ZIRCONIUM AND HAFNIUM

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All zirconium and hafnium, their oxides and salts, are derived from the minerals zircon sand (zirconium silicate $ZrO_2.SiO_2$) or baddeleyite (ZrO_2). It is often thought that zirconium and hafnium are rare elements, but they occur in 0.028% of the Earth's crust, being more plentiful than copper. All zirconium compounds contain 1.5 - 3.0% of hafnium unless separated for nuclear applications. Interest in these materials has increased over the past decade as they offer very diverse properties and are considered environmentally safe.

Zircon Sand (zirconium silicate)
Zircon sand showed an increase in output in 2001 over the previous year, with demand also increasing so that supply and demand were approximately in balance. Prices continued to strengthen throughout 2001, but started to fall in the first quarter of 2002.

Zircon sand is the most abundant naturally-occurring zirconium mineral, with deposits in many countries. Processing of zircon is always connected with the recovery of titanium bearing ores - generally rutile and ilmenite. Total known world resources of zircon ore are estimated to exceed 55 Mt, but it is thought that there could be at least as much again present in unknown/unworked deposits. Major producers remain Australia, South Africa and the US. Zircon is mined from heavy mineral sands (predominantly beach sands) by either dredging or the dry mixing technique, depending on the location and type of deposit. Further processing involves mechanical abrasion or acid/base chemical reaction together with heating in a calciner. This produces zircon sand with varying physical and chemical properties. The actual grading of the product is made on the basis of chemical purity and end-use application.

Zircon sand is used in its mined form and also milled into finer particle size grades. Sand is used in abrasive, foundry, refractory (glass and steel), zirconium chemical and television tube manufacture. In its finer particle size form, as a ground product such as a 95% below 45 micron sizing, it is used in these markets and also in large volumes in ceramic frits (special glasses) where it produces a white opaque colour in the final ceramic glaze due to light reflection. In the finest particle sizes (typically averaging 5 micron and below) it is consumed in large quantities as the major opacifier additive in tile, table and sanitaryware glazes.

In such applications where colour is critical, the requirement is for a ceramic-or premium-grade quality with low transition metal impurities - max. 0.10% TiO_2, 0.05% Fe_2O_3. Where impurity levels are higher, typically 0.25% TiO_2 and 0.15% Fe_2O_3 zircon is used in refractory and foundry markets. Older terms to describe grading such as prime, intermediate and coarse grades are still found.

Zircon sand production in 2001 totalled around 1.02 Mt, some 50,000 t over 1999 output of 970,000 t (5% increase). Australian output increased to 398,000 t (17,000 t more than 2000 output) despite fears that it would decline. South African shipments were approximately 340,000 t (figures for year 2000 range from 317,000 t to 355,000 t depending on the source of information). In the US, output fell marginally to around 180,000 t, (some 5,000 t - 10,000 t less than 2000). Production elsewhere increased from 80,000 - 90,000 t in 2000, to over 100,000 t with output from Ukraine, India, Vietnam, Brazil, Malaysia, China and Russia.

A number of factors is contributing to these changes. Australian output is predicted to fall owing to a drop in production at Cable Sands, Iluka Resources Ltd, Tiwest and CRL. Iluka has recently gained a 50% shareholding in

CRL and has ambitious plans for its Murray Basin mineral sands project. Southern Titanium's Mindarie mineral sands testwork has exceeded expectations.

Ticor South Africa (formerly Iscor Heavy Minerals) based in Kwa Zulu-Natal Province near Richards Bay, has made rapid progress and trial shipments of some 17,000 t have been made. In the US, Iluka is investing US$23 million to increase zircon (and rutile) production capacity at its Old Hickory operation in Virginia. Titanium Corp Inc. is also working deposits from Maitland at its Halifax Nova Scotia pilot plant.

In the markets, demand increased in 2001 to approximately 1.02 Mt, close to the world output. Ceramic applications in tile, table and sanitaryware moved up to consume around 500,000 t, notably through growth in China. Applications in grés porcelenato tile bodies did not grow as predicted, particularly in Spain. Sand, flour and opacifier prices rose to reflect tighter supplies. Further increases in ceramic demand are predicted.

Zircon Sand/Flour/Opacifier Prices 2001

Shipping Terms	April 2001	April 2002
Sand US$/t bulk		
fob Australia	330 - 360	330 - 390
fob South Africa	350 - 390	350 - 400
fob US	350 - 390	350 - 400
Flour (95% below 45 micron) US$/t bagged		
fob Europe	440 - 460	470 - 530
fob Asia	450 - 470	510 - 550
Micronised (d50 5 micron) US$/t bagged		
fob Europe	560 - 580	540 - 580
fob Asia	610 - 620	580 - 610

Fob: Free on Board

Foundry applications declined marginally to around 168,000 t and are forecast to remain at this level for the near future. Zircon usage in investment casting lies in equal second position with refractories, after ceramics. With a slowdown in steel output, demand for refractories remained fairly steady and consumed some 160,000 t. This demand is also forecast to remain fairly level over the next one to two years.

In special glass applications, eg television and computer monitor screens where zircon is incorporated to screen X-rays, usage grew slightly to over 80,000 t and further increases are predicted to over 85,000 t.

Growth in the production of synthetic ZrO_2 and Zr chemicals led to stronger demand of around 90,000 t. A 5 - 10% increase is likely in 2003. Other market consumptions remained steady at around 20,000 t. Predictions for 2002/03 suggest that the supply/demand balance will remain tight with little surplus material.

Baddeleyite (zirconium oxide/ore)

2001 was a dramatic year in the history of baddeleyite output, with South Africa halting output, thereby bringing to an end its 35-year dominance in the supply of this material. As a result, world output fell significantly, putting pressure on the only other baddeleyite producer, based in Russia, and on alternative synthetic zirconias. The markets reacted strongly to these changes. With global steel output only 1% lower than in 2000, the demand for refractories remained strong and the loss of baddeleyite as a raw material caused significant problems. Similarly, in ceramic colours, substitution of baddeleyite by synthetic zirconias has not been an easy task, since each zirconia produces a different shade of product.

To counteract the loss of baddeleyite feed, significant new capacity in synthetic zirconia plants fed by zircon sand were installed in Australia, China, South Africa and the US. Production of synthetic zirconia also commenced from a mixed zircon/baddeleyite mineral in the US.

Baddeleyite with ZrO_2 + HfO_2 typically 99% has been mined in commercial quantities in the Northern Province of South Africa and in the Kola Peninsula in the northwestern part of Russia on the border with Finland.

In Phalaborwa, South Africa, two operators have been involved in baddeleyite extraction: Palabora Mining Co. (PMC), with largest shareholder Rio Tinto based in London, has recovered the mineral as a by-product of its open-pit copper mine since 1972; and Foskor Ltd, a wholly-owned subsidiary of the state-owned Industrial Development Corp. (IDC), started production of the mineral from phosphate rock feedstock derived from Foskor's own mine and from PMC's open pit where Foskor owns the phosphate mining rights. PMC has been the world's largest producer of baddeleyite but as the open pit became deeper, the 80,000 t/d ore body produced less baddeleyite as a proportion of the product mix of copper, magnetite and precious metal slimes. With copper removed by flotation, the resultant heavy metal stream was beneficiated by gravity separation, then fed to a magnetic separation/acid leaching plant. This produced a refractory and ceramic pigment grade of zirconium ore. Some of this feed was further converted to zirconium (ortho) sulphate (Grade 4) by reaction with sulphuric acid coming from the copper smelting operation.

With a continuing fall in ZrO_2 grade from PMC's open pit due to geology and geometry, it was expected that baddeleyite recovery would cease. This was predicted to take place when the mine moved over to feed from its underground project, which was set to commence in 2002. In May 2001, PMC decided to close its Grade 4 zirconium sulphate plant in order to conserve baddeleyite feedstock. Soon afterwards, PMC workers went on strike and this led to a supposed temporary shut down of the baddeleyite plant. In July 2001, PMC management decided not to reopen this plant and so brought an end to baddeleyite production at PMC after nearly 30 years. Shipments continued to be made from finished stockpiles until the fourth quarter of 2002. With no synthetic zirconia plant following on, this meant that PMC would exit from zirconium ore markets after being market leader for most of its history.

In contrast, Foskor has been building up its synthetic output in recent years, initially installed in the early 1990s to offset a rapidly diminishing baddeleyite output. Like PMC, this decline was due to a lower ZrO_2 grade in the phosphate feedstock. In 2002, Foskor lifted synthetic zirconia output to 4,500 t - 5,000 t with the addition of a new furnace. Continuing demand has since led to further investment and additional plant. Sales of fused monoclinic and stabilised zirconia have balanced output, though the development of the synthetic pigment grade has been slower due to competition and insufficient capacity. The latest expansion may address this point somewhat.

The only remaining baddeleyite producer in the southwest part of the Kola Peninsula, some 20 km from the Finnish-Russian border, A.O.Kovdorsky GOK (Kovdor) recovers iron ore, apatite and baddeleyite from a complex orebody. Production of baddeleyite started in 1975 and has grown to counter the depleting reserves in South Africa. Kovdor is now the only commercial source of baddeleyite and this has led Kovdor management to rethink its strategy in recent months.

Investment over the past few years has led to quantity and quality improvements, and annual output has been lifted to over 6,500 t, with most being sold to abrasive and refractory markets, particularly in Japan. The emphasis has been to increase output whilst reducing impurities with various techniques including acid leaching. The mine has considerable feedstocks, both from the open pit and from stockpiled tailings accumulated over the past 20-years.

Kovdor has been considering collaboration with companies already involved in the zirconia field in Norway, UK, Japan and South Africa in order to maximise its position. Agreements have been reached with Nako Narvik AS, (previously Nako AS), Scatec AS (an advanced technology group) to restart the Narvik operation. At the end of 2001, Foskor also concluded an arrangement to market Kovdor baddeleyite alongside it own fused zirconia products in the Middle/Far East and South American markets.

2001 saw the entry of new players in the fused zirconia field, together with several plant expansions at existing suppliers.

In China, Shenyang Astron Mining Industry Ltd, Shenyang, installed a 4,000 t/y fused monoclinic zirconia furnace to make refractory/ceramic colour grades to replace baddeleyite. These grades are being marketed by MinChem Ltd UK, as alternatives to PMC baddeleyite Grades 1 and 5, alongside the sale of zirconium chemicals also made by Astron at its new Yingkou, Dalian plant. Astron has already announced further expansions at Yingkou, which will lift fused monoclinic output to 7,000 t/y.

In Australia, Sepr redeveloped its Pinkenba, Queensland site from the manufacture of cruciform/wear resistant materials to 2,500 t/y of fused zirconia and, in France, began sales of Chinese-produced zirconia.

UCM plc/Universal America Inc. (UAI) is increasing capacity at its Greenville, Tennessee, US operation from 4,000 t/y to 14,000 t/y at a reported cost of US$5.2 million. Part of this new production, scheduled for mid 2002, will be used to produce stabilised zirconia for the North American market. This will avoid the need to ship intermediate grades to the UK for finishing before their final delivery in the US.

Also in the US, Washington Mills further developed its range of fused monoclinic/ stabilised zirconias, some of which are used to replace baddeleyite.

Daiichi Kigenso Kagaku Kogyo Co. Ltd (DKK) in Japan maintained output of its IDU fused stabilised zirconia plant, but because of PMC's closure it has been forced to look at substitute feedstocks. AFM, Australia sold all of its output and continued discussions on a new furnace.

One new name to emerge, in July 2001, was the Energy Corp. - CMS Energy, based in Michigan, US. CMS began processing Brazilian caldasite at a revamped uranium processing plant in Canon City, Colorado, US. Approximately 16,000 t of ore, originally purchased from Brazil in 1946 by the US Government as a uranium strategic stockpile, is planned to be split into uranium feedstock, monoclinic zirconia, and high-grade silica. The ore is a mixture of baddeleyite and zircon and contains around 0.25% uranium.

2001 had its share of technical issues on baddeleyite/replacement products and zircon sand, but radioactivity concerns were somewhat overshadowed by commercial events such as lack of supply and fears of price increases. Markets continued to change in 2001, as shown below. With world steel output approximately 1% down over 2000, demand for refractories should have softened though falls in the US, EC and Japan were offset by growth in Africa, Asia and China. This led to a similar demand to 2000. Abrasive markets remained steady but also had to find baddeleyite substitutes.

Prices for Fused Monoclinic ZrO_2 /Baddeleyite (US$/t cif Main Ports EC, US, Japan)

Grade	2000	2001
Monoclinic Zirconia		
Refractory / Abrasive*	2,300 - 2,600	2,400 - 2,800
Ceramic Pigment*	2,700 - 3,200	2,700 - 3,200
Structural / Electronic	3,200 - 4,500	3,200 - 4,700
Stabilised Zirconia		
Refractory	3,500 - 3,900	3,700 - 4,200

** Baddeleyite price levels in the lower half*

Ceramic pigment markets were strongly affected by the loss off baddeleyite from PMC since producing equivalent shades of colour from other zirconia sources is difficult.

Prices for fused monoclinic zirconia and baddeleyite remained similar to 2000, with some gains and losses depending on availability and competition. The increased capacity in zirconia feedstocks worldwide will possibly depress prices in the coming months as pressure mounts to win market share.

Zirconium Metal, Oxide and Chemicals

World output of all zirconium products continued to increase in 2001 and new producers of zirconium oxides and chemicals emerged. The range of applications for these versatile materials diversified even more, with zirconium derivatives replacing long-established products such as lead compounds that are now considered environmentally unfriendly. Key markets for zirconium metal, oxides and chemicals are shown below. Major zirconium (and hafnium) chemicals production and applications are shown on the next page.

Markets for Baddeleyite / Synthetic Zirconia 2001 (t)

	Baddeleyite	Synthetic Zirconia	Total	Growth
Refractories	9,000	8,000	17,000	Level
Ceramic pigments	2,000	7,000	9,000	Rising
Abrasives	1,000	2,500	3,500	Level
Electronics	0	2,500	2,500	Rising
Oxygen sensors	0	850	850	Level
Glass/gemstones	0	750	750	Level
Advanced ceramics/ catalyst	0	3,400	3,400	Rising
Total	**12,000**	**25,000**	**37,000**	

Zirconium metal is made in alloyed and unalloyed forms; for nuclear applications hafnium is removed. Zirconium metal's extreme resistance to temperature and corrosion allows it to be used in challenging engineering applications, such as chemical plant fabrication. Hafnium-free zirconium metal is used in nuclear fuel rod claddings and reactor cores, both for new units and replacement parts. Applications in non-nuclear fields continue to grow and now represent a higher percentage of total zirconium output.

Zirconium oxide in natural and synthetic forms is available in various chemical purities and particle size distributions. Synthetic forms include fused monoclinic and fused stabilised grades (stabilised with a cubic oxide such as CaO, MgO or Y_2O_3 to prevent catastrophic volume changes with temperature).

In 2001, zirconium chemicals continued to find increased uses in catalyst, paint drier (siccative) and personal hygiene products. Key players are zirconium acetate (ZAC), zirconium basic carbonate (ZBC), ammonium zirconium carbonate (AZC), zirconium oxychloride (ZOC), zirconium acid sulphate (ZOS/ZST) and basic sulphate (ZBS).

Most zirconium metal, oxides and chemicals are derived from zircon sand using a variety of techniques such as desilication by thermal or chemical means. The powerhouse of zirconium chemical production continued to be in China with several new plants and extensions being announced. Increased zircon sand costs and freight increases following the September 11 events did not translate into increased selling prices. The pressure to move increased tonnages, together with high inventories, led to falling prices.

The first and highest tonnage zirconium chemical made from zircon sand is ZOC. Chinese output is now approaching 50,000 t/y, though a considerable part of this is converted to other downstream species such as ZBS and ZBC. ZOC continues to replace ZOS/ZST

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.
Zr oxychloride	ZOC	$ZrOCl_2.8H_2O$	50,000	Manufacture of other Zr chemicals, titania coating, antiperspirant, oil field acidising agent.
Zr sulphate	Acid/ZST Orthosulphate	$Zr(SO_4)_2.4H_2O$	8,000	Manufacture of other Zr chemicals, titania coating, leather tanning reagent.
Zr basic sulphate	ZBS	$Zr_5O_8(SO_4)_2.xH_2O$	10,000	Manufacture of other Zr chemicals, titania coating, leather tanning reagent.
Zr basic carbonate	ZBC or BZC	$ZrOCO_3$.xH2O	20,000	Manufacture of other Zr chemicals, paint driers, siccatives, antiperspirant.
Ammonium Zr carbonate	AZC	$(NH_4)_3ZrOH(CO_3)_3.2H_2O$	10,000	Paper coating (insolubliser), fungicidal treatment of textiles.
Zr acetate	ZAC	$H_2ZrO_2(C_2H_3O_2)_2$	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.
Potassium hexafluoro zirconate	KFZ	K_2ZrF_6	1,000	Grain refiner (Mg/Al alloys), flame proofing of textiles.
Zircon[1] (Zr silicate)		$ZrO_2.SiO_2$	1,020,000	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.
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 Available

[1] Zircon is generally considered a mineral, not a chemical, but is included in this table for comparison purposes.

in pigment coating applications owing to its lower cost and higher solubility. Selection of ZOC or ZOS/ZST depends on a number of factors including plant design, manufacturing process and product finishing techniques.

As mentioned earlier, ZST (Grade 4) production ceased at PMC in May 2000 and market share has now been replaced by Chinese and other South African production. Applications in leather tanning continued to be depressed owing to the aftermath of the foot and mouth disease outbreak in the UK and general market decline.

PMC's ZBS remains the only zirconium chemical now made at Phalaborwa, South Africa, following the closure of the ZST (Grade 4) and baddeleyite plants. A new furnace has been installed to increase output/profitability, but full operation of this plant has been hindered by a serious fire in early 2002. The plant continues to use zircon sand from sister company Richards Bay Minerals.

Sepr (part of the Saint Gobain Group), based in France, started to sell ZBC and oxides from its Shanghai plant, with material being shipped to Le Pontet, France.

Shenyang Astron Mining Industry Ltd (Yingkou Astron Chemicals Co Ltd), based in Shenyang but actually an Australian public-listed company, significantly increased sales of zirconium chemicals from the Yingkou plant in collaboration with MinChem Ltd, UK. This plant, built alongside Astron's single crystal manufacturing operation, also now includes two fused monoclinic zirconia furnaces with a third to be added by mid 2002.

Yixing Xinxing Zirconium Co Ltd, one of the largest producers in China, continued to press ahead and reduced costs by closing its US office. Several other new Chinese zirconium chemical producers emerged, all making ZOC from zircon sand as a first stage to other products.

In Japan, production of high-purity oxides and chemicals continued to grow, but with some refocusing because of a slower market in structural ceramics. DKK pressed ahead in catalyst in fuel cell applications and Tosoh Corp./Sumitomo Osaka Cement Co. Ltd (SOC) continued plant expansions.

In the US, Southern Ionics Inc. further developed its product mix; Eka part of the Akzo Group (formerly Hopton Technical) continued to be strong in AZC sales and Wah Chang Albany (part of Allegheny Technologies) lost production owing to a strike.

MEL UK (and sister company MEI, US) continued to move away from commodity zirconium chemicals to advanced technology markets.

Predicted shortages in zircon sand feedstocks did not translate into higher prices. Increased competition led to a fall in 2001 levels over the previous year.

Hafnium Metal and Chemicals

Hafnium normally represents 1.5 - 3.0% of the weight of zirconium in zircon and baddeleyite, and owing to its great similarity to zirconium is only removed when necessary. All hafnium metal and chemicals are derived from zircon sand during the manufacture of hafnium-free nuclear grade zirconium metal. Hafnium metal is used in similar ways to zirconium (as metal/alloy in forms such as plate, strip, sheet, foil, rod, wire and tube). It is also sold as the oxide and in various reactive chemical forms. Hafnium's strong neutron absorption property is used in the manufacture of control rods for nuclear reactors. It is also used in aerospace, medical and other high technology applications.