PREPARATION OF HIGH QUALITY ZIRCONIUM OXYCHLORIDE FROM ZIRCON OF VIETNAM

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ABSTRACT: This paper introduces a sodium hydroxide decomposition method for zirconium oxychloride production from zircon sand of Vietnam such as Ha Tinh, Hue, Binh Thuan seaside. Techniques for separation of impurities in ZOC final product such as SiO_2, Fe_2O_3, TiO_2, rare earths, uranium, and thorium have also been introduced. Content of uranium and thorium in the final product of ZOC is less than 1 ppm.

Key words: Zircon oxyclorua, zirconium silicate, uranium, thorium.

Introduction

Zirconium oxychloride is a very important precursor for preparation of many other zirconium compounds. At present, the zirconium oxychloride is widely used in various fields such as textile dyeing; oil-field acidizing; antiperspirants, water repellents and TiO_2 pigment coating. In addition, it is also applied in ceramic, electronic and nano material technology...

Zircon sand is initial material for producing zirconium oxychloride. This technology consists of three stages:

- Decomposition of zircon sand with sodium hydroxide at 600-700^{0}C.

- Precipitation of base sulfate of zirconium for removing unwanted impurities such as Fe, Ti, Al, U, Th, etc.

- Crystallization of the final product of zirconium oxychloride.

Experiment, Results and discussion

1. Preparation of zirconium oxychloride having high quality by decomposition method with sodium hydroxide

1.1. Chemical composition of samples and chemical for experiment

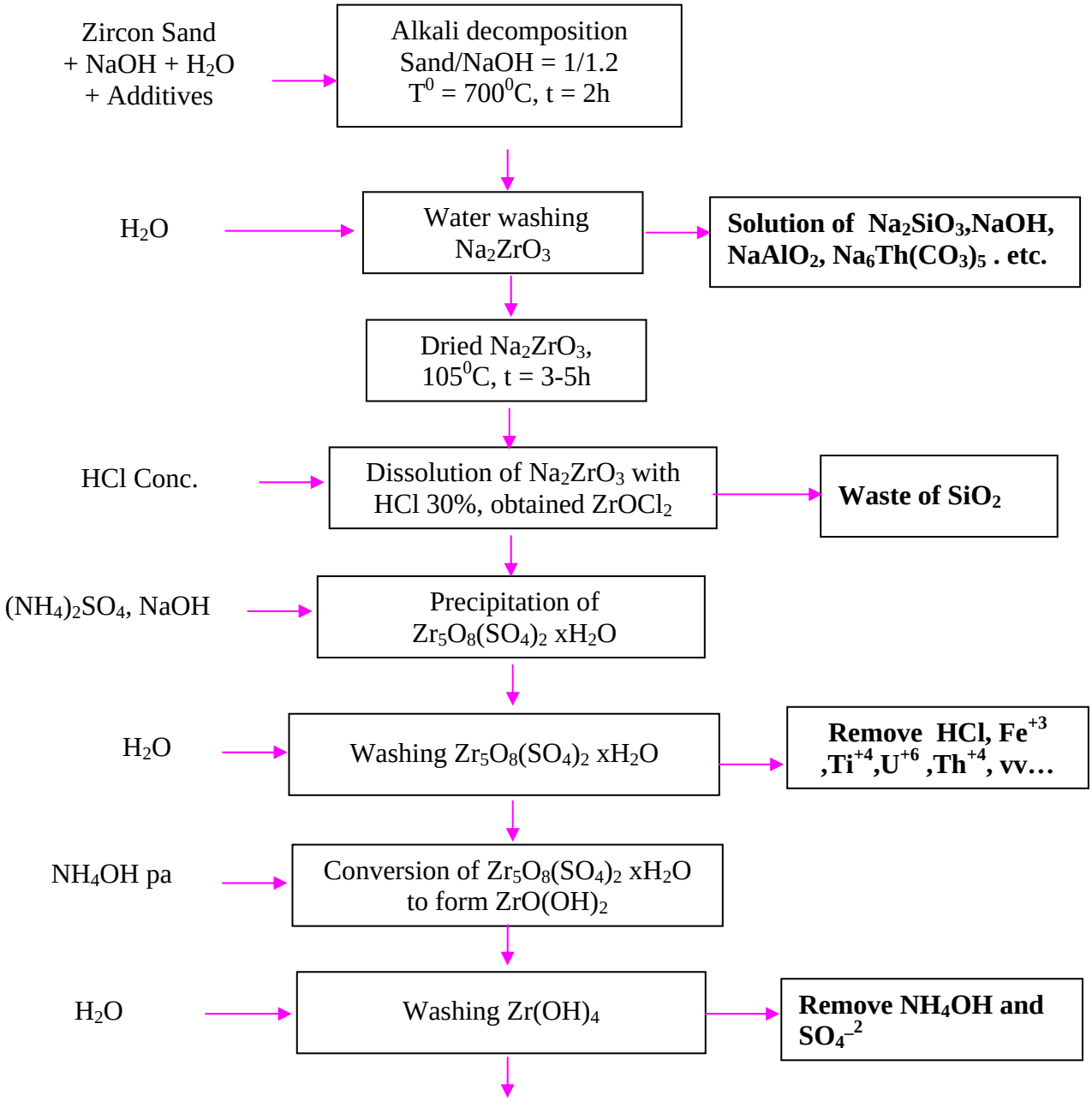
Table 1 shows composition of zircon sands used as initial material. Chemicals for experiments include NaOH, HCl, $(NH_4)_2SO_4$ in industrial grade and HCl, NH_4OH are in analytical grade.

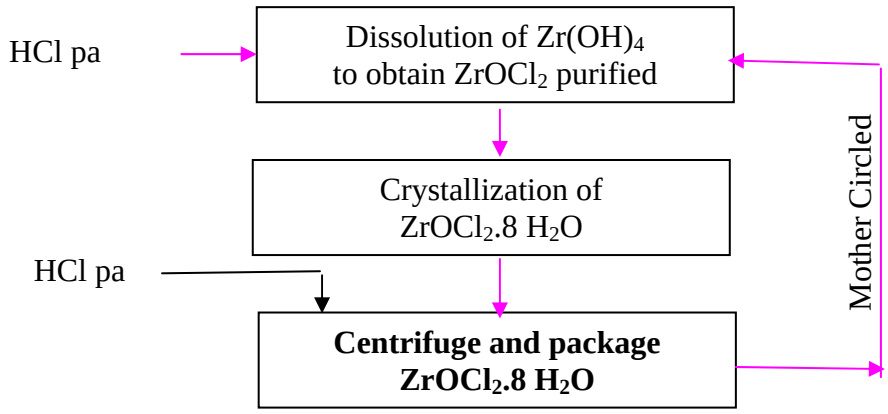
Composition of Zircon sands

No	Samples	Component content (%)							
		TiO_2	*Fe_2O_3*	*Cr*	*SiO_2*	*ZrO_2*	*U*	*Th*	*Al_2O_3*
1	$ZrSiO_4$ Hue	0.28	0.081	0.002	33.34	63.1	0.0659	0.0631	0.52
2	$ZrSiO_4$ Ha Tinh	0.12	0.071	0.0016	34.21	62.6	0.070	0.028	0.55

3	$ZrSiO_4$ BinhThuan	0.56	0.118	0.0018	34.32	61.9	0.064	0.039	0.59
4	$ZrSiO_4$ Ti west US	0.15	0.14	0.0014	34.23	62.1	0.025	0.019	0.48
5	$ZrSiO_4$ Iluka China	0.21	0.14	0.0013	34.31	61.5	0.027	0.018	0.53

1.2. Flow chart of ZOC preparation





2. Experiment Procedure

- Decomposition of zircon sand by alkali NaOH

All experiments are carried out in a steel pipe furnace with volume of 2 liters. For each experiment, 500 grams of zircon sand is perfectly mixed with NaOH, NaF, Na_2CO_3 and H_2O in a ratio of $NaOH/ZrSiO_4/H_2O/NaF/Na_2CO_3$ is 1.2:1:0.1:0. 015:0.015. The mixture is heated to 400^0C and continuously stirred for 35 min. At the moment, the reaction occurs drastically and the mixture becomes liquid that is easy to overflow. After that, the temperature is increased to 670-700^0C for 3hrs. Decomposition yield of the process achieves up to 93%. The final product is a fine soft powder that is easy to take out of the furnace. The powder is leached with water in a ratio of solid/liquid equal 1/8. After 5 times of the leaching, about 80% of SiO_2 and 75% of total of U, Th is removed from the final product named sodium zirconate.

- Dry sodium zirconate for getting para SiO_2

Obtained sodium zirconate from alkali decomposition and water leaching of zircon sand consists of ZrO_2 (80.4%), SiO_2 (6.21%), TiO_2 (1.76%), Fe_2O_3 (0.31%), Al_2O_3 (0.25%), CaO (0.27%), Cr_2O_3 (<0.015), P_2O_5 (<0.01%). The sodium zirconate is dried at 105^0C for 4hrs to fix silicon compounds in para SiO_2 that is difficult to dissolve by acids.

- Acid leaching

The sodium zirconate is dissolved by HCl of 20-30% at temperature of 90-100^0C. The acid addition is about 35% higher than theoretical requirement. Obtained solution is zirconium oxychloride consisting of ZrO_2 (65-70g/l) ; Fe (0,8-1g/l); TiO_2 (0,6-0,8g/l); SiO_2(1,2-1,5g/l) and solid waste containing a small amount of origin starting material and silicon colloid. Then the next step is precipitating base sulfate of zirconium.

- Precipitation of zirconium base sulfate

Precipitating zirconium base sulfate is a characteristic and high selective method for removing unwanted impurities to get the pure zirconium compounds. The precipitation is carried out as bellows: Adding $(NH_4)_2SO_4$ or Na_2SO_4 in ratio of SO_4^{-2}/ZrO_2 = 0.5 /1 (M) to zirconium oxychloride solution then stirring it in 150 rpm and heating it up to 80 - 90^0C. The pH of the solution is controlled in a range of 1.8-2.0 using 10% NaOH solution. Zirconium base sulfate precipitates ($4\ ZrO_2.3SO_3.14H_2O$) formed and has some

characteristic properties as filterable, well form, solid and thus it is easy to remove impurities of Ti, Fe, Si, U, Th, etc. by 5 times of washing.

- Conversion of $ZrO_2.3SO_3.14H_2O$ to $ZrO(OH)_2$ form

Obtained zirconium base sulfate in slime form is converted to zirconium hydroxide, NH_4OH 10% is used as precipitation agent. Reaction conditions include as below:

Temperature is of about 70-80^{0}C.

Stirring speed is of 150 rpm.

Reaction time is of 1.5hrs.

Velocity of NH_4OH is 3 liters/min.

Final pH is of 10.

Then the zirconium hydroxide is washed by water in 5 times to remove all SO_4^{-2}.

- Dissolution of resulted $ZrO(OH)_2$

A slury in ratio of $ZrO(OH)_2/H_2O$ = 1/1 is dissolved used HCl concentrate in analytical grade. Dissolution conditions are below:

Temperature is about 70-80^{0}C.

Stirring speed is of 150 rpm.

Reaction time is of 30 min.

Ratio of HCl/ZrO_2 = 5/1 (M)

C_{HCl} odd: 4-6M

C_{ZrO2} : 1.5 M.

The last step is filtration and waste of SiO_2 gel and to obtain clarified and pure solution of zirconium oxychloride.

- Crystallization of ZOC

The obtained ZOC solution is concentrated to get C_{ZrO2} : 2 M, C_{HCl} : >6 M. Then cooling to room temperature and maintain for 24hrs for perfect crystallization.

- Centrifuge washing ZOC crystal and packing

Separation of resulted ZOC crystal and mother solution is performed in centrifuge machine. After that the crystal is washed by used HCl 5.5 M with ratio of L/S= 1/10. Recovery yield is more than 60%. The mother solution contains C_{HCl} : 6 M, C_{ZrO2} :1.1 M and reused in the dissolution of zirconium hydroxide.

The last stage is packing in PVC.

Table 2: Composition of final zirconium oxyclorua determined by MeiWa, Japan.

No	Name of Product	Composition of components							
		$Zr(Hf)O_2$ (%)	*Fe_2O_3 (ppm)*	*Na_2O (ppm)*	*SiO_2 (ppm)*	*TiO_2 (ppm)*	*Al_2O_3 (ppm)*	*U (ppm)*	*Th (ppm)*
1	ZOC1	≥ 32.7	≤ 10	≤ 10	35.78	51	≤ 36	≤ 0.133	2.97
2	ZOC2	≥ 26	≤ 10	≤ 10	0.15	≤ 5	≤ 36	≤ 0.133	0.84
3	ZOC3	≥ 29.5	≤ 10	≤ 10	2.85	68	≤ 36	≤ 0.133	0.72
4	ZOC4	≥ 28	≤ 10	≤ 10	2.33	6	≤ 36	≤ 0.133	0.35
5	ZOC5	≥ 28	≤ 10	≤ 10	2.18	≤ 5	≤ 36	≤ 0.133	0.33

ZOC1 : ZOC from zircon sand Hue

ZOC2 : ZOC from zircon sand Ha Tinh

ZOC3 : ZOC from zircon sand Binh Thuan

ZOC4 : ZOC from zircon sand ILuka (china)

ZOC4 : ZOC from zircon sand TiWest (US)

Conclusion

Preparation of high quality zirconium oxychloride $ZrOCl_2 8H_2O$ contained U, Th < 5 pap from zircon sand of Binh Thuan, Ha Tinh, Vietnam is possible.

Alkali decomposition method with additives of NaF, Na_2CO_3 and H_2O have been applied for ZOC preparation in this paper that is not only achievement of a fine soft reaction mass with a high yield of more than 93% but also easy to remove > 80% SiO_2 and > 75% total of U,Th of starting material by water washing.

The sodium zirconate is dried at temperature of 105^0C for 4hrs to fix silicon compounds in para SiO_2 . That is difficult to dissolve by acids and easy to separate from ZOC solution.

It is possible to separate perfectly impurities of Fe, Ti, Al, U, Th, etc. from Zr by application of zirconium base sulfate precipitation method at acid medium and temperature of 90-100^0C. The method can achieve a recovery yield of more than 98% and able to develop up to large scale.

Zirconium base sulfate is easy to convert to zirconium hydroxide by using NH_4OH at room temperature. Removal of SO_4^{-2} from $ZrO(OH)_2$ is very simple. Dissolution of $ZrO(OH)_2$ by means of HCl at temperature of 70-80^0C occurs very fast.

Crystallization of ZOC from purified solution of zirconium oxychloride is carried out in a strong acid medium and washing the product with HCl pure 5.5M hence preparation of high quality ZOC contained total of U, Th less than 1ppm is possible.

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