

ZIRCONIUM AND HAFNIUM

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The minerals zircon sand (zirconium silicate, $\text{ZrO}_2 \cdot \text{SiO}_2$) and baddeleyite (ZrO_2) are the starting point for the preparation of all zirconium and hafnium compounds, including the metal, oxides and salts. With the fall in baddeleyite output in 2001, zircon sand is now the primary source. Zirconium and hafnium are not rare elements and occur in 0.028% of the Earth's crust, mostly associated with titanium and iron. Hafnium is present in all zirconium compounds (around 1.5 – 3.0%) and is removed for zirconium nuclear applications.

Zircon sand

Demand for zircon sand continued to outstrip production throughout 2002, and China's insatiable consumption seems set to cause further price increases as output falls further behind market requirements.

Zircon sand is found in most parts of the world and is the most abundant zirconium mineral. Zircon is mainly recovered from heavy mineral sands (predominantly beach sands) where titanium minerals – generally rutile and ilmenite – are separated out. Additional production also comes from rare earth processing. Total world reserves of zircon are estimated at over 100 Mt. Major producers remain Australia, South Africa and the US.

Zircon recovery from beach sands is achieved by dredging and/or dry mixing operations – with the actual technique dependent on orebody location and chemical make-up. Zircon is often further processed by abrasion, acid attack, or heat (calcination). The result is zircon sand with a range of chemical and physical properties. It is these properties that determine its end use.

A large proportion of zircon sand is used in its mined form; in abrasives, foundries, refractories (steel and glass), TV tubes and for zirconium oxide/chemical production. Zircon is also milled to finer particle sizes such as in zircon flours (generally <200 or <300 mesh), or in even smaller sizes (5 micron and below) as opacifier grades. These products are used predominantly in ceramic frits (special glasses), where they impart a white opaque colour in the final ceramic glaze due to light reflection. Such frits are used in large quantities in tile, table and sanitary-ware glaze production. These applications require careful control of colour, particularly that imparted by transition metal ions such as Fe and Ti. Consequently, the higher-quality grades (known as ceramic or premium grades) are used with low impurities – maximum 0.10% TiO_2 and 0.05% Fe_2O_3 . Zircon with higher levels of these impurities is used in refractory and foundry applications.

Output of zircon in 2002 totalled around 1,100,000 t (2001: 1,020,000 t). Shipments from Australia increased to approximately 420,000 t (2001: 398,000 t) and South Africa equalled this amount (2001: 340,000 t). In the US,

output continued to fall, to approximately 130,000t (2001: 180,000t). Other producers include Ukraine, India, Vietnam, Brazil, Malaysia, China and Russia, contributing around 130,000 t.

Titanium output remains the key to zircon supply since titanium ore and zircon are inextricably linked. With titanium ores in oversupply, there has been little incentive to crank up output, even though this would produce more zircon. Consequently, zircon will remain in short supply for at least 2 – 4 years, until major new projects come on stream.

The largest world producer is Iluka Resources Ltd, with operations in Australia and the US, and production/sales of approximately 360,000 t (an increase over 2001). Production in Western Australia should increase as the new South Tails mine is developed. Iluka is also active in the Murray Basin in southeast Australia, which is predicted to become the focus of future mineral sands activity. Production at Iluka's Douglas project is set for late 2004. The company's US plants in Old Hickory Virginia and Green Cove Springs Florida, both saw lower tonnages owing to a variety of factors: weather – both water shortages and flooding; changing mine plans; and general market conditions. In the next year or so, Iluka expects to increase output in order to meet sales demand.

In South Africa, Richards Bay Minerals (RBM), owned by Rio Tinto plc and BHP Billiton plc, is the world's second-largest producer and increased output to around 270,000 t in 2002. Namakwa Sands lies in third place, with operations in the Western Cape. It is owned by Anglo American plc and last year it reaped the benefits of earlier expansion and produced 100,000 t. Tigor South Africa (Kumba Resources 60%, Tigor 40%) is located close to Richards Bay in Kwa Zulu-Natal Province, and produced 55,000 t of zircon in 2002.

Other key players include the Ti-West joint venture, a 50/50 JV between Kerr McGee and Tigor Resources Pty Ltd, with a mine at Cooljarloo in Western Australia. It produced around 80,000 t in 2002, with a similar output predicted for 2003. RZM/Cable Sands (WA) Pty Ltd, owned by Nissho Iwai Corp. of Japan, also has a Murray Basin project, currently producing around 10,000 t/y. This is predicted to grow to 30,000 t/y. In the US, Du Pont's Florida plant maintained output, thought to be around 60,000 – 70,000 t/y.

Indian Rare Earths, with plants in Kerala and Orissa, India, produced around 20,000 t, with expansion planned. China also produced a similar quantity of zircon, mainly from Hainan Island, and both Indian and Chinese outputs were used domestically.

Zircon markets all showed growth in 2002, with a total demand of around 1.1 Mt, similar to world output. Ceramics (mainly tile and sanitary-ware) grew rapidly in China, pushing world demand for these applications closer to 600,000 t, much of this fuelled by housing development. Usage in grés porcelenato tile bodies in Europe gained momentum, and this application uses more zircon than a conventional glaze, so could push zircon demand even higher.

Refractory markets also showed some growth, and now consume around 170,000 t/y. All refractory users in steel and glass have been looking to increase the lifetime of the product, and this requires careful selection of zircon, thereby adding more strain on the producers.

Foundry uses for zircon in investment casting (a method of precision-casting of metals using moulds made from zircon) also moved up, to around 170,000 t, possibly due to increased usage in sports goods (golf clubs) and precision-engineering parts – again mainly in China. Consumption in television and computer monitor screens, where zircon blocks X-ray emissions, also rose, to around 90,000 t, with most production in the Far East.

Production of ZrO_2 and Zr chemicals absorbed a further 90,000 – 100,000 t of zircon, particularly of higher-grade product (to avoid the inclusion of impurities such as Fe and Ti).

Overall the tightening of supplies throughout 2002, coupled with stronger demand, has led to price increases despite strong resistance by customers. Prices are shown in Figure 1.

The outlook is for increased demand and for a continuing shortfall of supply. New developments, such as Australia's Murray Basin and the Corridor Sands Project (CSP) in Mozambique, are critical to the continuing growth in zircon output and the narrowing of the supply/demand gap in years to come.

Baddeleyite

2002 has seen significant changes in the traditional markets for baddeleyite, with several synthetic zirconia producers scrambling to win the market share left open by the cessation of South African-supplied baddeleyite during 2001.

Since the 1970s, baddeleyite output had been dominated by two operators based in Phalaborwa South Africa. Palabora Mining Co. (PMC), a Rio Tinto subsidiary, recovered the mineral as a by-product of its open-pit copper mine. This operation produced a varied product mix including magnetite and precious metal slimes. With a continuing fall in ZrO_2 grade from PMC's open pit due to geology and geometry, baddeleyite output was halted in 2001 as the mine moved to an underground operation. In May 2001, PMC decided to close its zirconium sulphate plant, and soon after this a strike led to full closure of the zirconium plant. This brought to an end PMC's position as market leader in zirconium ore and sulphate after some 30 years. At the peak of production, PMC shipped around 13,000 t/y of oxide and 3,000 t/y of sulphate. Replacement products to these are now predominantly covered by Chinese, French and Australian production (see later). PMC's only remaining part of its zirconium activity is a state-of-the-art zirconium basic sulphate (ZBS) plant (also see under Chemical section).

PMC's main rival in baddeleyite output was South Africa's state-owned Foskor Ltd. With Foskor's baddeleyite output declining in the early 1990s, it purchased a synthetic zirconia plant from Japan. This activity has now grown

to include fused monoclinic and stabilised zirconias, with annual output totalling well over 5,000 t. Foskor's main sales are in the refractory and ceramic pigment markets.

The world's only remaining source of baddeleyite is in the southwest part of the Kola Peninsula in Russia, just 20 km from the border with Finland. This remotely- situated mine, operated by AO Kovdorsky Gok (Kovdor) and owned by the huge MDM Chemical Group based in Moscow, recovers iron ore, apatite and baddeleyite from a complex orebody. Annual production of baddeleyite now exceeds 6,500 t and Kovdor is trying to maximise both output and revenue. Various investigations to add value have been studied, including the production of higher-grade and downstream products. Kovdor's main sales are to the abrasive and refractory markets, particularly in Japan. The mine has very considerable feedstock, both from the open pit and stockpiled tailings.

Kovdor's link with Nako Narvik AS (previously Nako AS) in Norway continues, and fresh studies by Scatec AS and others have been undertaken in a bid to restart the plant which is located in a fjord. Much depends on the price of the raw baddeleyite and on the pricing of the end products (fused monoclinic/stabilised zirconia).

Radioactivity issues concerning baddeleyite abated last year as PMC's output fell and customers were short of product. Synthetic zirconias can also have significant uranium and thorium content, depending on the zircon source and processing, so these concerns will continue. Replacement of baddeleyite with synthetic product in all markets has been difficult since the natural form reacts differently to the man-made product.

Figure 3 summarises the markets for baddeleyite and replacement fused monoclinic zirconias.

Production of steel refractories using baddeleyite/synthetic zirconia remained at a similar level to 2001, despite a 6.5% rise in world steel demand, although new plants were established in cheaper areas to offset closures in high labour/land cost areas. Similar events took place in the glass and refractories sectors.

The manufacture of ceramic and plastic colour pigments increased in 2002, with particularly strong demand in Far Eastern markets to support increased tile output. Reformulation of specific grades, away from baddeleyite raw material, required considerable effort and this has led in some cases to a complete review of all colour-making raw materials. Electronic markets in filters, buzzers and related lead zirconate titanate (PZT) applications grew, whereas use in glass and synthetic gemstones peaked and started to decline.

The latter markets are also strongly linked to fashion trends. The use of zirconia in advanced ceramic areas showed both decline and growth, depending on the application; with some precision-components sales falling

(eg optical fibre connectors) and use in industrial and autocatalyst systems rising.

Prices for baddeleyite and fused monoclinic zirconias generally saw some weakening from 2001, but there were gains and losses, depending on grade availability and competition. The question for the coming year is whether increased price and lower availability of zircon sand will translate into higher oxide prices. Production volumes have increased, but much of this has been absorbed by the loss of PMC's baddeleyite (approximately 6,000-8,000 t/y) in the market place.

Zirconium metal, oxide and chemicals

Demand for all zirconium products continued to increase in 2002 and this led to further new manufacturing capacity. Established markets were buoyant, though some geographical movement occurred where customers moved their manufacturing output to lower cost areas – particularly in China/Far East. Applications for these versatile materials continued to diversify, particularly in fuel cell, catalyst, surface coatings and healthcare applications.

Key markets for zirconium metal and oxide are shown in Figure 3. Zirconium (and hafnium) chemicals production and applications are shown in Figure 4. Zirconium metal is an important refractory material, and is made in alloyed and unalloyed forms. It is zirconium metal's outstanding resistance to high temperatures and to chemical attack that leads to the majority of its use in difficult engineering applications such as chemical reactors and hot, corrosive environments. Hafnium's ability to capture neutrons means that hafnium has to be removed where the zirconium metal is used in nuclear applications, eg, nuclear fuel rod claddings, reactor cores, and associated engineering. With fewer new reactors being built, most of the demand for hafnium lies in replacement units.

Although zirconium oxide is available in natural form as the mineral baddeleyite, it is also made synthetically by removing silica from zircon sand (zirconium silicate) using a variety of techniques including thermal and chemical dissociation. The synthetic forms include fused monoclinic and fused stabilised grades; the latter have a cubic oxide such as CaO, MgO, or Y₂O₃ added to prevent catastrophic volume changes on heating/cooling. High-purity stabilised grades, with full or partial stabilisation (PSZ) are made chemically and are used in a wide range of applications (see Figure 5).

Zirconium chemical markets continue to expand in catalyst, paint drier (siccative), paper and healthcare products. Major items were 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 remains the main producer of zirconium chemicals, with much smaller output found in India, South Africa, the UK and the US.

The largest tonnage produced is ZOC, with Chinese output now over 50,000 t/y. ZOC forms the starting point for downstream species such as ZBS and

ZBC, and is also used to make zirconium oxide by calcination. Higher-purity oxide and other chemicals are made from ZBS/ZBC. In pigment (TiO_2) coating, ZOC continued to replace ZOS/ZST due to its lower cost and higher solubility, though the choice is dependant on the particular manufacturing process and type of scrubber used in the acid treatment system.

The use of zirconium acid sulphate (ZOS/ZST) in leather tanning remained static because of ongoing poor markets. This application was expected to show some growth, however, following the recovery from the foot-and-mouth disease outbreak in the UK.

PMC's ZBS output from its plant at Phalaborwa, South Africa slowly resumed operations after a fire in early 2002, with the majority of its shipments going to the Far East. RBM, a sister company to PMC, supplies the feed zircon sand. Also in South Africa, Geratech Zirconium Beneficiation Ltd, founded in 1992, and closely associated with AEC, produces ZST/ZOS and other compounds. Sepr France (part of the Saint Gobain Group, which includes Norton USA) continued to expand. A significant portion of the market covered by PMC's zirconium ore Grade 5, which ceased production in 2001, has been covered by synthetic oxide made in Le Pontet, France. Sepr's joint venture in Shanghai continued to make ZOC and ZBC, with Western sales co-ordinated from France.

Some of PMC's zirconium ore Grade 5 market has also been won by Sepr's Australian associate, Fused Materials Pty Ltd (AFM) based in Rockingham, Western Australia. AFM has concentrated on glass and steel refractories, and also ceramic pigment markets, particularly in the Far East. Disagreements between AFM shareholders hindered further expansion and this has led to changes in the Chinese market.

Shenyang Astron Mining Industry Ltd (Yingkou Astron Chemicals Co. Ltd), with headquarters in Shenyang, pressed ahead with further expansion of its zirconium chemicals, fused and stabilised zirconium oxide, and other products, and is now one of the largest producers. Although based in Shenyang, Astron is an Australian public-listed company. Zirconium oxide production based on two furnaces began in 2001 when Astron ceased to be AFM's agent in China. A third furnace was added in 2002, and additional chemical plant was added, lifting annual capacities to 7,000 t (fused monoclinic/stabilised zirconium oxide) and over 15,000 t (advanced zirconium chemicals).

A close working relationship was developed between MinChem Ltd of the UK and Astron, initially to replace products made by the PMC plant which closed in 2001. MinChem now represents Astron in significant markets outside China for many zirconium products. Astron is also a major importer of zircon sand (around 45,000 t/y) and this is used for chemical production, for sale into refractory/ opacifier markets, and for milling in its Zibo and Bayuquan plants (3,000 t/y and 9,000 t/y capacities respectively). ZOC is produced by Jiaozou Astron Wangfeng Chemical Ltd, in which Astron holds a 49% interest. Astron also purchased the UK-based Merck single crystal plant in 1998 and moved

its production to China. This operation now makes high-purity zirconium (and other oxides/chemicals for optical/electrical coatings such as spectacle lenses). Further growth for Astron is predicted.

Another major Chinese producer, Yixing Xinxing Zirconium Co. Ltd (associated companies Asia Zirconium Ltd and Jiangsu Xinxing Zirconium Group Corp.), continued to reduce prices to maintain market share.

During 2002, Canadian-based rare-earth producer AMR invested US\$15 million in new product capacity at its plant in China, to include zirconium chemicals and oxide for the catalyst, fuel cell and electronics markets. Japanese production of high purity oxides and chemicals faced tougher market conditions and, as output declined, prices fell. Daiichi Kigenso Kagaku Kogyo Co. Ltd (DKK), based in Osaka, further developed its catalyst, fuel cell, and advanced ceramic grades of monoclinic and PSZ. Tosoh Corp. and Sumitomo Osaka Cement Co. Ltd (SOC) also found sales conditions more difficult, and accumulated large stockpiles of advanced ceramic components such as optical fibre connectors.

In the US, CMS Energy Corp. sold its Canyon City Colorado plant to the operator, Cotter Corp. and feasibility studies continue. Southern Ionics Inc. remained strong in the chemical/catalyst markets, and the introduction of a viable home dialysis unit for kidney patients (which utilises a zirconium resin) neared completion. This system will bring a major improvement in the lifestyle of kidney patients. Eka (part of Akzo Group and formerly Hopton Technical) majored in AZC sales and Wah Chang Albany (part of Allegheny Technologies) recovered from its 2001 strike; MEI continued to refocus on advanced-technology markets.

In the UK, MEI's sister company MEL continued to move away from zirconium 'commodity' chemicals at low prices. UCM Group plc (formerly Universal Abrasives and including Unitec Ceramics Ltd), manufactures fused monoclinic and PSZ from zircon sand but decided to close its UK production facility and consolidate this at its expanded facilities at Universal America Inc. (UAI) in Tennessee, US. This transfer should be completed by mid-2003.

In India, Bhalla Chemical refocused grades and pressed ahead in chemicals. In Ukraine, Vilnohirsk State Mining and Metallurgical Plant (VSMMP) developed zirconium oxides alongside its zircon sand output.

Producers of oxides and chemicals all saw prices falling as supply tended to overtake demand. The strengthening price of zircon sand did not stem this fall. All manufacturers are now close to marginal profits and a more difficult zircon supply situation will require some changes in market share, sales prices and operating base, to survive the coming year.

Hafnium metal and chemicals

Hafnium is normally present at 1.5 – 3.0% weight percent of zirconium in zircon and baddeleyite, and is removed when zirconium is used for nuclear applications. All hafnium compounds derive from this extraction process. The

metal is used in alloyed and unalloyed forms such as plate, strip, sheet, foil, rod, wire and tube – similar to zirconium. It is also sold as the oxide and in reactive chemical forms. Hafnium's strong ability to absorb neutrons led to its use as control rods in nuclear reactors, these being raised or lowered to increase or decrease reactor output. It is also used in various aerospace, medical and special products.

Hafnium is produced in the US (Westinghouse Electric Co, Wah Chang Albany), in Europe (Cezus France), in China, and the Ukraine (VSMMP). It is likely that the Iraq war led to increased military requirements during 2002. However it is thought that world output and pricing remained similar to 2001.

Figure 1: Zircon sand/flour/opacifier prices

Shipping terms	Pricing	April 2001	April 2002
Sand			
fob Australia	US\$/t bulk	330 – 390	365 – 410
fob South Africa	US\$/t bulk	350 – 400	360 – 410
fob US	US\$/t bulk	350 – 400	350 – 410
Flour (95% below 45 micron)			
fob Europe	US\$/t bagged	470 – 530	510 – 540
fob Asia	US\$/t bagged	510 – 550	450 – 550
Micronised (d₅₀ 5 micron)			
fob Europe	US\$/t bagged	540 – 580	600 – 630
fob Asia	US\$/t bagged	580 – 610	610 – 660

fob = Free on Board

Figure 2: Prices for fused monoclinic ZrO₂ /baddeleyite

US\$/t cif main ports EC, US, Japan		
	2001	2002
Monoclinic zirconia		
*Refractory / Abrasive Grade	2,400 – 2,800	2,000 – 2,400
*Ceramic Pigment Grade	2,700 – 3,200	2,400 – 3,500
Structural / Electronic Grade	3,200 – 4,700	3,100 – 4,500
High Purity Advanced Ceramic Grade	17,000 – 25,000	15,000 – 25,000
Stabilised zirconia		
Refractory Grade	3,700 – 4,200	3,000 – 4,200
High Purity Advanced Ceramic Grade	30,000 – 75,000	20,000 – 70,000

* Baddeleyite price levels in the lower half

Figure 3: Markets for baddeleyite/synthetic zirconia 2001

	baddeleyite (t)	synthetic zirconia (t)	Total (t)	Growth
Refractories	5,500	11,500	17,000	Level
Ceramic pigments	-	11,000	11,000	Increasing
Abrasives	1,000	2,500	3,500	Level
Electronics	0	3,000	3,000	Increasing
Oxygen sensors	0	850	850	Level
Glass/gemstones	0	650	650	Decreasing
Advanced ceramics/catalyst	0	4,000	4,000	Increasing
Total	6,500	33,500	40,000	

Figure 4: Major zirconium (Zr) and hafnium (Hf) chemical production and applications

Product	Abbreviation	Formula	Capacity (t/y)	Applications
Zr metal	Zr	Zr	10,000	Chemical processing plant, nuclear fuel rod/core components, explosives, alloys, pyrotechnics, military.
Zr Oxychloride	ZOC	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$	60,000	Manufacture of other Zr chemicals, titania coating, antiperspirant, oil field acidising agent.
Zr Sulphate	Acid/ZST Ortho-sulphate	$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	10,000	Manufacture of other Zr chemicals, titania coating, leather tanning reagent.
Zr Basic Sulphate	ZBS	$\text{Zr}_5\text{O}_8(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$	20,000	Manufacture of other Zr chemicals, titania coating, leather tanning reagent.
Zr Basic Carbonate	ZBC or BZC	$\text{ZrOCO}_3 \cdot x\text{H}_2\text{O}$	20,000	Manufacture of other Zr chemicals, paint driers (siccatives), antiperspirant.
Ammonium Zr Carbonate	AZC	$(\text{NH}_4)_3\text{ZrOH}(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$	15,000	Paper coating (insolubliser), fungicidal treatment of textiles.
Zr Acetate	ZAC	$\text{H}_2\text{ZrO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$	3,500	Manufacture of other Zr chemicals, water repellant in textiles / paper, catalyst production.
Zr Tetrachloride		ZrCl_4	NA	Production of Zr metal, Zr chemicals, catalyst.

Figure 4 continued

Potassium Hexafluoro zirconate	KFZ	K_2ZrF_6	1,000	Grain refiner (Mg/Al alloys), flame proofing of textiles.
Zircon ^(a) (Zr silicate)		$ZrO_2 \cdot SiO_2$	1,100,000	Foundry sand, refractories, opacifiers, manufacture of Zr/Hf metals & chemicals.
Hf Metal		Hf	NA	Aerospace alloys, nuclear reactor control rods, cutting tips, sputtering agent, plasma coatings, military.
Hf Dichloride		$HfCl_2$	NA	Catalyst.
Hf Dibromide		$HfBr_2$	NA	Special refractories.
Hf Oxide		HfO_2	NA	Optical coatings, electronics.
Hf Carbide		HfC	NA	Nuclear control rods.
Hf Nitride		HfN	NA	Cutting tools, coatings.

NA = information Not AvailableNote^(a): Zircon is generally considered a mineral, not a processed chemical, but is included in this table for comparison purposes.

Figure 5: Applications for stabilised zirconia (particularly PSZ)**A. Utilizing ZrO₂'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. Utilizing ZrO₂'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 (utilizing sound rather than electrical power).
Catalysts	For industrial and automobile exhaust applications using ceria-doped ZrO ₂ .

Writer's data compared with published information from TZ Minerals Sands Report 2003, and *Industrial Minerals*, May 2003.