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Production of zirconia powders from the basic disintegration of zircon, and their characterization

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Monoclinic ZrO_2 has been prepared through the decomposition of $ZrSiO_4$ with soda ash and lime, followed by leaching in hydrochloric acid and sodium hydroxide. The resulting zirconia powders are characterized in terms of their physical and chemical properties.

1. Introduction

Zircon is the most common and widely distributed raw material for the production of zirconia. The oxide is commercially manufactured from the silicate through a variety of processes, most of which involve a treatment to form an aqueous solution of zirconium from which the fine zirconia particles are precipitated. In each case, the process for the fabrication of the oxide is chosen according to cost, raw material availability, and the purity and properties required in the final product.

This paper reports on the development of two novel methods for the fabrication of zirconia powders from zircon which do not involve an aqueous solution of the element. Instead, the silicate raw material is reacted with soda ash or lime to form monoclinic zirconia. Silica, and Na- or Ca-silicozirconate, are also formed as by-products, which are leached out with hydrochloric acid and alkali, respectively. In the first route, the zircon raw material is decomposed with soda ash; in the second route, lime is used. Both approaches are described below.

2. Experimental procedure

2.1. Raw materials and equipment

The zircon ores used in this study were commercial grade products; their physical and chemical characterization is summarized in Tables I and II. Chemical composition was determined with X-ray fluorescence for the major elements (Zr, Hf and Si), and atomic absorption spectrometry for Fe, Mg, K, Na, Ti, Ca and Al. True density was measured with a helium autopycnometer (Micromeritics, Inc. Norcross, GA, USA). Specific surface area was measured by the Brunauer-Emmett-Teller adsorption equation (BET method) with nitrogen at the temperature of liquid nitrogen as the adsorbate (Micromeritics, Inc.). As shown in the tables, true density and surface area of the different zircon raw materials were very uniform (around 4.6 $g\,cm^{-3}$ and 1 $m^2\,g^{-1}$, respectively). They exhibited, however, widely different particle size distributions: average (d_{50}) particle sizes for powders B and D were 15 and 130 μm, respectively. The same analytical techniques were applied to the characterization of the zirconia powders. Sodium carbonate, hydrochloric acid and caustic soda were commercial grade products.

Thermal decomposition of the zircon was made in a high-temperature muffle furnace capable of reading 1650 °C (Lindberg, Inc. Chicago, IL, USA). Preliminary work in the alkali and acid leaching of the decomposition products was carried out in teflon-lined stainless steel acid digestion bombs (Parr Instruments); once the optimum digestion parameters had been established, alkali digestion was made in an autoclave (Parr Instruments), and acid leaching was performed in a glass reactor provided with mechanical stirring.

2.2. Synthesis of zirconia powders by the soda-ash process

2.2.1. Zircon disintegration

It is well known that zircon is decomposed at high temperature in reducing media [1]. The decomposition temperature, however, is lowered when the silicate is mixed with a fluxing agent such as NaOH [2], Na_2CO_3 [3, 4], $CaCO_3$ or $MgCO_3$ [5, 6].

Samples of grade G zircon were mixed with 5, 8, 10 and 20 wt % soda ash by dry ball milling with zirconia media; the mixed powder was compacted into small pellets with a hand press. Thermal treatment was carried out at temperatures between 1100 and 1600 °C; soak times varied between 5 min and 3 h. As evinced by X-ray diffraction (XRD), reaction products depended on reaction temperature, reaction time, and the concentration of soda ash in the solid mixture. For samples with 20% soda ash, the reaction was not complete at temperatures below 1300 °C, even when long reaction times (180 min) were used. Reaction products included monoclinic zirconia, $Na_4Zr_2Si_3O_{12}$ [7] (Fig. 1), amorphous silica and unreacted zircon. At 1350 °C, decomposition was complete in only 5 min.

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TABLE I Chemical composition of zircon

	Composition (wt %)									
Zircon	ZrO_2	HfO_2	SiO_2	Fe_2O_3	MgO	H_2O	Na_2O	TiO_2	CaO	Al_2O_3
A	64.30	1.52	32.84	0.14	0.02	0	0.03	0.04	0.07	0
B	62.64	1.50	33.00	0.23	0.03	0.01	0.02	0.15	0.08	0
C	59.89	1.52	32.88	0.36	0.04	0	0	0.09	0.07	0
D	59.89	1.52	32.58	0.36	0.04	0	0	0.09	0.07	0
E	57.76	1.47	33.42	0.36	0.04	0.03	0.04	0.06	0.04	0
F	56.64	1.42	33.02	0.12	0.05	0.02	0.02	0.09	0.07	0
G	62.60	1.52	32.70	0.50	0.11	0.15	0.47	0.18	0.50	0

TABLE II Physical characteristics of zirconium silicates

Zircon	Open porosity (%)	Total porosity (%)	Macro porosity (%)	Micro porosity (%)	Apparent density ($g\,cm^{-3}$)	Bulk density ($g\,cm^{-3}$)	True density ($g\,cm^{-3}$)	d_{50} porosity (μm)	d_{50} particle size (μm)	BET $m^2\,g^{-1}$
A	35.6	46.5	16.5	20.1	3.91	2.52	4.71	2.19	125	0.8
B	37.1	54.9	7.4	29.7	3.35	2.10	4.66	2.38	15	0.4
C	17.3	46.7	11.2	6.1	3.01	2.49	4.67	2.34	80	0.9
D	33.6	54.6	33.4	0.2	4.11	2.72	4.67	35.32	130	0.7
E	39.2	52.4	8.6	30.4	3.61	2.19	4.60	2.72	100	0.3
F	35.7	50.1	7.4	28.3	3.68	2.37	4.83	2.12	77	0.6
G	43.7	56.4	9.8	33.9	3.57	2.01	4.65	2.11	30	0.6

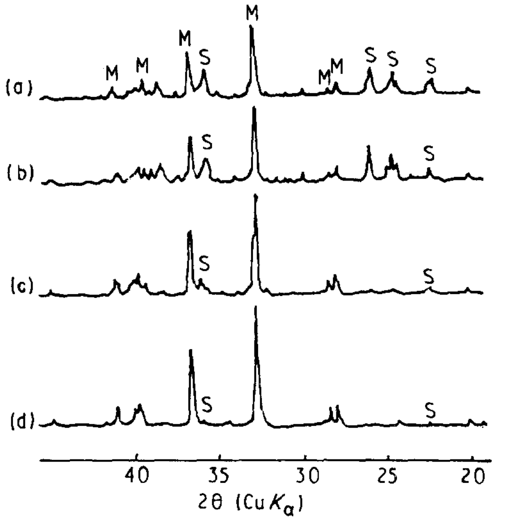

Figure 1 X-ray patterns of samples with 20% Na_2CO_3 heated at different temperatures. (a) 1350; (b) 1400; (c) 1450; (d) 1500 °C; M = m-ZrO_2; S = $Na_4Zr_2Si_3O_{12}$.

Higher temperatures were required to complete the decomposition of samples containing 10% soda ash. Decomposition of this material was complete only after a thermal treatment at 1500 °C, while samples reacted for 1 h at 1400 °C still exhibited 15% of unreacted zircon. Higher reaction temperatures (1600 °C) were necessary to complete the decomposition of samples containing even lower amounts (5–8%) of soda ash.

2.2.2. *Alkali leaching*

The product from the complete decomposition of the silicate with soda ash consists of a mixture of monoclinic zirconia, Na–silicozirconate, and amorphous silica. The purpose of the alkali leaching step is the removal of this amorphous silica through a wet chemistry process.

A parametric study was carried out first, in which approximately 0.5 g of the product from the previous step was treated with 10 ml of a NaOH solution in an acid digestion bomb, which was heated in a stove at 200 °C for 24 h. The leached sample was then filtered and washed with distilled water. It was found that a 20% solution of NaOH was most effective in the removal of silica from the samples that had been decomposed with 10% Na_2CO_3. In these conditions, silica removal increased with increasing leaching time to an optimum value at 24 h, after which it did not improve appreciably any further.

Once the parametric study was completed, further research was carried out with products which had been decomposed at 1350, 1400, 1450, 1500 and 1600 °C. Samples were leached in the autoclave. For a given alkali leaching procedure (5 h at 200 °C with 20% NaOH), the best results were obtained with the material that had been decomposed with 10% Na_2CO_3, the average ZrO_2 content in the filtered, washed and dried powder was 74%, while the corresponding figure was less than 64% for the material that had been decomposed with 20% Na_2CO_3.

To determine the optimum concentration of caustic soda, leaching experiments were carried out at three different alkali concentrations (10, 15 and 20% NaOH) with the materials which had been decomposed at 1500 °C with 10% Na_2CO_3. As shown in Table III, results improved with increasing concentration of caustic soda: a product of 76% ZrO_2 was obtained with a 20% NaOH solution at 200 °C, while the zirconia content of the product was only 74% when a 15% NaOH solution was used.

The effects of pulp density on the leaching of silica were also studied. No large differences were exhibited

TABLE III Zirconia and silica content averages of products elaborated with mixtures of zircon with 10% Na_2CO_3 heated at 1500 °C after caustic leaching

NaOH (wt %)	Temperature (°C)	Time (h)	ZrO_2 (wt %)	SiO_2 (wt %)
10	200	6	72.8	14.36
10	220	6	70.1	16.06
15	200	10	73.7	11.13
15	200	24	70.6	11.71
15	220	10	74.5	10.07
20	180	8	74.3	12.18
20	180	10	74.6	10.01
20	180	24	75.1	11.90
20	200	5	70.5	16.87
20	200	6	72.8	14.32
20	200	8	76.0	12.17
20	200	10	75.8	10.57
20	200	24	75.7	10.16
20	220	8	74.1	11.99
20	220	10	75.0	11.13
20	220	24	75.8	11.42

by treatments involving pulp densities in the 10–30 wt % range. There was in any case enough excess of alkaline reactive.

2.2.3. Acid leaching

After the silica had been eliminated from the samples via an alkaline leaching, Na–silicozirconate still remained unattacked in the product. This compound can be removed through solution in hydrochloric acid [8]. As in the previous step, a parametric study was performed first in acid digestion bombs, while subsequent work used a heated glass reactor provided with a mechanical stirrer. The effects of HCl concentration, temperature and reaction time were studied.

$Na_4Zr_2Si_3O_{12}$ is attacked by HCl preferentially to ZrO_2, but dissolution and loss of the zirconia will also take place once the Na–silicozirconate has reacted. For this reason, optimum conditions were found to include the lower acid concentrations (preferably 10%), room temperature, and shorter reaction times (Fig. 2). As an example, the use of 10% HCl yielded a product consisting of 98% ZrO_2, while this figure decreased to 91.6% ZrO_2 when 30% HCl was used in the acid leaching step. Results are summarized in Table IV.

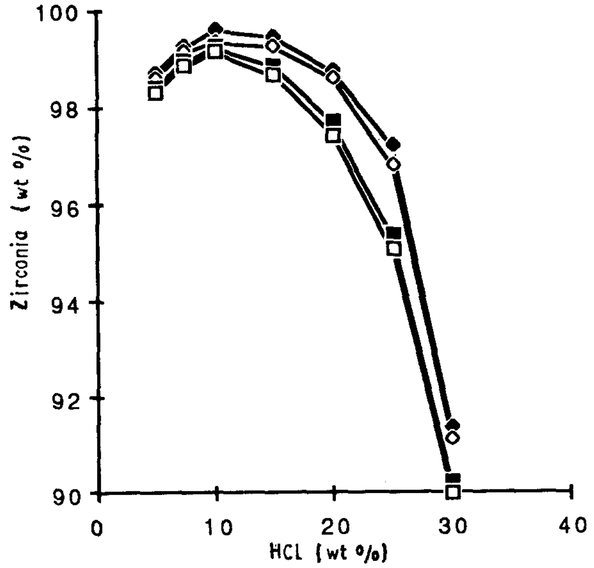

Figure 2 Effect of temperature, time and hydrochloric concentration on acid leaching. Treatments: diamonds, room temperature; squares, boiling temperature; closed symbols, 1 h; open symbols, 2 h.

Differences in pulp density within the 5–30% range had negligible effect on the results of the acid leaching; there was in any case enough excess of acid reactive.

2.3. Synthesis of zirconia powders by the lime process

As an alternative to the use of soda ash, zircon can be decomposed by lime [5, 6, 9, 10]. The synthesis of zirconia by the lime process also includes three steps: decomposition of the silicate, acid leaching to remove the resulting wollastonite phase, and removal of the silica with alkali.

2.3.1. Zircon disintegration

Mixes of zircon powder with 5, 10, 15, 20 and 30 wt % lime were prepared by dry ball milling with zirconia media. Samples of the compacted powder mix were heated in a Lindberg furnace for 2 h at 1450, 1500 and 1550 °C. Results indicated that decomposition of the zircon was enhanced by higher lime contents and higher temperatures. Samples with lime contents below 20% exhibited only partial decomposition in the temperature range studied. For 20% lime content, total decomposition took place only at temperatures of 1500 °C or higher. Samples with 30% lime, however, were totally decomposed even at the lowest temperature. Monoclinic zirconia and wollastonite [7] ($Ca_3Si_2ZrO_9$) were identified by XRD analysis as the two crystalline phases in the reaction products (Fig. 3).

2.3.2. Acid leaching

Wollastonite is soluble in hydrochloric acid [8]. When the products of the decomposition of zircon with CaO

TABLE IV Chemical composition of zirconias manufactured by soda ash and lime processes

Zircon	$ZrO_2 + HfO_2$ (wt %)	SiO_2 (wt %)	Fe_2O_3 (wt %)	MgO (wt %)	K_2O (wt %)	Na_2O (wt %)	TiO_2 (wt %)	CaO (wt %)	Al_2O_3 (wt %)
Ca:A	94.68	2.34	0.14	0.48	0	0.25	0.04	1.26	0
B	91.21	4.83	0.21	0.70	0.04	0.64	0.04	2.59	0
C	94.27	1.36	0.14	0.29	0	0.15	0.09	0.91	0
D	90.57	4.23	0.14	0.47	0	0.25	0.04	1.19	0
E	92.71	5.81	0.26	0.51	0.06	0.46	0.05	1.34	0
F	92.39	3.06	0.21	0.42	0	0.19	0.08	1.34	0
G	96.82	1.28	0.14	0.16	0.05	0.37	0.05	0.98	0
Na:A	90.53	5.05	0.25	0.11	0.06	0.12	0	0.21	0
B	93.66	6.10	0.28	0.29	0.06	0.19	0.05	0.21	0
C	95.96	1.40	0.14	0.17	0.01	0.07	0.05	0.07	0
D	90.07	5.58	0.14	0.16	0.07	0.23	0.07	0.14	0
F	95.48	3.40	0.14	0.06	0.15	0.30	0.04	0.07	0
G	98.10	0.57	0.14	0.09	0.01	0.05	0.03	0.07	0

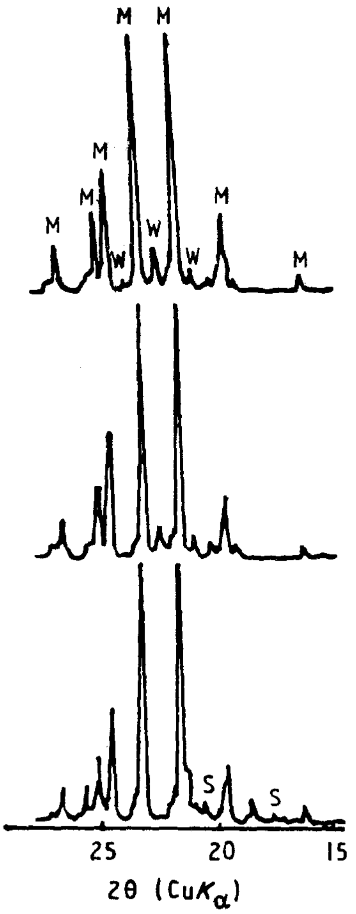

Figure 3 X-ray patterns of samples with 20% CaO heated at different temperatures. S = $ZrSiO_4$; M = m-ZrO_2; W = $CaSiO_3$.

were leached with HCl at high temperatures and pressures, a ZrO_2-rich gelatinous precipitate was obtained which was not produced when leaching took place at atmospheric pressure.

Leaching with 10 and 20% HCl produced a precipitate containing 74 and 76% ZrO_2, respectively; the corresponding values for the silica content were 17 and 14%. An HCl concentration of 20% was therefore considered optimum. Reaction rate increased with increasing temperature up to the boiling point of the mixture (106 °C).

Optimum reaction time at 106 °C was determined as 30–60 min. Results were similar in this time range within the error of the analytical procedure [11]; shorter or longer residence times resulted in poorer zirconia yields. The preferred reaction time was therefore fixed as 30 min after the mixture had reached the boiling temperature.

The effect of pulp density was also studied. There was in any case enough excess of acid reactive. Zirconia yields decreased with increasing pulp density. A solids loading of 20% was preferred in order to optimize the process economics.

2.3.3. Alkali leaching

Since the products from the acid leaching step still contained large amounts of silica, they were treated with caustic soda in order to produce zirconia powders of high purity. Samples were treated with 20% NaOH solution at 200 °C for 5 h, according to the optimum conditions that had been derived in the work with soda-decomposed zircon (section 2.2.2.).

A study of the effect of pulp density in the 30–50% range revealed that lower densities were preferred. As an example, alkali leaching with a pulp density of 30% yielded a product with zirconia content of 98%, while only 91% ZrO_2 was obtained with a pulp density of 50%.

3. Results and discussion

3.1. Zirconia purity

Purity of the zirconia products obtained in this work ranged between 90 and 98%. Reports available in the literature indicate that the purity of zirconias produced by hydrothermal processes range between 84 and 99.9%; plasma methods have produced zirconias in the 94.5–99.6% range. The processes proposed in this work produce zirconia powders in the upper region of those ranges.

3.2. Zirconia density and porosimetry

Apparent density for the zirconias obtained in this study ranged from 3.1 to 4.5 g cm^{-3}. These values are lower than those reported for the commercial monoclinic zirconias (typically 4.7 g cm^{-3}). The same applies to the bulk density: values obtained in this study

TABLE V Physical characteristics of zirconias manufactured by soda ash and lime processes

Zircon	Open porosity (%)	Total porosity (%)	Macro porosity (%)	Micro porosity (%)	Apparent density (g cm^{-3})	Bulk density (g cm^{-3})	True density (g cm^{-3})	d_{50} porosity (μm)	d_{50} particle size (μm)	BET (m^2 g^{-1})
Na:A	52.1	65.5	8.4	43.7	3.66	1.75	5.09	1.13	4.5	5.3
B	50.9	60.0	7.1	43.8	4.47	2.20	5.50	0.33	5.5	2.8
C	59.2	67.9	6.0	53.2	4.38	1.78	5.55	0.37	8.0	10.2
D	42.9	63.0	7.2	35.7	3.49	1.99	5.39	0.49	6.0	3.1
F	54.3	64.9	10.7	43.6	4.37	1.99	5.70	0.51	8.0	0.5
G	52.6	68.0	8.7	45.9	4.09	1.94	5.69	0.34	8.0	5.0
Ca:A	53.2	63.0	8.2	45.0	4.44	2.07	5.61	0.54	70	3.6
B	60.9	69.3	15.2	45.7	4.06	1.59	5.18	0.24	53	5.5
C	53.4	64.0	6.7	46.7	4.35	2.04	5.67	0.27	14	4.4
D	52.9	61.5	8.1	44.5	4.44	2.09	5.44	0.20	9	6.9
E	62.4	70.7	12.3	50.1	4.09	1.54	5.25	0.14	10	13.4
F	37.7	65.7	7.2	30.5	3.06	1.90	5.55	0.13	7	6.8
G	53.6	65.3	11.4	42.4	4.25	1.97	5.67	0.85	58	2.0
Mon. Com.*	40.0	52.1	8.7	31.3	4.60	2.81	5.87	1.68	60	0.6

*Monoclinic commercial product.

ranged between 5.1 and 5.6 g cm^{-3}, while the corresponding value for commercial zirconias is typically 5.9 g cm^{-3}. As shown in Table V, total porosity is approximately the same (about 65%) for all zirconias produced in this study. It should be noted, however, that microporosity (approximately 10%) is small compared with the macroporosity (around 45%). In general, pore size distribution for the zirconias obtained in this work is coarser than for commercial monoclinic zirconias.

3.3. Zirconia surface area: particle size and shape

Specific surface area for the zirconias obtained in this study is generally higher than the typical values for the commercial powders (0.6 m^2 g^{-1}), and similar to those of the zirconias produced by plasma methods (5–8 m^2 g^{-1}). Powders derived from hydrothermal processes [15–18] exhibit a much wider range (4–123 m^2 g^{-1}). Different grain morphologies of our zirconias are shown in Fig. 4. In general, powders with high purity such as those derived from ores C, F and G exhibit a spherical grain shape; lower-purity zirconias (such as those derived from ore A) show small impurity grains adhering to the zirconia particles. This applies to zirconias fabricated by both lime and soda methods. Particle size distribution for zirconias fabricated by the lime method varies widely: d_{50} is 70 μm for zirconia A, and only 7 μm for zirconia F. It is much more consistent for the products derived from the soda ash method, with d_{50} ranging between 4.5 and 8 μm (Figs 5 and 6). For comparison purposes, commercial monoclinic zirconias exhibit a d_{50} of approximately 60 μm, and the products obtained from hydrothermal processes have a d_{50} value in the 3–35 μm range.

3.4. Effects of raw material purity

The chemical composition of the raw material used, and the amount of lime or soda ash used in the decomposition step, had a large influence on the results of the process. As a general rule, products of higher purity were obtained from ores containing higher amounts of zirconium when leached with alkali solutions of higher concentrations (Table IV). When two zircon ores with similar particle sizes were used (ores C and F, d_{50} = 80 μm), a slightly better product was obtained in both methods from the ore C with a higher ZrO_2 content.

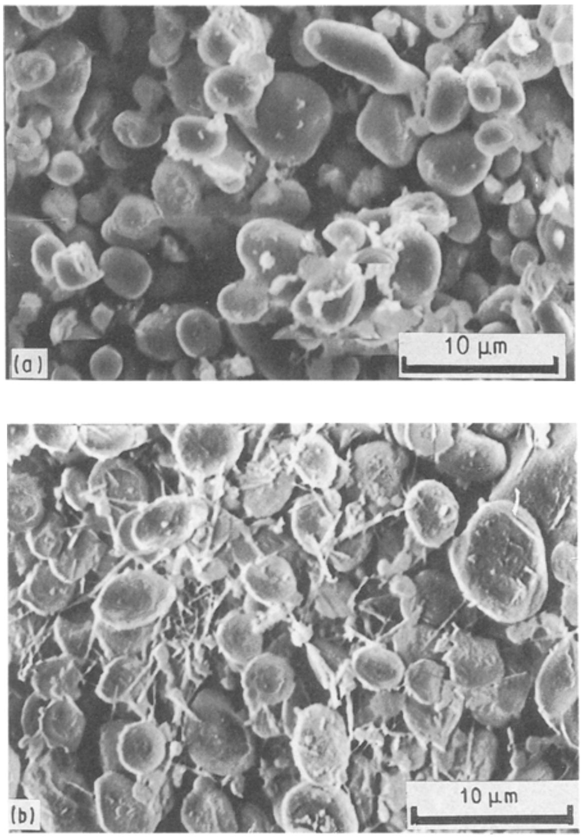

Figure 4 Scanning electron micrographs of zirconias: (a) via soda ash, Na–G; (b) via lime, Ca–G.

3.5. Influence of zircon particle size

The particle size distribution of the zircon ore had an important role in the purity of the zirconia manufactured from both the soda and the lime processes. A

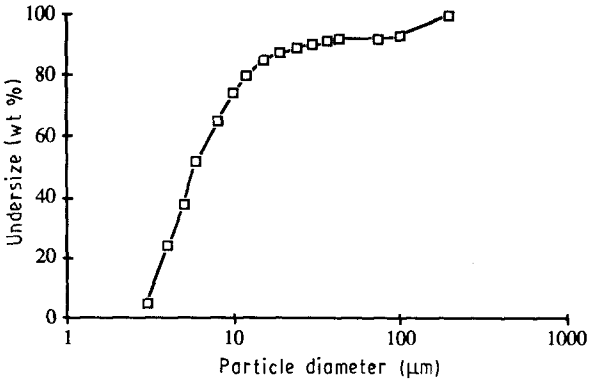

Figure 5 Particle size distribution of zirconia D, Na–D.

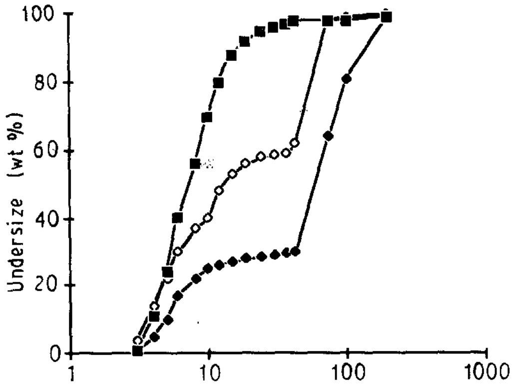

Figure 6 Particle size distribution of zirconias via lime, ◆, Ca–G; ◇ Ca–C; ■, Ca–F.

coarser particle size distribution in the zircon ore usually resulted in a decreased purity of the zirconia powder. This effect is illustrated by a comparison between the behaviour of ores C and D, which exhibited similar chemical composition but different particle size distributions. The zirconia from ore C (the finer of the two) was richer in ZrO_2 than the powder resulting from the much coarser ore D.

3.6. Effects of pulp density

Zirconia purity could be improved with lower pulp densities in the leaching steps.

4. Conclusions

Two methods are proposed for the fabrication of zirconia powders from zircon. The two methods differ in the fluxing agent used for the decomposition of the silicate: soda ash in the first case, and lime in the second. In both approaches, zircon decomposition is achieved with smaller amounts of fluxing agent than those previously reported.

The optimum parameters for the thermal decomposition of zircon with Na_2CO_3 were defined as follows: 10 wt % Na_2CO_3 and 2 h at 1500 °C. After this treatment, zirconium is crystallized as monoclinic zirconia, while silica remains in the mixture as both amorphous silica and as $Na_4Si_3Zr_2O_{12}$. This product is reacted in an autoclave with 20 wt % NaOH to remove the silica; optimum parameters in this step are a pulp density of 30%, temperature of 200 °C, pressure of 14 atm, and residence time of 5 h. This step is followed by an acid leaching of the filtered, washed powder mixture in order to remove the $Na_4Si_3Zr_2O_{12}$. Optimum parameters for the acid leaching step include the use of a 10% HCl solution, room temperature, atmospheric pressure, 1 h residence time, and 20% pulp density.

For the lime process, the optimum parameters in the disintegration of the zircon ore are: 20 wt % CaO, and a thermal treatment at 1500 °C for 2 h. The resulting product consists of monoclinic zirconia, β-wollastonite, and amorphous silica. The β-wollastonite phase is then leached out with hydrochloric acid under the following preferred conditions: 20% HCl solution, boiling temperature (106 °C), atmospheric pressure, 30 min residence time, and 20% pulp density. The last step is the removal of the amorphous silica via alkaline leaching with 20 wt % NaOH at 200 °C and 5 h; preferred pulp density is 15%.

The ZrO_2 content of the zirconias fabricated by these methods lies in the 90–98% range, depending on the chemical purity of the zircon ore. Higher purity can be achieved with lower pulp densities in the leaching steps. True, apparent and bulk densities of the zirconias were measured in the ranges 5.1–5.7, 3.1–4.5, and 1.5–2.2 g cm^{-3}, respectively. Total porosity was approximately 65%, most of which (45%) was microporosity. Morphological analysis showed a grain shape factor close to 1. The zirconias derived from the soda ash process exhibited smaller and more uniform grain size distribution than those derived from the lime method. Chemical composition of the starting zircon, and the amount of soda ash or lime used for disintegration, had an important effect on the quality of the resulting zirconia.

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