NaOH/ZrSiO₄. The moisture was carefully charged into an iron crucible and set in an electric furnace. The alkaline fusion reaction was conducted following thermal treatment: first heating at rate 20°C/min up to 100°C, remained at this temperature for 1h and then heating at rate 20°C/min up to 200°C, remained for 1h and finally the temperature was increased to 600°C for 2h, at that time the alkali fusion reaction takes place and caustic frit is formed, a mixture of sodium zirconate and sodium silicate. This frit was washed with water, removing the soluble sodium silicate and hydrolyzing the zirconate to an impure hydrous zirconium oxide. The water-leached frit was treated in cold 8M HCl at 80°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. The separated zirconyl chloride solution was kept overnight at room temperature for silicic acid coagulation (precipitation of silica in form of silica gel) and zirconyl chloride crystallization. Dissolution of once-crystallized zirconyl solution in water and stirring produced mushy semi-solid solidified mass and permitted the removal of coagulated silicic acid by filtration. The separated silica gel was exhaustively washed with water and filtered until no chloride was detected by AgNO₃ test, dried and calcined resulting silica powder for chemical and physical characterization. The filtrate consisting of zirconium oxychloride solution free from silica was then heated on a hot plate to reduce the volume to obtain zirconium oxychloride crystals. Those crystals are separated by filtration and exhaustively washed with ethanol. The obtained white crystals are dissolved in water to achieve clear solution of zirconium oxychloride, and then it was neutralized with ammonia to precipitate zirconium hydroxide, which was dried and calcined at 550°C for 1h. After calcining, white zirconia powder was produced for characterization. Both zirconia and silica

powders were analyzed by XRF (X-ray fluorescence) and BET method. Laser Quasi Elastic Light Scattering (QLS) technique was used for agglomerate size distribution determination. SEM (scanning electronic microscopy) was used for powders morphology observation. To indicate the degree of conversion in the fritting of the zircon, the filtrate produced by hydrolysis was analyzed gravimetrically [12].

Results and Discussion

The particle distribution size of the zircon sand is provided in Table 1. Table 2 gives its chemical analyses.

Table 1- Particle size distribution of zircon sand

Particle size		
[mesh]	[μm]	[wt%]
65	$\leq 250\mu\text{m} \leq 210\mu\text{m}$	0.29
65/115	$\leq 250 \mu\text{m}, \leq 125 \mu\text{m}$	43.8
115/200	$\leq 125 \mu\text{m} \leq 74\mu\text{m}$	55.9

It is observed that the mean size of zircon sand is between 205 and 74 μm .

Table 2- Analytical results of zircon by XRF

Composition [wt%]									
ZrO ₂	HfO ₂	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	Y ₂ O ₃	U ₃ O ₈	ThO ₂	CaO
66.1	1.63	30.3	0.10	0.30	1.02	0.14	0.06	0.11	0.08

Fritting results as a function of NaOH/ZrSiO₄ ratio to recover ZrO₂ is showed in Table 1.

Table 1- ZrO₂ recovery at 600°C for 1h reaction as function of NaOH/ZrSiO₄ ratio

Sample	NaOH/ZrSiO ₄ [wt/wt]	Zirconium recovered % [ZrO ₂ + Hf O ₂]
1	1.0	62.77
2	1.2	74.04
3	1.5	87.26

In Table 1, the percentage of zirconium recovered from the frit is used to express the extent of decomposition of zircon. The degree of decomposition depends on parameters such as particle size of zircon sand, alkali/zircon ratio, temperature and time of decomposition. According to the literature DTA results of the caustic reaction with NaOH, revealed that the optimum temperature in actual fritting operation ranges from 600°C to 650°C [4]. Higher temperatures than 650°C are not beneficial for the further improvement of decomposition [4]. In view of those literature results, the decomposition of our zircon can be improved by increasing the time of reaction or a reduction of particle size of zircon sand, since the selected temperature is in the optimum range. XRD analysis of the water washed frit after dried at 100°C for 1h, compared with the XDR patterns of start zircon sand are showed in Fig. 1.

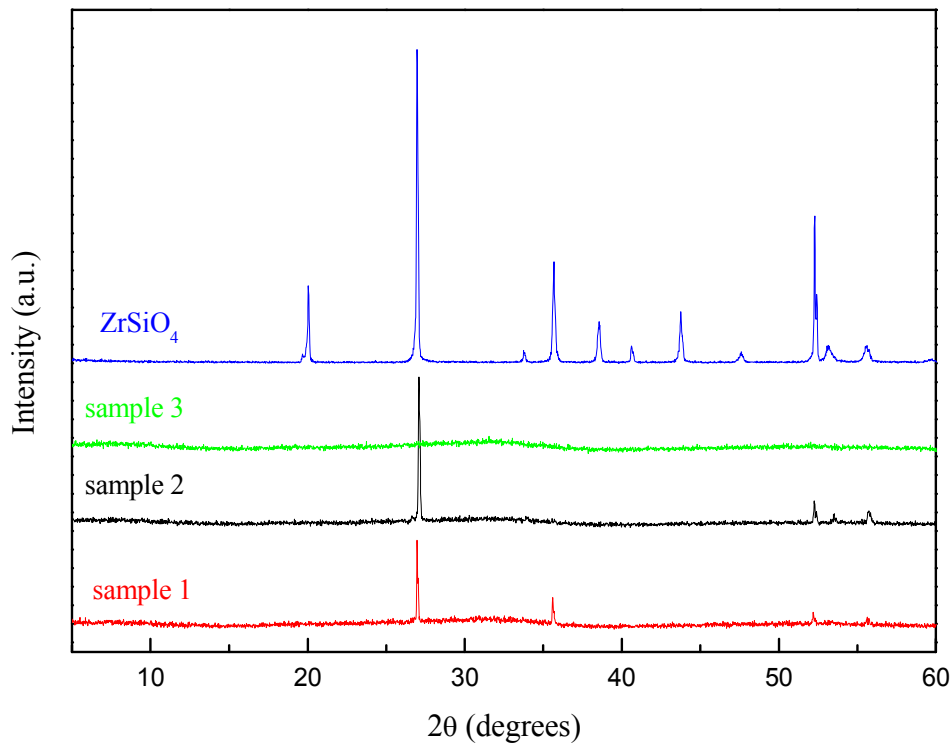


Fig. 1- XRD patterns of $ZrSiO_4$ and fused products water leached samples using $NaOH/ZrSiO_4$ (wt/wt) of 1.0 (sample 1), 1.2 (sample 2) 1.5 (sample 3).

From Fig. 1, it can be verify the presence of zircon in samples 1 and 2 since the observation of the high-intensity line (2,0,0) of zircon [13] in both of samples. The presence of zircon in those samples reveals that the amount of NaOH was not sufficient to the total reaction of zircon. From XRD analysis of sample 3, it seems to indicate that the most of the zircon was reacted. No lines of zircon are observed. XRD pattern of sample 3 observed in Fig. 3 is typical of amorphous material. This is because of the most of zirconates formed at alkaline fusion reaction were hydrolyzed during the washing of the frit with water and convert to the amorphous hydrous oxide complex, according to the following equation [14]



Agglomerate diameter size distribution determined by QLS (Quasi Elastic Light Scattering) technique is presented in Fig. 2. It is observed that the agglomerate diameter size of zirconia powder falls between 20 to 75 nm (Fig. 2 A), the d_{50} size is ~ 40 nm. The agglomerate size of silica is larger than zirconia agglomerates, between 100 and 550 nm (Fig.2 B). The d_{50} agglomerate size determined by QLS technique was 275 nm.

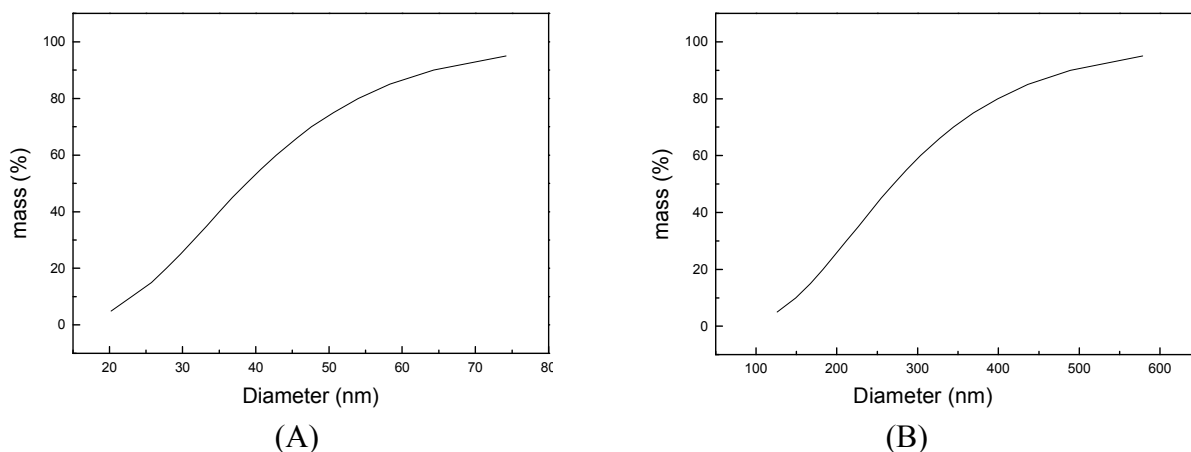


Fig. 2 - Agglomerate diameter size distribution of zirconia calcined at 550 °C for 1h, obtained by crystallization of zirconyl chloride followed by zirconium hydroxide precipitation (A) and recovered silica gel calcined at 800 °C for 1h.

SEM image of zirconia powder, in Fig. 3 A, shows that the morphology of the agglomerates is spherical like with sub micron size, confirming the results of size distribution determined by QLS. In Fig. 3 B it is observed SEM micrographs of silica. It can be seen agglomerates with morphology not exactly spherical like but the agglomerate size confirms the results determined by QLS.

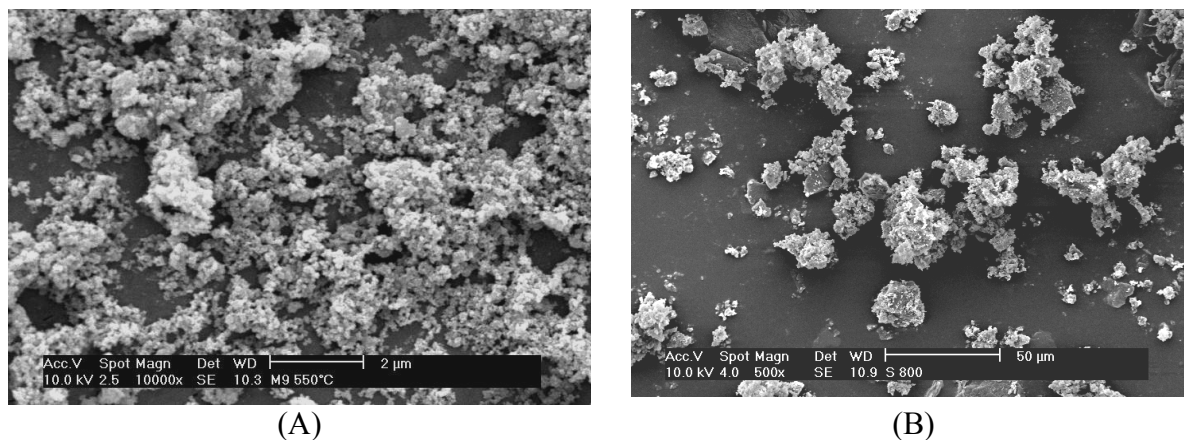


Fig. 3- SEM images of zirconia calcined at 550 °C for 1h, obtained by crystallization of zirconyl chloride followed by zirconium hydroxide precipitation (A) and recovered silica gel calcined at 800 °C for 1h.

The specific surface area measurements determined by BET method revealed $72.29\text{m}^2\cdot\text{g}^{-1}$ and $501.32\text{m}^2\cdot\text{g}^{-1}$ for zirconia and silica powders, respectively. XRF analysis indicated that zirconia presented 98.5 % of purity and silica with 99.51 % of purity was recovered.

Conclusions

By using 1.5 ratio of $\text{NaOH}/\text{ZrSiO}_4$ at 600 °C for 2h in the process of alkaline fusion of zircon sand, it can improve 87.26 % of ZrO_2 . The obtained product is suitable for preparing ZrO_2 with 98.5 % of purity, $72.29\text{m}^2\cdot\text{g}^{-1}$ specific surface area and sub micron agglomerate size. Silica can be recovered via acid catalyzed reaction; at the same time sodium zirconate (product of alkaline fusion of zircon)

is solubilized with HCl. Silica with 99.51 % of purity has been obtained. Silica powders with high specific surface area ($501.32\text{m}^2\cdot\text{g}^{-1}$) were obtained, presetting agglomerates of about 300 nm.

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