ZIRCONIUM AND HAFNIUM

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All zirconium and hafnium compounds, including the metal, oxide and salts, are derived from zircon sand (zirconium silicate ZrO_2 SiO_2) and baddeleyite (ZrO_2), with zircon being the primary feedstock. Often, zirconium and hafnium are thought to be rare elements, but in fact they occur frequently in the Earth's crust, being more plentiful than copper, with a concentration of 0.028%. They are generally found alongside titanium and iron ore, and these are mined commercially to recover zircon and baddeleyite. Hafnium is present in all zircon sand and baddeleyite (around 1.5-3.0%) and has an almost identical chemistry to zirconium. This makes separation of the two difficult, and is only done when absolutely necessary, such as for zirconium nuclear applications and the preparation of hafnium compounds.

Zircon sand
2003 saw further dramatic moves in the world of zircon sand producers and consumers. The undersupply that developed in 2002 deepened further, leading to a shortage of some 50-80,000 t globally. The net result of this has been yet another spike in zircon prices, major concerns about short- and long-term supplies and resulting changes in downstream product manufacture. Zircon markets have seen a modest growth over the past few years but it has been the rapid expansion of the ceramics and zirconium chemical production in China that has led to the huge shortfall in supply.

Zircon sand occurs in most parts of the world and is the most abundant zirconium mineral. Zircon is mainly recovered from heavy mineral sands (found predominantly in beach deposits) where the associated titanium minerals – generally rutile and Ilmenite are recovered separately. Some zircon sand is also produced during rare earth processing. Total world reserves are thought to be in excess of 100 Mt. Australia, South Africa and the US continue to be the main players.

Zircon recovery from heavy mineral sands is normally achieved by dredging and/or dry mixing operations – the technique used being dependent on the orebody location, concentration and chemical makeup. There is a trend for zircon to be processed further by mechanical abrasion, chemical attack and heat processing (calcination). This results in zircon with a wide range of physical and chemical properties, which determine its end use.

A large proportion of zircon sand is used as mined – in a coarse particle size– in abrasives, foundries, refractories (steel, glass, cement, metal), cathode ray tubes (CRT) for televisions and for zirconium metal, oxide and chemical production. In uses where the material is not so aggressively attacked (as it is in fusion and chemical processing) the surface area needs to be increased. This is achieved by milling to finer particle sizes as found in zircon flours (generally <200 or <300 mesh), or in smaller sizes (5 micron and below) as opacifier grades. These products are used predominantly in ceramic frits, which are special glasses. The zircon particles reflect light and so impart a white opaque colour to the final ceramic glaze. Generally, zircons with a finer particle size and narrower distribution lead to the best opacifiers. Such frits are used in large quantities in tile, table and sanitary ware production. Since the desired effect is the formulation of an intense white colour, impurities such as colouring transition metal ions, (Fe and Ti) need to be minimised. Consequently the higher quality grades (generally referred to as ceramic or premium grades) have a maximum 0.10% TiO_2 and 0.05% Fe_2O_3. Lower-quality grades with higher Ti and Fe levels are used in refractory and foundry applications.

In 2003, world zircon output totalled some 1.1 Mt, similar to 2002. Shipments from Australia increased to approximately 450,000 t (2002: 420,000 t), South African movements fell to around 375,000 t (2002: 420,000 t) and US sales increased to some 140,000 t (2002: 130,000 t). Output from Ukraine, India, Vietnam, Brazil, Malaysia, China and Russia showed little change, with a combined contribution of around 130,000 t (similar to 2002).

The ongoing problem of zircon being inextricably linked to titanium minerals and markets continued. Historically, titanium ores and downstream TiO_2 pigments have been in oversupply. This has led to little price improvement and, with increasing environmental, social and other operating costs, has led to low profitability. The heavy mineral sands mining industry has always centred more on titanium ore recovery than zircon – with zircon being considered a by-product. Hence, with low demand for titanium ores, there has been no incentive to increase output and this has resulted in little growth in zircon recoveries. This situation may be changing as zircon demand and pricing increase. Recently, however, ores with high TiO_2 content are in more demand – also easing the situation.

The largest world producer is Iluka Resources Ltd, with operations in Australia and the US, and production and sales of approximately 375,000 t (2002 360,000 t). Plans to increase output in the short-term rest on improved operational efficiencies and product recoveries at all existing sites, particularly in Virginia US and at Eneabba in Western Australia. Recently, Iluka began commissioning its' new Lulaton mine and plant in Georgia, US. Developments in the Murray Basin in southeast Australia are spearheading Iluka's medium- to long-term plan to boost output. On an even longer scale, Iluka sees exploration and the discovery of new orebodies, particularly with high zircon contents, as paramount. Iluka informed its customers in late 2003 of its intention to raise prices in the first half of 2004 and again in the second half of 2004. This sets the picture for 2004, with all zircon producers quoting on a quarterly basis. Also in Australia, Tiwest maintained output at around 80,000 t (similar to 2002).

In South Africa, Richards Bay Minerals (RBM) owned by Rio Tinto plc and BHP Billiton plc is the world's second-largest producer. Production difficulties, mainly due to an organic coating on the zircon led to a fall in output in 2003, to approximately 240,000 t (2002: 270,000 t).

Anglo American's subsidiary Namakwa Sands lies in third place, with operations in the Western Cape. A serious fire in the mineral separation plant in October 2003 halted production for three months and led to a fall in output to about 80,000 t in 2003 (2002: 100,000 t). The plant is now running again but the lost production further pressurised the zircon supply/demand situation. Also in South Africa, Ticor SA (Kumba Resources 60%, Ticor 40%) located close to Richards Bay in Kwa Zulu-Natal Province, saw output fall marginally to 50,000 t in 2003 (2002: 55,000 t). In the US, Du Pont's Florida plant maintained output at approximately 70,000 t/y.

All zircon markets showed growth in 2003, with total demand well over 1.1 Mt. Ceramics (mainly tile and sanitary ware) consumed around 50% of total output of zircon, with China's demand rising to 125,000 t, from 100,000 t in 2002. (China now produces 36% of the world's tiles.) European demand grew only marginally in this period and is now some 270,000 t.

Refractory requirements for zircon saw a small increase to 180,000 t (2002: 170,000 t). Chinese demand grew to 30,000 t (25,000 t), mainly because a number of Western refractory producers have moved production to China, eg, RHI and Vesuvius. All refractory users, particularly steel-makers, have pressed for increased performance and consequently there has been a continuing fall in refractory consumption per tonne of product made. For example, in China, the steel industry has seen a fall from 55 kg used per tonne steel output to around 20 kg/t steel in 2002. This increased performance has not been mirrored with increased refractory prices, leading to pressures to cut costs and the move to cheaper manufacturing bases.

Foundry uses for zircon in investment casting (a method of precision-casting of metals using moulds made from zircon) moved up only marginally and consumption was similar to the 170,000 t consumed in 2002. This may have been due to a slowdown in the aerospace industry (turbine blades). Sports goods, such as golf club production, remained buoyant. The use of zircon to block X-ray emissions in cathode ray tubes (CRT) in computers and TV monitors also continued to rise slowly and consumption in 2003 was broadly similar to the 2002 level of 90,000 t). In the longer term, the development of alternative electronic display methods, for example liquid crystal displays/thin film transistors, may temper the growth of zircon usage in this industry.

In addition to the movement in the ceramics industry, the use of zircon in zirconium chemicals and synthetic zirconia in China jumped significantly in 2003 by some 10,000 t, to 45,000 t. In world terms this lifted zircon usage for zirconium metal, oxide and chemical manufacture to over 110,000 t (95,000 t). This market, like the ceramic opacifiers, needs good-quality zircon containing low impurity levels. Premium grade is in very short supply and this has added extra pressure, particularly in China, with some zirconium chemical producers unable to find material and so chopping output.

Taking all the world markets together, Europe continued to absorb the largest zircon share in 2003, at 400,000 t, with China next at 225,000 t (2002: 190,000 t). North America followed, at 175,000 t (150,000 t). The Japanese market reduced by 20,000 t to 55,000 t, mainly because of improved refractory performance and some substitution. Prices increased steeply during the year, with some inventory and panic buying adding to the severe shortage in supply. Table 1 shows the significant price moves with zircon opacifiers edging over US$1,000/t in Asia.

The outlook is for continuing tightness in zircon supply well into 2004-05, with further increases in price. Demand is expected to move closer to 1.2 Mt and, with no new major output imminent, significant problems are likely across all markets. Over the next two years it is envisaged that the annual shortfall in supply could grow to as much as 100,000 t. Further ahead, the supply/demand balance should be restored; the main producers are trying to maximise output from existing mines, and there are new developments in Australia's Murray Basin and the Corridor sands project (CSP) in Mozambique, together with prospects in Sri Lanka, India, Canada (Alberta) and the Former Soviet Union.

Baddeleyite

In 2003, the traditional markets for baddeleyite moved further towards the use of synthetically derived products made from zircon sand, namely fused monoclinic and stabilised zirconia. With the closure of South African baddeleyite production in 2001, some 12,000 -13,000 t of annual consumption in refractory, ceramic, abrasive and other applications was forced to move to alternative supplies. Long-standing zirconia producers in the US, Europe and Australia (previously in competition with baddeleyite) increased output to fill this void. The largest change occurred in China where significant new zircon cracking plants were established.

Since the 1970s, baddeleyite output had been dominated by two operators based at Phalaborwa in the Northern Province of South Africa. Palabora Mining Co (PMC), a Rio Tinto plc subsidiary, and state-owned Phosphate Development Corp Ltd (Foskor). PMC recovered zirconium ore containing 99% ZrO_2 + HfO_2 as a byproduct of its open-pit copper mine. This complex ore-body produced a varied product mix including magnetite and precious metal slimes. As a result of the changing geology and mine geometry, output of baddeleyite came to an end in 2001, with PMC switching to underground block-cave mining. PMC also closed the world's only plant making a zirconium salt from baddeleyite (zirconium sulphate or acid zirconium sulphate – AZST or orthosulphate) as the feedstock disappeared.

This ended PMC's position as market leader in zirconium ore and sulphate after some 30 years. Maximum annual output was achieved by PMC in the late 1980s when around 13,000 t of oxide and 3,000 t of sulphate were sold annually. Around this time, PMC investigated the possibility of building a zirconium chemical plant in the US but this was shelved because another competitor in the US expanded output. Instead, PMC completed a state-of-the-art zirconium basic sulphate (ZBS) plant in the early 1990s at Phalaborwa. (refer to zirconium chemical section). This plant was based on using zircon sand taken from PMC's sister company Richards Bay Minerals

(RBM). After significant operational problems, including a serious fire, PMC offered this plant for sale in the second quarter of 2004.

Foskor also ran out of baddeleyite in the early 1990s after reaching a maximum yearly output of 6,000-7,000 t. However, Foskor retained and developed its markets for zirconium ore products by purchasing a synthetic zirconia plant from Fukushima Steel, Japan. This operation, also based on zircon sand as a starting material, manufactures monoclinic and fused stabilised zirconia, and has an annual capacity in excess of 6,500 t. These products are sold to refractory and ceramic pigment markets.

The world’s one remaining commercial source of baddeleyite lies in the southwest part of the Kola Peninsula in Russia, very close to the border with Finland. This remote mine, operated by A O Kovdorsky GoK (Kovdor) and owned by MDM Chemical group based in Moscow, recovers iron ore, apatite and baddeleyite from a complex ore-body. Over the past few years, Kovdor has slowly increased annual output and this now approaches 7,000 t. Following the curtailment of production at PMC, Kovdor received much attention from the various markets but ore-body availability and processing constraints would not allow volumes to be lifted to replace South African market share. Knowing this, Kovdor has concentrated on maximising the revenue potential of available material, and work continues to find high added value products. Kovdor’s main sales continue to be to the abrasive and refractory markets, particularly in the East, and recently they have been focusing on baddeleyite use in ceramic colours.

The mine operates around the year despite harsh winters and there is considerable feedstock from the open pit and part-processed tailings. It is expected that baddeleyite and/or downstream product output will continue for at least a further 20-30 years. After some early difficulties, quality issues have now been stabilised. As further developments occur in the ore recovery, separation and purification stages, there is potential to develop new products and applications.

The Norwegian fusion plant Nako Narvik AS, built to take baddeleyite feedstock from Kovdor, remains closed, despite attempts by the bank owners to find a partner or buyer. Higher zirconia prices and developing shortages may lead to the reopening of this plant, based either on baddeleyite or zircon sand feed.

Technical matters relating to the uranium and thorium content of baddeleyite and synthetic zirconia (fused monoclinic and stabilised grades) continue to be debated at specific radioactivity conferences and related mineral user group meetings. There is a continuing trend by the legislators to tighten up on acceptable levels of U + Th contained in baddeleyite (and zircon sand) from a production, shipment, bulk storage and end-use consideration. Specifically, this is controlled with regard to worker, environment/waste and transport regulations. Work has been focused on the education of likely problem sites, with emphasis on risk assessment. Varying levels of legislation around the world have been subject to comparison and attempts are being made to harmonise the variations. In general, synthetic zirconia are less radioactive than baddeleyite but this is dependent on the zircon sand feedstock used.

Table 2 outlines the market position for baddeleyite and synthetic zirconia, including both fused monoclinic and stabilised zirconia.

Around 70% of refractories produced worldwide are used in the steel industry (with cement, chemicals, ceramics, glass, others each accounting for 4-6%). Despite a 6.7% rise in world steel output the use of baddeleyite/synthetic zirconia increased only marginally in 2003. This is due to the continuing reduction in the rate of refractory consumption per tonne of steel produced. China increased its steel output by 73% over the period 2000-03 (by 21% in 2003) and this has led to a significant movement of Western refractory production to plants in China (either wholly owned or joint ventures). Similar moves are happening in the glass, ceramic and other refractory fields. Ceramic and plastic colour pigment output increased in 2003, with Asia and specifically China, showing gains. This is being fuelled by China's spectacular growth in ceramic tile manufacture for example from 252 million m^2 in 1990 to 2,240 million m^2 in 2002.

Alumina-zirconia (AZ) abrasives were first made by Norton of the US. An AZ alloy can contain up to 40% zirconia and is made by fusing alumina, zircon and baddeleyite/fused monoclinic zirconia in an electric arc furnace. These products offer an exceptional cutting action with increased lifetime of use. These developments, along with changes in the metal-forming market (more precise casting), have led to much-improved performance and product life, and hence almost zero growth in consumption.

Electro-ceramic markets utilising zirconia's insulator/conductor properties continued to grow slowly in the filter, buzzer, spark generator and other leading zirconate titanate (PZT) applications.

In glass applications there have been new developments in frit and other surface coatings. This has been offset by market saturation in the cubic zirconia field, and some replacement by alumina leading to little or no growth in this sector.

The varied uses of zirconia in the advanced ceramic, fuel cell and catalyst (industrial and autocatalyst) areas continue to grow. Zirconia of much higher purity (and price) can be made in partially (PSZ) or fully stabilised (FSZ) forms by careful chemical processing under controlled conditions. These grades offer novel mechanical and electrical properties.

The advanced ceramics field saw no major changes, although interest in fuel cells, catalyst (industrial and automotive) continued. Other applications using zirconia's superior mechanical properties continued to grow slowly – although volumes remain relatively small (refer to zirconium metal, oxide and chemicals section).

Prices for baddeleyite and synthetic zirconia (Table 3) edged upwards into 2004 in response to increases in zircon sand prices, higher shipping charges, increased costs for other raw materials and fuel, and Chinese export tax rebate reductions. Higher zirconia output, particularly in China, led to more fierce competition, and this limited price increases, with some grades more affected than others.

Zirconium metal, oxide and chemicals

2003 saw a further jump in demand and manufacturing capacity of various zirconium chemical products – particularly in China. Key markets for metal, oxides and chemicals are given in Table 4.

Zirconium metal continues to be an important refractory material and is used in alloyed and unalloyed forms. Its outstanding metallurgical properties such as resistance to high temperatures and chemical attack leads to its use in challenging engineering applications such as chemical reactors with hot, corrosive environments. Recently, zirconium is also finding increased use in professional flute manufacture because of its ability to lift the musical quality. Hafnium's ability to capture neutrons means that hafnium has to be removed where zirconium metal is used in nuclear applications eg, nuclear fuel rod claddings, reactor cores and related engineering. With the slowdown in new nuclear reactor installations worldwide, zirconium metal producers have concentrated on developing new markets.

Zirconium oxide occurs naturally as the mineral baddeleyite but the majority of the world's supply is made synthetically by removing silica from zircon sand (zirconium silicate) using a variety of techniques based on a) thermal dissociation (where the resulting product is referred to as fused monoclinic zirconia) and b) chemical splitting (where the resulting zirconium chemical is then converted to chemical grade zirconia). These include:

- Electric arc fusion process to dissociate the ZrO_2 from SiO_2
- By plasma dissociation followed by leaching.
- Attack with carbon at 2,000°C or carbon/chlorine to make carbide, tetrachloride, and then hydrolysis/calcination.
- Reaction with alkali or alkali earth oxide (sodium hydroxide/carbonate or lime) followed by hydrolysis/calcination/acid leaching.

Chemical grade (monoclinic) zirconia are generally made by onward processing and calcination of zirconium oxychloride (ZOC), basis carbonate (ZBC) or other species.

Monoclinic zirconia suffer from an 8% volume change when they are heated to 1,170°C where the tetragonal form occurs. Continued heating results in a further charge to the cubic phase at 2,370°C. This catastrophic volume change in the monoclinic/tetragonal transformation is avoided by the addition of a cubic oxide (eg, MgO, CaO or Y_2O_3) to form baddeleyite or fused monoclinic zirconia during processing at high temperatures. This results in fused, fully stabilised zirconia (FSZ) in the cubic phase, which is stable from room temperature to its molten state. This material has a uniform thermal expansion curve, hence rapid volume changes are eliminated, which means that the ceramic article being produced does not crack or shatter on cooling.

Similar cubic additions are used in chemical grade zirconia, particularly yttria. These tend to be added during chemical processing and result in an intimate contact of cubic oxide/zirconia. Where the stabilised oxide is present in concentrations less than those required for complete stabilisation in the cubic phase, then the resulting zirconia will be a combination of cubic and tetragonal and/or monoclinic phases – so called partially stabilised zirconia (PSZ). The development of PSZ in the 1970s led to the start of the zirconia advanced ceramics markets. It was realised that these new materials offered superior mechanical properties to metals (stronger, better heat and wear resistance) and had a novel electrical make up (conductor as well as insulator). This led to a wide range of applications (Table 5).

The range of applications for zirconium chemicals, as seen in Table 4, diversified even more, with major uses in catalyst, chemical manufacturing, healthcare, metals, paint drier (siccative), paper, textile and titania coatings. Key items made are zirconium acetate (ZAC), zirconium basic carbonate (ZBC), ammonium zirconium carbonate (AZC), zirconium oxychloride (ZOC), zirconium acid sulphate (ZOS/ZST) and zirconium basic sulphate (ZBS). China has added significant new capacity in 2003 and remains the powerhouse of zirconium chemical production with a total capacity of over 100,000 t. Smaller volumes emanate from India, South Africa, the UK and the US.

ZOC continues to be the basic building block chemical used to make other species and Chinese capacity now exceeds 60,000 t. However, in recent months the shortages in zircon sand supply and resulting price increases have led to changes. Several ZOC producers have been forced to close or cut back output and this has led to concerns throughout the whole industry. With zircon spot prices now exceeding USS600/t and large increases in other raw material costs, ZOC prices have jumped by over US$400/t – the largest increase ever.

Since ZOC is used to make ZBS, ZBC and chemical grade zirconia, these increases have been pushed down the line, leading to large cost increases for the various customers.

ZOC continues to replace ZOS/ZST in pigment (TiO_2) coating owing to its lower cost and higher solubility, with the choice being dependent on the manufacturing process and type of scrubber used in the acid treatment system. Antiperspirant markets also moved ahead as personal hygiene sales grew in markets outside the EC and the US. The use of ZOS/ZST in leather tanning saw little or no growth possibly because of substitution by synthetics and low fashion interest.

ZBS continued to be used primarily as an intermediate for ZBC, AZC and other products, with China again a major source. PMC's ZBS plant in South

Africa was rebuilt after the fire in 2002 and additional equipment added. PMC recently decided to end its interest in this plant and a management buy-out has been agreed.

Major consumers of ZBC all pushed ahead. ZBC's use in paint driers is closely linked to its role as a catalyst, where the zirconium compound speeds up the physical change from the liquid to the solid state (O_2 is absorbed leading to oxidative cross linking). The catalyst industry uses ZBC as a precursor to other zirconium compounds/special oxides.

AZC is mainly used in paper coating to improve print adhesion and in textiles to fix antifungal species such as Cu, Cr or Hg to the cellulose fibre.

As mentioned, China continued to increase its capacity to produce zirconium products. Shenyang Astron Mining Industry Ltd (Yingkou Astron Chemical Co Ltd), with headquarters in Shenyang, saw major growth in fused and stabilised zirconium oxides (new furnaces lifting annual capacity to 13,000 t) and chemicals (production doubled at its Yingkou plant). Although based in Shenyang, Astron is an Australian public-listed company. Being a major importer and user/seller of zircon sand into the Chinese market, Astron has also been working to secure long-term supplies. In a joint venture with Carnegie Corp Ltd of Australia, the former British Titan Products' mineral sand deposit in Gambia has been converted to produce zircon concentrate, which is shipped to China for further processing. Some 12,000 t was shipped in 2003.

Astron also acquired 100% of Zirtanium Ltd, which owns large zircon deposits in the Murray Basin in western Victoria. The Jackson and Donald heavy minerals deposits, discovered in the 1980s by CRA/Rio Tinto but relinquished by CRA because the very fine grain size posed separation problems, should yield 30,000 t/y of zircon, together with other titanium minerals, once large-scale mining begins.

Asia Zirconium Ltd (Jiangsu Xinxing Chemicals Group), one of the first Chinese makers of zirconium chemicals in the 1970s, was floated on the Hong Kong Stock Exchange during 2003. With total production capacity listed at 35,000 t/y of ZOC and 6,000 t/y of ZBC, it is one of the largest manufacturers. New developments include nanometric zirconium oxide and further plant expansions. There are now a total of approximately 40 zirconium chemical plants in China although, with the shortages in zircon supply, this may decline. The Canadian-based rare-earth producer AMR Technologies continued with developments at its Chinese and Thailand plants, adding zirconium oxide and chemicals for the catalyst, fuel cell and electronic markets. Its 2003 results showed higher operating profits despite a fall in sales revenue. Sydney-based rare earth company Lynas Corp has increased its shareholding in AMR to approximately 20%.

In Japan, four companies, namely Daiichi Kigenso Kagaku (DKK), Fukushima, Tosoh Corp and Sumitomo Osaka Cement (SOC), were involved in fused zirconia/chemical production. DKK based in Osaka/Gotsu further developed its catalyst, fuel cell and advanced ceramic grades of PSZ but slower market conditions were experienced. Its main competitors, Tosoh and SOC, also saw continuing stockpiles of advanced ceramics components.

In the US, Southern Ionics pressed ahead in the chemical, catalyst and renal dialysis markets. Eka (part of Akzo Group and formerly Hopton Technical) moved forward in paper coating, and ATI Wah Chang continued to grow in aerospace, automotive and nuclear applications, with its speciality materials such as zirconium and hafnium metal/alloys. MEI continued to refocus on advanced technology markets. New York-based Aremco Products launched a high ZrO_2 (>90%) refractory paint for sealing ceramic/metal surfaces.

In the UK, Magnesium Elektron Limited Chemicals (MEL Chemicals), a sister company to Magnesium Elektron Inc (MEI) US, moved further away from commodity zirconium chemicals, concentrating on higher added-value products. UCM Group (formerly Universal Abrasives and incorporating Unitec Ceramics UK and Universal America US), moved production from the UK to the US, thereby streamlining its operations. The company has manufactured electro-fused zirconia for over 30 years. Its advanced ceramics grades will continue to be made in Stafford, UK at the newly enhanced site. Sales and marketing responsibilities also changed under the new management structure.

In India, Bhalla Chemical announced a further expansion at its zirconium chemicals plant. A new 500 t/y zirconia and 250 t/y zirconium sponge plant owned by Nuclear Fuel Complex (NFC) of Hyderabad, is nearing construction at Tuticoru in Tamil Nadu. In Ukraine, Vilnohirsk State Mining and Metallurgical Plant (VSMMP) introduced yttria stabilised zirconia to augment its zirconium oxide, zircon and other mineral range.

In Australia, Australian Fused Materials (AFM) 4,500 t/y fused zirconia output was fully sold. AFM has seen growth in sales to ceramic pigment manufacturers at the expense of refractory/abrasive markets. An additional furnace is required to lift output but shareholder differences have prevented this.

The largest zirconia producer is the French industrial giant, Saint Gobain, with plants in Australia, the US, China and France. Total capacity of zirconium chemical and zirconia production is thought to be approximately 40,000 t/y of which, around one third is fused monoclinic and chemical grade zirconia. In South Africa, Geratech Beneficiation Ltd won more government backing and announced a further plant expansion.

All producers of zirconium metal, oxides and chemicals have been affected by the increasing shortage of zircon sand and this has led to worries about security of supply. Around 100,000 t/y of zircon is consumed in making these products, or some 10% of world zircon sand output. Some producers, eg Astron, have secured ownership of zircon deposits, to provide adequate feedstock and also to develop business in the related titanium minerals field. Large increases in prices of other raw material, and fuel and freight costs, particularly in China, mean that the prolonged downward spiral of zirconium chemicals prices is being reversed. This will lead to changes in market shares worldwide and may lead to significant shifts in the world's distribution of zirconium products.

Hafnium metal and chemicals

Hafnium is normally present at 1.5-3.0 weight percent of zircon sand and baddeleyite, and is removed when zirconium is used for nuclear applications. All hafnium compounds derive from this difficult extraction process, which is based on the Kroll process. Hafnium is used in various alloyed and unalloyed forms such as plate, strip, sheet, rod, wire and tube – similar to zirconium metal. It is also converted into oxide and other reactive chemical species (Table 4). Hafnium's strong ability to absorb neutrons led to its use in controlling nuclear reactors. Rods containing hafnium are raised or lowered to regulate the nuclear reaction. Hafnium metal finds extensive use in aerospace alloys, in medical and in other special products.

Hafnium metal and compounds are produced in the US (Westinghouse Electric Co, ATI Wah Chang, in Europe (Cezus, France), in Russia, China and Ukraine. Additional, nuclear-related material is no doubt produced clandestinely. World output of hafnium compounds in 2003 was similar to 2002 but the higher cost of the zircon feedstock will lead to increased pricing.

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Table 1: Zircon sand/flour/opacifier prices

Shipping Terms	Pricing	April 2003	June 2004
Sand			
fob Australia	US$/t bulk	365 – 410	420-550
fob South Africa	US$/t bulk	360 – 410	410-550
fob US	US$/t bulk	350 – 410	400-530
Flour (95% below 45 micron)			
fob Europe	US$/t bagged	510 – 540	800-940
fob Asia	US$/t bagged	450 – 550	800-950
Micronised (d_{50} 5 micron)			
fob Europe	US$/t bagged	600 – 630	900-1050
fob Asia	US$/t bagged	610 – 660	900-1100

fob = free on board
The prices given are the most up to date at the time of writing

Table 2: Markets for baddeleyite / synthetic zirconia 2003

	baddeleyite (t)	synthetic zirconia (t)	Total (t)	Growth
Refractories	5,500	13,000	18,500	Increase
Ceramic pigments	500	13,000	13,500	Increase
Abrasives	1,000	2,500	3,500	Level
Electronics	0	3,000	3,000	Level
Oxygen sensors	0	850	850	Level
Glass/gemstones	0	650	650	Level
Advanced ceramics/catalyst	0	5,000	5,000	Increasing
Total	**7,000**	**38,000**	**45,000**	

Table 3: Prices for fused monoclinic ZrO_2/stabilised ZrO_2 and baddeleyite

	US$/t cif Main ports EC, US, Japan	
	2002	**June 2004**
Monoclinic zirconia		
* Refractory / Abrasive Grade	2,000 – 2,400	2,200 – 2,800
* Ceramic Pigment Grade	2,400 – 3,500	2,700 – 3,700
Structural / Electronic Grade	3,100 – 4,500	3,300 – 4,800
High Purity Advanced Ceramic Grade	15,000 – 25,000	15,000 – 25,000
Stabilised zirconia		
Refractory Grade	3,000 – 4,200	3,400 – 4,200
High Purity Advanced Ceramic Grade	20,000 – 70,000	25,000 – 75,000

* baddeleyite price levels in the lower half
The prices given are the most up to date at the time of writing

Table 4: Major zirconium (Zr) and hafnium (Hf) chemical production and application

Product	Abbre-viation	Formula	World Capacity (t)	Application
Zr silicate		$ZrO_2.SiO_2$	1,100,000	Opacifier in ceramic tiles, sanitary ware and table ware. Steel/glass refractories. Foundry/investment casting. TV/computer glass. Production of Zr chemicals/oxides. Manufacture of Zr/Hf metal/ chemicals
Zr oxychloride	ZOC	$ZrOCl_2.8H_2O$	60,000	Manufacture of other Zr chemicals Titania coating. Antiperspirant Oil field acidising agent
Zr sulphate	ZOS	$Zr(SO_4)_2.4H_2O$	10,000	Manufacture of other Zr chemicals Titania coating Leather tanning reagent
Zr basic sulphate	ZBS	$Zr_5O_8(SO_4)_2$ x H_2O	25,000	Manufacture of other Zr chemicals Titania coating Leather tanning reagent
Zr basic carbonate	ZBC or BZC	$ZrOCO_3$ x H_2O	20,000	Manufacture of other Zr chemicals Paint driers (siccatives) Antiperspirant Catalyst
Ammonium Zr carbonate	AZC	$(NH_4)_3ZrOH(CO_3)_32H_2O$	15,000	Paper coating (insolubiliser) Fungicidal treatment of textiles
Zr acetate	ZAC	$H_2ZrO_2(C_2H_3O_2)_2$	2,000	Manufacture of other Zr chemicals Water repellent in textiles/paper Catalyst production
Potassium hexafluorozirc-onate	KFZ	K_2ZrF_6	1,000	Grain refiner - Mg/Al alloys Flame proofing of textiles
Zr oxide		ZrO_2	45,000	Refractories. Ceramic colours Abrasives. Electronics Oxygen sensors. Glass/gemstones. Catalyst Advanced ceramics. See Fig 2&5
Zr metal		Zr	10,000	Chemical processing plant Nuclear fuel rod/core components Explosives. Alloys.Pyrotechnics. Military

Hf metal		Hf	N/A	Aerospace alloys, nuclear refractories, control rods, cutting tips, sputtering agent, plasma coating, military
Hf dichloride		$HfCl_2$	N/A	Catalyst
Hf dibromide		$HfBr_2$	N/A	Special refractories
Hf oxide		HfO_2	N/A	Optical coatings, electronics
Hf carbide		HfC	N/A	Nuclear control rods
Hf nitride		HfN	N/A	Cutting tools, coatings

N/A = information Not Available

Table 5: Applications for zirconia in advanced ceramics

A. Utilising ZrO_2's superb mechanical properties

Use	Application
Structural ceramics	Various components, pumps, bearings, seals, valves, optical fibre connectors.
Bioceramics	Hip replacement joints, dental ceramics.
Low wear ceramics	Grinding medias, engine components, textile thread guides, printer heads.
Forming dies	Extrusion of copper / wire.
Metal filtration	Removal of impurities during casting.
Cutting applications	Blades, scissors, cutting tools.
Coatings	Plasma spray.
Gemstones	Zirconia single crystal in various colours.
Glass	Lenses, glass fibre, laboratory equipment.
Jewellery/Watches	Scratch resistant bracelets/faces.

B. Utilising ZrO_2's interesting electrical properties

Use	Application
Fuel Cells	ZrO_2 is used in solid oxide fuel cells as the electrolyte.
Oxygen sensors	Oxygen concentrations affect yttria stabilised ZrO_2 conductivity and this property can be used to control emissions in auto engines, furnaces and gas boilers.
H_2 from water electrolysis	This is the reverse of the fuel cell.
MHD electrodes	Magneto-hydrodynamic generators for current generation where zirconium electrodes are used
Filters, transducers, resonators, other PZT uses	Use in mobile phone filters, acceleration and underwater detection sensors. Production of buzzers for clocks, timers, automobiles etc. Ultrasonic motors (utilising sound rather than electrical power).
Catalysts	For industrial and automobile exhaust applications using ceria-doped ZrO_2.