



Beneficiation of zircon sand in South Africa

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Synopsis

South Africa and Australia are the biggest suppliers of zircon sand to the international zirconium industry. However neither South Africa nor Australia is well known for zircon beneficiation.

Geratech Zirconium Beneficiation Ltd (GZB) continued with additional research on sodium hydroxide (NaOH) cracking of zircon sand during 2002–2003. In 2003 GZB started extracting zirconium from zircon sand by means of NaOH cracking on a commercial scale.

Experience has shown that temperature profile and atmospheric control inside the furnace is crucial for the beneficiation of zircon sand. Silica carryover to zirconium chemicals could result if a high temperature is used.

Once the sodium silicate is extracted from the sodium zirconate and dissolved in hydrochloric acid, two distinct routes can be followed to precipitate various zirconium chemicals. The most common route is to precipitate zirconium oxychloride crystals (ZOC), with subsequent purification from all contaminants (crystal route). Less known is the process (liquid route) that involves the direct precipitation of zirconium basic sulphate (ZBS). This route will yield a less pure product, with contaminants such as silica and titanium. An important factor in this route is the prevention of silica gel formation, which could hamper final product filtration.

For applications like paint drying (zirconium octoate) or antiperspirants (zirconium hydroxychloride) low levels of contaminants have no effect on the final product. The advantage of the liquid route is fewer production stages compared to the crystal route. The disadvantage of the liquid route is that the market for the products will be significantly smaller. The optimum solution could be a plant design that could cater for both routes.

Another example of an application of zirconium chemicals is the use of ammonium zirconium carbonate (AZC) in the paper industry. Zirconium basic carbonate (ZBC) is dissolved in ammonium carbonate to produce AZC solution. AZC is used mainly in European countries in the paper industry. For example, carton boxes were initially produced with formaldehyde as the binder, however, it has now been replaced with AZC since formaldehyde is considered toxic. AZC reacts with the cellulose fibres in the paper to act as the binder. The resulting product is not toxic, and printing ink dries very quickly due to the porous paper structure.

Other applications of zirconium chemicals involve the use of acid zirconium sulphate tetrahydrate (AZST), zirconium orthosulphate (ZOS), potassium zirconium carbonate (KZC), and zirconium hydrous oxide (ZHO). Fluoride-based zirconium chemicals like zirconium tetra-fluoride (ZrF_4) and hexafluoro-zirconic acid (H_2ZrF_6) are used in the aluminium industry.

Zirconium oxide (ZrO_2) can be produced from any of the abovementioned precipitated chemicals via a high-temperature decomposition process. The physical properties of such oxides can differ tremendously, depending on the final application. The fired density of sanitaryware is typically 5.8 g/cm^3 , compared to milling media at $>6.1 \text{ g/cm}^3$. The required fired density is achieved by controlling the precipitation and decomposition conditions for these two oxides. The same applies to stabilized and mixed oxides, for example where zirconium oxide acts as an oxygen carrier in fuel cells.

Introduction

Working with consortium partners, Geratech Zirconium Beneficiation Ltd. has developed the process technology to beneficiate zircon sand to produce various zirconium chemicals.

South Africa supplies approximately 45 percent of all zircon sand globally. Despite the large local zircon sand resources and established zircon sand mines, more than 95 percent of the beneficiation capacity for zircon sand is situated in China. This creates a beneficiation opportunity for South Africa, where value can be added locally.

The global demand for zirconium chemicals is currently 120 000 t/a with consistent growth expected annually; Geratech is targeting a niche market, and already has an approved customer list based on test samples from its demonstration plant in Chamdor, Krugersdorp.

This paper is a technical discussion on the beneficiation of zircon sand in South Africa.

Zircon beneficiation processing routes

In recent years, numerous zircon beneficiation processing methods have been developed. The following zircon beneficiation routes were investigated and are discussed below:

- Plasma-dissociated zircon (PDZ)
- H_2SO_4 dissolution of PDZ
- 40% HF dissolution of PDZ
- Dry HF desilication of PDZ
- Carbochlorination of zircon sand
- Alkaline fluxing of zircon with NaOH / Na_2CO_3 .

Plasma-dissociated zircon (PDZ)

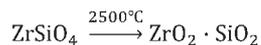
Zircon is chemically inert. Once zircon is heated to its melting point ($>2 \text{ 500 } ^\circ\text{C}$), the crystal structure re-arranges into separate amorphous silica and zirconium oxide phases. On fast cooling, fine zirconium oxide particles

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are entrapped inside an amorphous silica matrix.

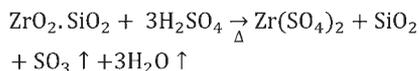


Necsa (Nuclear Energy Corporation of South Africa) investigated various plasma reactor configurations to research the dissociation of zircon. A V-type plasma configuration pilot plant was built and successfully commissioned.

Once zircon is dissociated to PDZ, it becomes vulnerable to acid attack and can be dissolved in sulphuric acid (H_2SO_4) and hydrofluoric acid (HF).

H₂SO₄ dissolution of PDZ

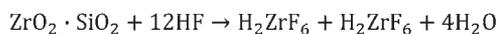
Since PDZ consists of individual ZrO_2 and SiO_2 phases, the ZrO_2 will be soluble in an excess of sulphuric acid at boiling point. The reaction rate is highly dependent on the surface area of the PDZ particles. The amorphous silica dehydrates during dissolution and can be filtered from the zirconium sulphate solution as a solid.



Due to the relative zirconium anion bonding strengths, the only chemical that can be precipitated successfully via this route is acid zirconium sulphate tetrahydrate $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (AZST). Additionally, the design of the furnace and scrubbing of the off-gas could be challenging.

40% HF dissolution of PDZ

ZrO_2 and SiO_2 are both highly soluble in hydrofluoric acid (HF).



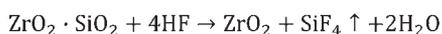
Since the reaction is extremely exothermic, the reaction temperature must be controlled. After dissolution of the PDZ, H_2SiF_6 is evaporated from the H_2ZrF_6 slurry. The H_2ZrF_6 is decomposed at high temperature to ZrO_2 .

The disadvantage of this process is the dangers of 40% HF. Additionally, fluoride forms a very strong bond with zirconium ions and is therefore very difficult to eliminate from zirconium chemicals. For example, low levels of fluoride contamination will prevent the precipitation of zirconium oxychloride crystals. The ZrO_2 produced from H_2ZrF_6 contains some fluoride contamination as ZrOF_2 .

Necsa registered a patent on the above process and proved the process by successfully commissioning a pilot plant during the late 1990s¹.

Dry HF desilication of PDZ

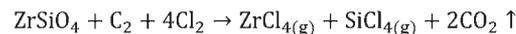
PDZ can be desilicated with dry HF gas in a fluidized bed, producing very fine ZrO_2 . The zirconium oxide produced has higher levels of impurities than the product from other processing routes. The resulting off-gas is oxidized to fumed silica and HF in a plasma reactor. The HF can be recycled back to the PDZ desilication reaction:



Carbochlorination of zircon sand

Zircon can be chlorinated at $>1\ 200^\circ\text{C}$ to produce zirconium tetrachloride (ZrCl_4) and silicon tetrachloride (SiCl_4). Due to zirconium's reactivity with oxygen, the process proceeds anaerobically. Both ZrCl_4 and SiCl_4 are removed from the reactor as gases. The ZrCl_4 deposits at 200°C and SiCl_4

condenses at -40°C .



ZrCl_4 can be converted to zirconium metal via the Kroll process. The main application of SiCl_4 's is in optical fibre production.

Alkaline fluxing of zircon with NaOH / Na₂CO₃

Both NaOH and Na_2CO_3 effectively flux zircon sand at high temperature. However, the zirconium extraction and separation processes differ.

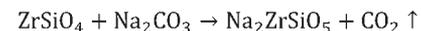
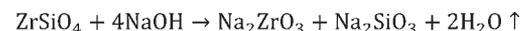


Table I indicates the main differences between the dissociation processes.

Commercial production routes for zirconium chemicals

From the above beneficiation routes, only two have been commercialized; namely alkaline fusion via sodium hydroxide (NaOH) and the alkaline fusion using sodium carbonate (Na_2CO_3). The latter process was used by MEI Chemicals in the USA, as well as by Palabora Mining Company (PMC) in the 1990s. The NaOH fusion process is used in China and in India at Bhalla Chemical Works. MEL in the UK, sister company to MEI, also used the NaOH route until all zircon cracking was stopped in the USA and the UK to focus on higher added value products.

Currently only the NaOH cracking of zircon is commercially employed to produce zirconium chemicals and high purity zirconium oxides. MEL used a slight variation of this route by precipitating zirconium basic sulphate (ZBS) directly from the HCl leach liquor (liquid route) without going through the ZOC crystallization step (crystal route). The differences between the liquid and crystal routes are discussed below.

Liquid vs. crystal route for zirconium chemicals production from zircon sand

There are two distinct routes that can be followed to produce zirconium chemicals via NaOH cracking of zircon sand (Figure 1). In the conventional route, the zircon is cracked, washed with water to remove the water soluble sodium silicate and leached with hot hydrochloric acid. Zirconium oxychloride (ZOC) crystals are then precipitated from this leach liquor. The water-soluble ZOC crystals are dissolved and the remaining insoluble silica is filtered and removed. ZOC is recrystallized to produce a pure ZOC crystal. ZBS is produced from the ZOC as an intermediate product or sold as a final product.

All the beneficiation steps for the crystal and liquid routes are essentially the same, except that the leach liquor is used for the direct precipitation of ZBS in the liquid route (Figure 1). As silica is a contaminant to all zirconium chemicals, using the liquid route, it is essential that the silica is kept soluble throughout the process.

The crystal route

NaOH fusion of zircon

Zircon reacts with NaOH at a temperature above 600°C according to the following reaction:

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	NaOH	Na ₂ CO ₃
Dissociation temperature	>600°C	>1200 °C
Furnace feed preparation	No mixing required	Normally pelletized
Heating profile	H ₂ O needs to be evaporated at low temperature (<400°C)	No specific profile
Containment	NaOH melts at >400°C and needs to be contained	Very limited liquid phase at 1 000°C
Furnace design	Batch furnace	Rotary kiln
Dissociated product	Final product is a soft powder	Hard pelletized product
Storage of dissociated product	Product is hygroscopic and must be protected against moisture	Can be stored for long period
Frit dissolution	Reaction is exothermic with water and temperature must be controlled	Reaction mixture solidifies with hydrochloric acid

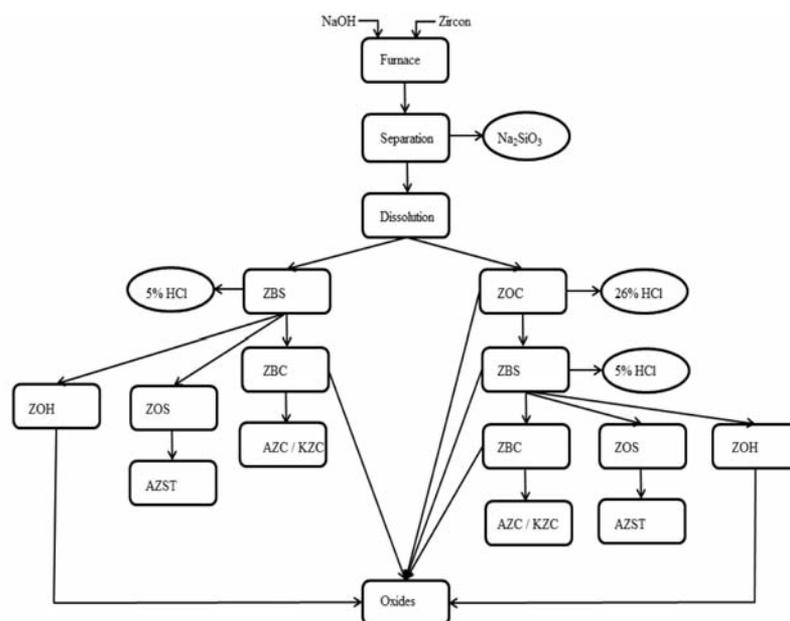
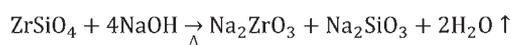
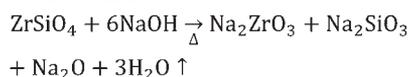


Figure 1—Schematic diagram of zircon sand beneficiation



Although this reaction will proceed as above, this results in a very hard unworkable solid product. In practice, an excess of NaOH is added:



This ensures that the resulting frit is soft and powdery.

Frit washing

Frit, consisting of two solid phases, namely water-soluble sodium silicate and water-insoluble sodium zirconate, is washed with water. More than 90 percent of all the silica in the zircon feed is removed as sodium silicate through filtration. The residual sodium silicate in the filter cake is removed later in the process.

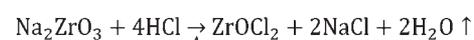
Silica conditioning

The sodium zirconate cake is reslurried in water and the pH is slowly adjusted using hydrochloric acid. By adjusting the pH to an acidic value, the sodium silicate is converted to a

range of silicon hydroxide compounds which are precipitated during leaching of sodium zirconate.

Acid leaching

The neutralized filter cake is leached with an excess of hydrochloric acid at boiling point according to the following reaction:



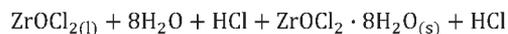
Silica precipitation

Zirconium oxychloride (ZOC) crystals precipitate from the leach liquor on cooling. The high acid concentration also results in the precipitation of the remaining silicon hydroxides. The solution is aged for several hours to maximize the precipitation of the silicon hydroxides. The ZOC is dissolved in water and the silica is removed by filtration.

Zirconium oxychloride (ZOC) precipitation

The acid concentration of the silica-free ZOC solution is increased in order to precipitate all zirconium in solution².

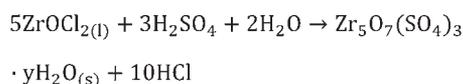
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The crystals are then washed and dried to the desired ZrO_2 concentration before packing and shipping. Alternatively it can be re-dissolved for further processing.

Zirconium basic sulphate (ZBS) precipitation

The ZOC crystals are dissolved in water. A source of SO_4^{2-} is added to precipitate ZBS at boiling point according to the following reaction:



Precipitation conditions are tightly controlled to ensure that specific properties of the ZBS crystals are achieved. These properties are application-dependant.

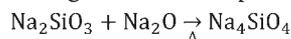
The ZBS is filtered and washed before drying and packing.

The liquid route

The main difference between the crystal and the liquid routes is the silica removal process. The aim of this processing route is to keep the silica in solution as long as possible. However, on aging, silica will eventually start to precipitate.

NaOH fusion of zircon

At higher reaction temperatures, different sodium silicate compounds form that are more stable (higher solubility) during the leaching process. The following reaction takes place at higher furnace temperatures:



Frit washing

Slurry temperature during frit washing is controlled. Too high a temperature will promote colloidal silica precipitation, which could result in filtration problems downstream.

Silica conditioning

This step is omitted for the liquid route.

Acid leaching

Washed frit cake is leached with hydrochloric acid at boiling point. After complete dissolution, this leach liquor is polished to remove any acid insolubles.

Zirconium basic sulphate (ZBS) precipitation from leach liquor

After polishing, ZBS is precipitated immediately from the acid leach liquor employing the same conditions used for ZOC

precipitation. The final product will still contain low levels of silica and titanium contamination.

Differences between the liquid and crystal routes

The main process differences are summarized in Table II.

Although Geratech produced several products using the liquid route, the levels of contaminants in the ZBS are higher than in ZBS produced from ZOC crystals (Table III).

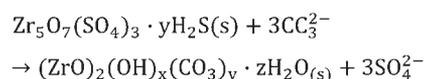
The contaminants in the ZBS produced via the liquid route cannot be removed in the subsequent processing steps and will be contained in the final products downstream. This limits the applications for zirconium chemicals produced via this route.

Other zirconium chemicals

All other zirconium chemicals are produced from ZBS as feed material. Purification is achieved during ZOC crystal precipitation for the crystal route and during ZBS precipitation for the liquid route. Subsequent production of zirconium chemicals is via conversion reactions. No further purification can be achieved.

Zirconium basic carbonate (ZBC)

Zirconium basic carbonate (ZBC) is produced from ZBS via an ion exchange reaction:

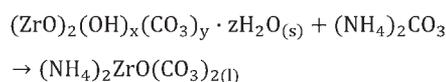


Properties of the ZBC such as reactivity and molecular mass can be controlled for specific applications by adjusting the key process parameters.

ZBC is produced by the addition of a carbonate reagent to a ZBS slurry. Once all ZBS is converted to ZBC, it is filtered, washed, and dried before packing.

Ammonium zirconium carbonate (AZC)

Ammonium zirconium carbonate (AZC) is produced by increasing the $\text{CO}_3:\text{Zr}$ mole ratio by the addition of ammonium carbonate.



This reaction takes place at ambient temperature. After dissolution, the solution is polished and stored. AZC has a limited shelf live due to polymerization.

Potassium zirconium carbonate (KZC)

Potassium zirconium carbonate (KZC) is preferred to AZC in

Table II

Process differences between the liquid and crystal routes

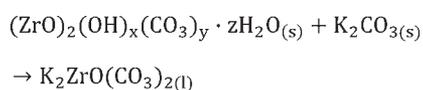
Process step	Liquid route	Crystal route
Fritting temperature	Critical control required	Some control required
Frit washing temperature	Critical control required	No control required
Silica conditioning	Not applicable	Critical control required
Acid leaching	Critical control required	Some control required
Acid recycling	No acid recycling	Some acid recycling
Product quality	TiO ₂ and SiO ₂ as contaminants	All contaminant concentrations are very low

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Table III
Difference in contaminant levels of ZBS produced via the liquid route compared to the crystal route

Contaminant	ZBS via the Liquid route	ZBS via the Crystal route
SiO ₂	<500 ppm	<20 ppm
TiO ₂	<2 000 ppm	<5 ppm
Fe ₂ O ₃	<10 ppm	<5 ppm
Na ₂ O	<100 ppm	< 10 ppm

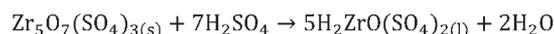
some applications due to the strong ammonia smell associated with AZC. The process to make KZC is similar to that for AZC, except potassium carbonate is used instead of ammonium carbonate.



KZC has the added advantage that it can be spray-dried to reduce shipping cost.

Zirconium ortho-sulphate (ZOS)

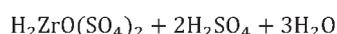
Zirconium ortho-sulphate (ZOS) is a liquid zirconium chemical produced by dissolving ZBS in sulphuric acid.



Since the ZBS is dissolved in a sub-stoichiometric amount of H₂SO₄, the solution tends to precipitate very fine ZrOH(SO₄) if the process is not well controlled.

Acid zirconium sulphate tetrahydrate (AZST)

Acid zirconium sulphate tetrahydrate (AZST) is precipitated from a ZOS solution by adding concentrated H₂SO₄.



AZST is filtered from the acid solution, washed, dried, and packed. The filtrate can be recycled to dissolve ZBS for ZOS production.

Zirconium oxides

Background

Zirconium oxide exhibits three well-defined polymorphs; i.e. monoclinic, tetragonal, and cubic phases. The monoclinic phase is stable up to about 1 170°C and then transforms to the tetragonal phase. The tetragonal phase is stable up to 2 370°C and then transforms to the cubic phase, which is stable up to the melting temperature of 2 680°C. On cooling to the transformation temperature, the structure reverts back to the original phase. Of greatest significance is the tetragonal to monoclinic transformation, which is associated with a large volume change⁵.

The volume reduction during tetragonal to monoclinic transformation can be used as an advantage to improve both toughness and strength of ceramics. The addition of stabilizing oxides with either CaO, MgO, Y₂O₃, CeO etc., stabilizes the cubic crystallographic phase of zirconium oxide at ambient temperature, thereby avoiding the volume change

during the phase change.

Most common precipitation and decomposition routes

There are various routes for precipitating and decomposing monoclinic zirconium oxide. The specific precipitation route will determine the physical properties of the final decomposed zirconium oxide.

The most common precipitation and decomposition routes are:

- ZOC precipitation and decomposition
- ZBC precipitation and decomposition
- ZHO precipitation and decomposition.

The difference between decomposition of ZOC and ZBC/ZHO are as follows:

- Off-gases
- Morphology and flowability
- Particle size
- Specific surface area (SSA).

High-value zirconium oxide precipitation at Geratech

By focussing on ZBS precipitation technology, Geratech was able to manipulate the physical properties of zirconium oxide. During ZBS precipitation one can effectively control the particle size as well as the crystallite size.

An example is the fired density of sanitaryware, which is typically 5.8 g/cm³ compared to milling media at >6.1 g/cm³. The required fired density is achieved by controlling the precipitation and decomposition conditions for these two oxides. The same applies to stabilized and mixed oxides, where zirconium oxide acts as an oxygen carrier in fuel cells.

Mixed and stabilized zirconium oxide precipitation.

Stabilized zirconium oxide is manufactured by adding a rare earth metal in the production process, whereas mixed oxides are combinations of rare earth oxides.

Co-precipitation

The stabilizing chemical, for example Y₂O₃, is precipitated onto the ZHO particle by means of a pH change. The disadvantage of this process is that stabilization may occur only in the outer layer of the particle. If these particles are crushed downstream, this may expose monoclinic zirconium oxide, which could result in product failures.

Simultaneous precipitation

The required chemicals are mixed simultaneously as a liquid and then slowly precipitated by changing the pH. A disadvantage of this method is a possible yield loss if the pH of the mixture is not carefully controlled.

Calcining and milling

On drying and calcining, the ZHO particles become hard and dense. This will have an impact on the energy required for size reduction. The density of the ZHO particles can be manipulated by controlling the drying process.

If a carbonaceous alkali is used, the particles will be porous due to the release of CO₂ during drying. The particles will have a bigger surface area, with an internal porous structure. Milling of these oxides will require less energy than oxides produced from ZHO.

Specific surface area (SSA) is dependent on the calcination temperature and particle size. Low calcination temperatures will yield higher SSAs and softer particles.

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These properties are, however, client-specific and should be controlled to achieve client specifications.

Waste management

The beneficiation of zircon for the production of zirconium chemicals produces a number of waste streams.

The highly alkaline waste from the frit washing step is combined with the acid waste from the rest of the process to produce a neutral waste that can be safely disposed.

Zircon contains low levels of the radioactive metals uranium and thorium. During the processing of zircon, uranium and thorium are diluted with the acid waste. Geratech has completed an environmental impact assessment (EIA) and is operating under a National Nuclear Regulator (NNR) approved waste management plan.

Examples of industrial applications

Table IV lists industrial applications of the zirconium chemical currently in use⁴.

Zirconium chemicals are used in a wide variety of industrial applications. In a number of cases the zirconium compounds replace harmful elements, like Cr⁶⁺ in leather tanning and formaldehyde in the papermaking industry.

Stabilized zirconium oxide is used as an oxygen ion conductor in solid oxide fuel cells. It is believed that these fuel cells will have a major influence on the supply of clean power in the next millennium⁵.

Commercialization in South Africa

Geratech Zirconium Beneficiation Ltd is a South Africa based company owned by the Industrial Development Corporation (IDC), the Technology Innovation Agency (TIA), the Swedish government through Swedfund, and private shareholders. Geratech, as part of a consortium, has developed the process

technology to beneficiate zircon sand for the production of various zirconium chemicals.

Thus far, Geratech is the only company in Africa to successfully produce 2 000 t of zirconium chemicals at a demonstration plant scale. Each product type was successfully marketed and approved by customers from the USA, Europe, Asia, and Africa. Although China is the largest producer of zirconium chemicals, Geratech is strategically positioned due to its access to the main raw material, zircon sand.

Conclusion

Various methods of beneficiating zircon sand can be employed; the most common route is by fluxing with an excess of sodium hydroxide. Once the resulting sodium zirconate is dissolved in boiling hydrochloric acid, two distinct routes can be used to precipitate various zirconium chemicals. The ZOC crystal route will yield a higher-purity range of products. The liquid route will produce a less pure product range at a lower production cost. Final product applications will therefore differ; both routes have approved customers worldwide.

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Table IV

List of industrial applications and an example of the zirconium chemical currently in use

No.	Industrial application	Zirconium chemical
1	Adhesives	Zirconium propionate
2	Aluminium industry	Hexafluorozirconic acid
3	Anti-perspirants	Zirconium hydroxychloride
4	Catalysts	Ceria-doped zirconium oxides
5	Ceramic colours	Zirconium oxide
6	Ceramic filters	Yttria-stabilized zirconium oxide
7	Coatings	Potassium zirconium carbonate
8	Dental implants	Zirconium oxides
9	Electroceramics	Zirconium barium titanate
10	Fuel cells	Yttria-stabilized zirconium oxide
11	Inks (printing)	Ammonium zirconium carbonate
12	Kidney dialysis	Zirconium phosphate
13	Leather tanning	Acid zirconium sulphate tetrahydrate
14	Metal treatment	Zirconium nitrate
15	Oil industry	Zirconium lactate
16	Oxygen sensors	Zirconium oxides
17	Paint dryers	Zirconium octoate
18	Paper	Ammonium zirconium carbonate
19	Pigments	Zirconium hydroxide
20	Polymers	Zirconium propionate
21	Prostheses	Zirconium oxides
22	Refractories	Zirconium carbide
23	Spark plugs	Zirconium oxides
24	Textiles	Zirconium oxychloride