Chemical Analysis of Local Zircon Concentrate and Preparation of Zirconium Oxychloride Octahydrate

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Abstract
Zircon is one of the most valuable mineral ore for production of important intermediate compound, zirconium oxychloride, and zirconium metal. Zircon has been found in heavy sands of river beds and ocean beaches in Myanmar. This work deals with the systematic study using locally available zircon concentrate from Moemeik Myitsone area; and the optimal conditions for the production of zirconium oxychloride from zircon were investigated. It was found that samples of zircon concentrate consist of 65.53 % of ZrO$_2$, 25.23 % of SiO$_2$, 0.34 % of FeO, 0.216 % of Fe$_2$O$_3$, 0.74 % of TiO$_2$ and 1.6 % of HfO$_2$. The process for the production of zirconium oxychloride, ZrOCl$_2$.8H$_2$O from zircon concentrate involves (i) fluxing with alkali, (ii) treating with 1:10 w/v ratio of concentrated hydrochloric acid and (iii) repeated crystallization via hydroxide gel. Within a fluxing time of one and half hour the optimal conditions for the fluxing of zircon was found to be 1:4 w/w ratio of zircon to sodium hydroxide at 650 ºC. Repeated crystallization via hydroxide gel was able to upgrade the purity of zirconium oxychloride up to 99.24 % with the yield % of about 69.8. It was characterized by XRD, EDXRF, FT IR, TG-DTA and chemical analysis. This work initiating with local zircon concentrate provides an efficient method for the production of an important zirconium oxychloride, of high purity which is justifiable to be used in the synthesis of zirconium sol and other zirconium compounds, and extraction of zirconium metal.

Keywords: zircon, analysis, zirconiumoxychloride ZrOCl$_2$.8H$_2$O, hydroxide gel

Introduction
Zirconium is classified in subgroup IV B of the periodic table with its sister metallic elements, titanium and hafnium. Zirconium forms a very stable oxide. The principal valence state of zirconium is +4, its only stable valence in aqueous solutions. Zirconium compounds commonly exhibit coordinations of 6, 7 and 8.
Zirconium is found in at least 37 different mineral forms but the predominant commercial source is the mineral zircon, zirconium orthosilicate. Other current mineral sources are baddeleyite and eudialyte (Nielsen et al., 1984). Although so widely distributed, large workable deposits are rare.

The largest commercial sources of zircon are in Kerala State in India, Sri Lanka, the east and west Coast of Australia, on the Trial Ridge in Florida, and at Richards Bay in the Republic of South Africa. These heavy mineral sands are processed for the recovery of the titanium bearing minerals ilmenite, rutile, and leucoxene, and the zircon is obtained as a co-product (Nielsen et al., 1984).

Most gem grade zircon comes from several eastern Asian countries, where it is found in placer deposits of rounded waterworn stones. These countries are Sri Lanka, Myanmar, Vietnam, Cambodia, Thailand, Madagascar and Brazil (Watt, 1980).

In Myanmar, zircon sand can be found in northern Shan State, Sagaing Region and Tanintharyi Region, occurring mostly as beach sands. In Mogoke Area, Mandalay Region, it occurs as a crystal zircon, hyacinth, accompanied by ruby and other gem-gravels, and it also occurred as heavy mineral sand, consisting of zircon, samarskite, uranite and monazite. Heavy sand containing monazite and zircon etc, radioactive bearing mineral (pegmatite) are also found in Sagaing Region. The presence of monazite (ThO₂) and zircon in heavy sand are also found in Dawei, Tanintharyi Region, as tailings from tin-tungsten ore dressing (United Nations, 1996). Mostly zircon can be found in heavy sand, of which promising deposits are in Myitsone Area, Moemeik Township, northern Shan State. It is also found in Rakhine Coast but further investigation and exploration should be undertaken.

Zirconium oxide dichloride, ZrOCl₂·8H₂O, commonly called zirconium oxychloride, is really a hydroxyl chloride, [Zr₃(OH)₈·16H₂O]Cl₈·12H₂O. Zirconyl chloride is the most commonly used zirconium compound from which to derive other zirconium compounds: hydrous oxide, carbonated hydrous oxide, acetate, sulfate, glycolate, lactate, and others. Its solutions precipitate acid dyes, and can be used to prepare high quality pigment toners and to improve the properties of color lakes. Zirconyl chloride is also important precursor for the production of advanced ceramic, zirconia and for the production of zirconium metal.
Materials and Methods

The chemicals used were of analytical and reagent grade. They were procured from British Drug House Chemical Ltd, Poole, England (BDH), Kanto Chemical Co. Ltd. Japan, and Sigma, Aldrich Co. Ltd., Poole, England. The chemicals were used as received unless otherwise stated.

In all analytical procedures of the experiments, recommended standard methods and techniques were applied (Vogel, 1961; Maxwell, 1968; Dean, 1995). All analytical determinations, instrumental analyses and monitoring of the process system were carried out by FT IR Spectrophotometer, Perkin Elmer 1600, Shimadzu model IR-408 TG-DTA, Hi-TGA 2950 Thermogravimetric Analyzer; X-ray Diffractometer, XRD - Rigaku - D - Max - 2200, Japan; EDXRF Spectrometer (Shimadzu EDX - 700) ; UV-visible Spectrometer, Ciba - Corning 259; Electromicroscope, BX 51 Biological Microscope attached by Olympus, PM 20 Automatic Photomicrographic System; AAS Perkin Elmer A.Analyst 800 AAS, Germany.

Sample Collection: The principal source of the sample is the heavy sand collected from Myitsone area, Moemeik Township, Northern Shan State. Figure 1 shows the location and site of the sample collecting area. Sample collected is pale yellow in colour. The sample used in this investigation is zircon concentrate. The beneficiated sample was subjected to dressing process such as screening, magnetic separation, high-tension separation, ball milling and air drying and then grinding (100mesh). The powdered sample (approximately 147 μm) were stored in plastic containers. Representative sample was taken systematically by Coning and Quartering method.

Figure 1. Location map of zircon sample

Figure 2. EM photograph of Zircon concentrate
Characterization of Zircon Sample: The powdered zircon concentrate was subjected to characterization by electromicroscope, XRD and EDXRF Technique.

Determination of Zirconium Content: Zirconium dioxide in zircon sample was determined by gravimetric analysis of fusion with a mixture of anhydrous sodium carbonate and sodium peroxide and precipitated with 15% mandelic acid solution.

Determination of Titanium, Total Iron, Silica and Other Trace Elements: Titanium dioxide in zircon was determined by colorimetric method. By preparing the calibration curve of standard TiO\textsubscript{2} solution, and the Ti content was determined from maximum absorbance $\lambda_{\text{max}}$ at 410 nm. The total iron content was determined by using Zimmermann-Reinhardt solution and titrated with 0.1 N potassium permanganate solution. The silica content was determined by gravimetric determination of fusion with sodium carbonate. Other trace elements in zircon concentrate were determined by the atomic absorption spectroscopic technique.

Preparation of Zirconium Oxychloride: The unit process of fusion with alkali and extraction with hydrochloric acid was used for the extraction of zirconium oxychloride from zircon. The altered process, crystallization via hydroxide gel was carried out to obtain purified ZrOCl\textsubscript{2} .8H\textsubscript{2}O. In order to find out the optimal conditions for the preparation of zirconium oxychloride, the sample was fused with sodium hydroxide with respect to variation of NaOH to zircon ratio within 1:1 to 5:1 w/w ratios. Fusion temperatures were varied from 600°C to 800°C and fusion periods were varied from 1 to 3 hr. Crystallization conditions were carried out by (i) recrystallization for several times and (ii) repeated crystallization via hydroxide gel methods.

Characterization of Prepared Zirconium Oxychloride: The extracted compound, zirconium oxychloride, was confirmed and characterized by electromicroscope, XRD, EDXRF, FT IR, TG-DTA and chemical analysis.
Results and Discussion

Analytical Assay of Zircon Sample: The authenticity as zircon, ZrSiO$_4$, was obvious by the XRD pattern as presented in Figure 3. The authenticity of the presence of zircon can be known by matched spectra included in the diffractograms. The high intensity and well resolution of the peaks regarding zircon sample indicated that the sample is a high purity type of zircon.

The presence of a high content of ZrO$_2$ in the sample is augmented by the semiquantitative data of EDXRF, shown in Figure 4. The data, although based on relative abundance present in the matrix, indicate high ZrO$_2$, content about 97%.

The chemical analytical assay data of the sample is shown in Table 1. Although the analytical data is semiquantitative in XRF technique the percent content of ZrO$_2$ is comparable with that of chemical analysis. It was observed that from XRF data and chemical analysis data, local zircon was high grade zircon.

In the analytical assay determination, all chemical methods for the determination of zirconium actually give the amount of zirconium plus hafnium. The latter can be determined only by physical methods such as emission spectroscopy or X-ray spectrography. From the XRF determination (Figure 4.) the hafnia content was found to be ca 1.6% in the sample. It is a common observation; that the zirconium and hafnium ratio is 100:2 in the...
zircon sample. The chemical analysis gives the composition of zirconium plus hafnium.

From the observation of XRD diffractogram, semiquantitative data of EDXRF and analytical assay data, it was observed that the zircon concentrate from Moemeik Myitsone Area is of a high grade sample.

**On the Aspect of the Preparation of ZrOCl$_2$.8H$_2$O :** Tables 2 – 4 showed optimal conditions for preparation of zirconium oxychloride, the investigated data as regard to the optimal conditions, found out with respect to the digestion step where NaOH was used as fluxing agent. The nature of digestion primarily depends on the fluxed mass cake where different proportions of NaOH to sample were used in Table 2. It shows that the fluxed mass, which decomposed by using different caustic soda to sample ratio, can give rise to different yields of ZrOCl$_2$. It can be observed that 4:1 caustic soda to sample ratio shows optimal yield of 69.42%.

Based on the ratio of 4:1 NaOH to sample, the effect of fusion temperature and time of fusion were found out. Thus, Tables 3 and 4 show the optimal fusion temperature to be 650°C and optimal fusion time to be 1.5 hr. At these optimal conditions the highest yield of ZrOCl$_2$ was achieved. It was observed that the optimum ratio of NaOH and zircon is 4:1. At lower ratio, the sample cannot be decomposed completely and at greater value, the yield was drop of little significance. The ratio above (5:1), sodium silicate interfered as a gel and it was difficult to filter and the separation is incomplete.

Table 1. Analytical assay results of zircon concentrate from Moemeik Myitsone area

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content (%)</th>
<th>Method of Assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>65.530 ± 0.02</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>25.234 ± 0.003</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.2165 ± 0.002</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>FeO</td>
<td>0.3419 ± 0.001</td>
<td>Chemical analysis</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.7424 ± 0.002</td>
<td>Spectrophotometric</td>
</tr>
<tr>
<td>HfO$_2$</td>
<td>1.608</td>
<td>XRF</td>
</tr>
<tr>
<td>Constituent</td>
<td>Content (%)</td>
<td>Method of Assay</td>
</tr>
<tr>
<td>------------</td>
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<td>----------------</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0014 ± 0.0002</td>
<td>AAS</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0015 ± 0.0002</td>
<td>AAS</td>
</tr>
<tr>
<td>Zn</td>
<td>0.0024 ± 0.0002</td>
<td>AAS</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0043 ± 0.0002</td>
<td>AAS</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0025 ± 0.0001</td>
<td>AAS</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0038 ± 0.0002</td>
<td>AAS</td>
</tr>
<tr>
<td>Ag</td>
<td>ND</td>
<td>AAS</td>
</tr>
<tr>
<td>Co</td>
<td>ND</td>
<td>AAS</td>
</tr>
</tbody>
</table>

ND = less than 0.0001 % for Ag and Co

At the fluxing temperature below 600°C, yield of ZrOCl₂ is lower than at the high temperature. It was due to the incomplete fusion of the sample. At temperature higher than 650°C, yield of ZrOCl₂ became low. It was due to the effect of high temperature, which favours various composition of oxide and silicozirconate formation when hydrolysed it formed zirconic acid or silicozirconic acid gelation. Table 4 shows the yield of ZrOCl₂ from fused mass by variation of fluxing time. At a short time fusion, the sample could not be fused completely and at longer time it did not change significantly. Thus, the optimal conditions for decomposition of zircon for the extraction of ZrOCl₂ by fluxing with alkali were 4:1 NaOH to zircon ratio, temperature 650°C and 1.5 hr heating time. The fused mass product was washed with deionized water and the moist cake was extracted with concentrated HCl by the ratio of 1:10 w/v.
Table 2. Yield percents of zirconium oxychloride from different NaOH to sample ratio fused mass

<table>
<thead>
<tr>
<th>NaOH: Sample (w/w)</th>
<th>Fusion Temperature (ºC)</th>
<th>Fusion time (hr)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>650</td>
<td>2</td>
<td>63.25 ± 0.02</td>
</tr>
<tr>
<td>2:1</td>
<td>650</td>
<td>2</td>
<td>64.54 ± 0.02</td>
</tr>
<tr>
<td>3:1</td>
<td>650</td>
<td>2</td>
<td>65.14 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>2</td>
<td>69.42 ± 0.02</td>
</tr>
<tr>
<td>5:1</td>
<td>650</td>
<td>2</td>
<td>69.37 ± 0.02</td>
</tr>
</tbody>
</table>

Table 3. Yield percents of zirconium oxychloride from fused mass by variation of fusion temperature

<table>
<thead>
<tr>
<th>NaOH: Sample (w/w)</th>
<th>Fusion Temperature (ºC)</th>
<th>Fusion time (hr)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>600</td>
<td>2</td>
<td>65.69 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>2</td>
<td>69.82 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>700</td>
<td>2</td>
<td>52.58 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>750</td>
<td>2</td>
<td>51.05 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>800</td>
<td>2</td>
<td>51.02 ± 0.02</td>
</tr>
</tbody>
</table>
Table 4. Yield percents of zirconium oxychloride from fused mass by variation of fluxing time

<table>
<thead>
<tr>
<th>NaOH: Sample (w/w)</th>
<th>Fusion Temperature (°C)</th>
<th>Fusion time (hr)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>650</td>
<td>1</td>
<td>65.45 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>1.5</td>
<td>69.87 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>2</td>
<td>69.52 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>2.5</td>
<td>69.51 ± 0.02</td>
</tr>
<tr>
<td>4:1</td>
<td>650</td>
<td>3</td>
<td>68.24 ± 0.02</td>
</tr>
</tbody>
</table>

Figures 5 and 6 are XRD diffractograms of extracted compound obtained from fifth time recrystallization and the extracted compound from repeated crystallization via hydroxide gel. Recrystallization is an important step to obtain desired crystals because the crystals from recrystallization route can be formed as mixture of crystals, such as hexahydrated, trihydrated and mixture of both hydrated crystals. In the crystallization via hydroxide gel route, it is considered that the desired crystals formed were only octahydrated crystals.

Studies on the Characterization of Zirconium Oxychloride Octahydrate: EM photograph (Figure 7) shows the extracted compound that has needle shape. Figures 8 and 9 show the EDXRF spectra of ZrOCl$_2$.8H$_2$O obtained from 5$^{th}$ time of recrystallization and crystallization via the hydroxide gel method. It was observed that, the crystal from hydroxide gel was more of a purer form than others (based on semi-quantitative data of EDXRF spectra). It shows 98% purity. Table 5 shows the percent purity and elemental data of ZrOCl$_2$.8H$_2$O. From these data, crystal from hydroxide gels, ZrOCl$_2$.8H$_2$O are more purified than recrystallization process. The percent purity of extracted compound was found to be 99.24% based on chemical analysis.

Figure 10 is FT-IR spectrum of extracted compound. This spectrum was identical to the reference standard ZrOCl$_2$.8H$_2$O spectrum (Nyquist and Kagal,1991). At the frequency range of 3650-3200 cm$^{-1}$, the very broad band
was observed. It was due to the stretching vibration of free - OH group of water molecule and polymeric -OH group. At 1619 cm\(^{-1}\) was due to the bending vibration of -OH group and 1010 cm\(^{-1}\) was due to the vibration of bridging - O - group attached with metal zirconium atom. Very broad overlapping band at 731-486 cm\(^{-1}\) can be referred to the monoclinic form of zirconia. In this spectrum, frequency at 850 cm\(^{-1}\) band was not observed. Thus, the compound has no = O bonding. Therefore, the extracted compound contained metal -O- bridging group, polymeric -OH and monoclinic character.

Figure 11 shows the TG-DTA curves for the decomposition of extracted ZrOCl\(_2\).8H\(_2\)O crystals. The compound is found to have decomposed into zirconia in two steps. It is shown by the DTA curve in Figure 11. There exists an exothermic peak at about 80\(^\circ\)C, which corresponds to the elimination of surface water and at about 160\(^\circ\)C dehydration of interstitial water of the compound occurred. The corresponding weight loss obtained from the TGA curve is about 44%. It is in agreement with the 8 moles of water molecules. There is an exothermic peak in the DTA profile around 400\(^\circ\)C. The exothermic peak may be attributed to the decomposition of compound with libration of HCl and transformation to zirconia.
Figure 7. EM photograph of zirconium oxychloride

Figure 8. EDXRF spectrum of extracted zirconium oxychloride by 5th time recrystallization

Figure 9. ED-XRF spectrum of extracted zirconium oxychloride

Table 5. Percent purity and elemental data of extracted zirconium oxychloride

<table>
<thead>
<tr>
<th>Extracted Compound</th>
<th>Zr (%)</th>
<th>Hf (%)</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
<th>SiO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 times Recrystallization ZrOCl₂</td>
<td>97.43</td>
<td>95.51</td>
<td>1.47</td>
<td>0.0010</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>± 0.01</td>
<td>± 0.01</td>
<td>± 0.01</td>
<td>± 0.0001</td>
<td>± 0.001</td>
</tr>
<tr>
<td>Recrystallization via hydroxide gel ZrOCl₂</td>
<td>99.24</td>
<td>98.45</td>
<td>1.33</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>± 0.01</td>
<td>± 0.01</td>
<td>± 0.01</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ND - less than 0.0001 % for Fe
* Hf may also be included
The results of this investigation revealed that local zircon concentrate has high zirconia content. It consists of 65.53% ZrO₂, 25.23% SiO₂, 0.34% FeO, 0.216% Fe₂O₃, 0.74% TiO₂, 1.6% HfO₂ and trace amounts of other elements. It is High Zircon.

It is evident from the results of investigation that ZrOCl₂·8H₂O can be extracted from hydroxide gel that was more pure (99.24%) than it is from recrystallization for several times (97.43% purity). Hf content in extracted ZrOCl₂·8H₂O was found to be 1.33%. Prepared zirconium oxychloride was characterized by conventional and modern instrumental techniques. From XRD diffractogram, it was confirmed that the extracted compound is pure ZrOCl₂·8H₂O crystalline form. From EM photograph, it was observed that the compound is needle shape crystal. FT-IR spectrum of ZrOCl₂·8H₂O indicates the existence of surface water and interstitial water which shows very broad band at 3650 cm⁻¹ - 3000 cm⁻¹, and monoclinic zirconia was also confirmed by the band at 731-486 cm⁻¹. From TG-DTA thermogram, the compound was in octahydrated form. It was dehydrated (surface water) at 160°C and further decomposition was completed at 400°C. The XRD diffractogram of prepared ZrOCl₂·8H₂O did not indicate any major impurities. According to the chemical analysis data by conventional and modern instrumental techniques, it did not contain other trace elements. Therefore, the extracted compound is justifiable to be used for the synthesis of zirconium sols, other zirconium compounds and extraction of zirconium metal.

Conclusion
Acknowledgements

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References