Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 1431–1438

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Analysis of water leaching and transition processes in zirconium oxychloride octahydrate production

Ran Liu[a,b,c], Jingkui Qu[b,c], Jing Song[b,c], Tao Qi[b,c], Ailing Du[a,*]

[a]School of Chemistry and Chemical Engineering, Shandong University, Jinan 250061, China
[b]National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Beijing 100190, China
[c]Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

Received 18 June 2013; received in revised form 4 July 2013; accepted 4 July 2013
Available online 16 July 2013

Abstract

The water leaching and transition process in manufacturing zirconium oxychloride octahydrate was examined. Results from X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectra showed that most of the soluble sodium silicate was dissolved and the residue hydrolyzed into H_2SiO_3 during the water leaching process. In addition, Na^+ from sodium zirconate ($NaZrO_3$) in the interlayer was removed during the first and second water leaching and the in-host layer was distinguished in the third water leaching. This process resulted in the hydrolysis of $NaZrO_3$ into $ZrO(OH)_2$. Results from the scanning electron microscopy (SEM), FT-IR spectra, nuclear magnetic resonance (NMR) and XRD of the transition process showed the main reaction and properties of the products at different pH values. Na_2ZrSiO_5 reacted with HCl at pH = 7, producing $ZrO(OH)_2 \cdot SiO_2$ and NaCl. $ZrO(OH)_2 \cdot SiO_2$ partially reacted with HCl, forming $ZrOCl_2$ and H_2SiO_3 with a decrease in pH.
© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Zirconium oxychloride; Water leaching; Transition

1. Introduction

Zirconium has attracted considerable attention as a material for high-tech industrial applications because of its excellent mechanical, thermal, electrical, chemical, and optical properties. This element is widely used in ceramic production and nuclear reactors to clad fuel rods. Zirconium is also used to remove residual gases in electron tubes as well as to fabricate pumps, valves and heat exchangers [1–3]. Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$), an important basic chemical product, is the main raw material for zirconium-based chemicals, such as zirconium oxide, zirconium sulfate, and zirconium carbonate. According to the survey conducted by the China Nonferrous Metals Industry Association, China ranked first in $ZrOCl_2 \cdot 8H_2O$ production because it produced more than 200,000 t of $ZrOCl_2 \cdot 8H_2O$ in 2011. Alkali fusion of zircon sand concentrate, the key method for producing $ZrOCl_2 \cdot 8H_2O$, is highly efficient and can be used for large-scale production, compared with the chloride and lime sintering method. The alkali fusion technology is shown in Fig. 1 [4–6].

During alkali fusion, zircon is sintered thoroughly with sodium hydroxide (NaOH) at 750 °C, according to the following reactions [7–9]:

$$ZrSiO_4 + 2NaOH \rightarrow Na_2ZrSiO_5 + H_2O \quad (1)$$

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \quad (2)$$

$$ZrSiO_4 + 6NaOH \rightarrow Na_2ZrO_3 + Na_4SiO_4 + 3H_2O \quad (3)$$

Water leaching separates sodium zirconate (Na_2ZrO_3), sodium metasilicate (Na_2SiO_3), and sodium orthosilicate (Na_4SiO_4) formed during the alkaline melting, which is critical for silicon removal in the whole line. Na_2SiO_3, Na_4SiO_4 and unreacted NaOH are supposed to be soluble in water, whereas Na_2ZrO_3 should be hydrolyzed, remaining in the water insoluble residue. During the water leaching, a certain amount of zirconium is entrained in the silicon slag and discharged. If optimum silicon removal is performed, we can reduce the amount of silicon slag and the corresponding zirconium entrained can be reduced. This process will reduce the production cost and improve the

*Corresponding author. Tel./fax: +86 13678819446.
E-mail address: duailing56@163.com (A. Du).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.07.026

zirconium extraction rate. Therefore, investigating the water leaching process is necessary.

Transition is performed not only to remove Na^+ from the material, but also influence the acid solution and flocculation process. However, its mechanism remains unclear; as a result denatrium is difficult to achieve. Thus, the transformation process is not performed and Na^+ remains in $ZrOCl_2 \cdot 8H_2O$. However, if the transition process is extensively studied, Na^+ removal and the quality of $ZrOCl_2 \cdot 8H_2O$ can be greatly enhanced.

Studies on the alkali fusion of zircon sand concentrate with NaOH have been conducted. However, the mechanism of the water leaching and transition technique has not been analyzed. To the best of our knowledge, the structural characterization of silicon and zirconium using X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), and nuclear magnetic resonance (NMR) has not been reported. With the use of these techniques, the present study explores the relationship between the preparation conditions and properties of the materials. The mechanism and several key techniques of the water leaching and transformation processes are discussed in detail. Results from this study are anticipated to be beneficial in the understanding of $ZrOCl_2 \cdot 8H_2O$ production through alkali fusion.

2. Experimental procedures

2.1. Materials

The fused mass was provided by Jiangxi Jing'an Hi-technology Co. Ltd. The chemical composition of the sample is shown in Table 1, and results from the XRD analysis are presented in Fig. 2a. The samples primarily comprised Na_2ZrO_3 and Na_2SiO_3.

2.2. Analyses and measurements

The concentrations of Na_2O, SiO_2 and ZrO_2 in the aqueous solution were analyzed using inductively coupled plasma atomic emission spectra (ICP-AES) (IRIS/AP, Thermo Electron Corporation). Hydrogen and nitrogen in the xerogel were determined using a Perkin-Elmer Series II CHNS/O Analyzer 2400 (USA).

The physical structure was evaluated using an X-ray diffractometer (D/max-RB, Rigaku, Japan), with the following conditions: 40-kV CuKα radiation with a graphite monochromator, and 40 mA electric current. The patterns were obtained within a 5–90° 2θ angular interval with 0.05° step and 1 s of counting time.

The chemical structure was evaluated by FT-IR spectra (Perkin-Elmer spectrophotometer). The samples were prepared by mixing the materials and KBr in a proportion 1:200(w/w). For all spectra, eight scans were accumulated with a 4 cm^{-1} resolution.

The SEM micrographs of the solid particles were taken using a scanning electron microscope (JSM-35CF, Japan Electron Optics Laboratory Co., Ltd.).

A Bruker Avance 400 (9.4 Telsa) operating at a frequency of 79.5 MHz for the ^{29}Si nucleus was utilized to collect the NMR spectra. A standard double-air-bearing cross polarization–magic angle spinning (CP/MAS) probe was used. Ground samples were loaded into 7 mm fused zirconia rotors, sealed with Kel-F™ caps, spun at a magic angle with a spinning rate of 5 kHz at a delay time of 5 s. The observed signals were quantified by directly comparing the areas of the peaks. All chemical shifts were externally referenced to tetramethyl silicane.

Diffuse reflectance spectra of the samples were recorded on a UV-2000 spectrometer equipped with an integrating sphere, using $BaSO_4$ as a reference material.

2.3. General procedure

2.3.1. Water leaching process

All experiments were conducted in batch mode and three level countercurrent water leaching processes. The leaching experiments were conducted in a 2-L volume plastic cup. The fused mass (200 g) was mixed with deionized water (L/S=4:1) of 50 °C, via mechanical stirring at 300 rev/min for 30 min. Solid–liquid separation was subsequently achieved. Sodium, silicon and zirconium contents of the final washed residue were analyzed by ICP-AES.

2.3.2. Transition process

The water leaching product (500 g) was mixed with deionized water (1000 g) in a plastic cup and put in a water bath at 65 °C. The pH value was adjusted using HCl (5.5 mol/L) to 1, 3, or 7 under mechanical stirring at 300 rev/min. The sample precipitated at a stable pH after 40 min. Deionized water (1500 g) was added to the plastic cup with constant stirring for 5 min. The water was filtered, washed thoroughly with deionized water (2000 g), and analyzed.

Fig. 1. Technological process of $ZrOCl_2 \cdot 8H_2O$ production by alkali fusion.

Table 1
Chemical composition of the fused mass.

Component	Na_2O	ZrO_2	SiO_2	HfO_2	Cl	K_2O	TiO_2	Fe_2O_3
Content (ω, %)	51.28	28.05	16.99	0.715	1.363	0.356	0.213	0.208

Download English Version:

https://daneshyari.com/en/article/1461826

Download Persian Version:

https://daneshyari.com/article/1461826

Daneshyari.com