ZIRCONIUM AND HAFNIUM

By Charles Skidmore
Minchem Ltd, UK

Zircon sand (zirconium silicate ZrO_2, SiO_2) and baddeleyite (zirconium oxide ZrO_2) are the mineral sources of all zirconium and hafnium metals, oxides and their salts. Zirconium and hafnium 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.

Zircon Sand (zirconium silicate)
Zircon sand output in 2000 fell less than 1% under the 1999 level but demand increased by around 6% which led to increasing tightness in the market. From July 2000, prices showed marked increases and this trend is predicted to continue well into 2001.

Zircon sand is the most commonly abundant naturally occurring zirconium mineral with deposits in many countries. Recovery, however, is always associated with titanium bearing ores - rutile and ilmenite. It is estimated that total known world reserves of zircon ore exceed 55 Mt with possibly double this amount present in the Earth's crust. Key producers remain Australia, South Africa and the US.

Zircon is mined from heavy mineral sands (typically beach sands) using either dredging or dry mixing methods; the choice dependent on the position, nature and size of the deposit. Onward processing by either mechanical abrasion or acid/base chemical attack together with heat (calcination) results in zircon sand products with varying chemical and physical properties. Actual grading and product name is made on the basis of chemical purity and application.

Zircon sand is used in its mined form and also milled into finer particle size products. Sand is used in a variety of applications: abrasive, foundry, refractory (glass and steel), zirconium chemical production and television tube manufacture. As a ground flour product (typically 95% below 45 micron) it is used in these markets and in large quantities in ceramic frits (special glasses) where it produces a white opaque colour due to light reflection. In its finest particle size (typically averaging particle size 5-6 micron and below) it is used in large quantities as the major opacifier in tiles, table and sanitaryware.

Applications where colour is important, such as in opacifiers require ceramic or premium quality grades with low impurities - max 0.10% TiO_2, 0.05% Fe_2O_3. Lower purity grades with 0.25% TiO_2, 0.15% Fe_2O_3 are used in refractory and foundry markets. Other terms such as prime, intermediate and coarse grade refer to specific qualities.

In general, the higher purity grades are needed for zirconium chemical production, though developing shortages have led to lower qualities being substituted.

Zircon sand shipments, in 2000, totalled around 978,000 t, a small decrease over reported 1999 output of 984,000 t. Australian output increased marginally to 381,000 t (1999:373,000 t) though this is predicted to fall due to cut backs at Iluka. This may be tempered by the extension of Mineral Deposits Ltd's (MDL) Fullerton mineral sands operation (based Newcastle, eastern Australia) which produces 60,000 t/y zircon.

In South Africa, production increased marginally to 355,000 t (1999:352,000 t) with Richards Bay Minerals (RBM) (50%-owned by Rio Tinto), increasing output with a fifth dredge. Namakwa Sands pressed ahead with its second smelter and steel giant Iscor Ltd is well advanced in its Hillendale mineral sands operation in Kwa Zulu Natal and work also progressed at the Gravelotte mine in the Northern Province.

In the US, Iluka plans to increase output at its Old Hickory operation by 70% over the next five years.

Production elsewhere in the world, remained steady at around 80,000 t with contributions from Ukraine, India, Vietnam, Brazil, Malaysia and China.

In the markets, demand increased in the ceramic applications in tile, table and sanitaryware, and showed an increase of some 9% over 1999. This was due to continuing recovery in the Far East and use of zircon in grés porcelenato tiles in the EU (where much higher loadings of zircon are needed to produce the whitening effect). Sand, flour and opacifier prices moved up in these markets as a result of the increased demand. Some substitution of zircon opacifiers with kaolin, alumina or feldspar may occur if prices climb too high.

Foundry applications showed a very slight increase to around 168,000 t (1999:166,000 t). The forming of complex shapes such as golf club heads, and turbine blades using investment casting, continues to develop. In these markets, prices have seen an increase though this is less than seen in ceramic grades.

Refractory markets also saw gains, in both glass and steel output, with around 2% growth in zircon usage (2000:158,000 t, 1999:155,000 t).

Zircon usage in television and computer monitor screens, where it is added to absorb X-rays, showed an 8% increase (2000:80,000 t, 1999:74,000 t) and is predicted to reach 100,000 t/y in the near future.

Production of zirconium chemicals saw a 7% gain with usage of 88,000 t in 2000 (1999:82,000 t). Supplies are now becoming increasingly tight for this specific market since, in general, high purity feedstock is preferred.

Consumption in other applications remained steady at around 20,000 t.

Last year's prediction that zircon would be in surplus has again proved false with demand outstripping supply. The coming months will again be a demanding time for producers and consumers.

Baddeleyite (zirconium oxide / ore)

Worldwide output of baddeleyite showed a marginal increase in 2000. This was due to improved performance in South Africa and continued output from Russia. Refractory and ceramic markets continued to show strong demand with synthetic zirconias taking up the shortfall in supplies of baddeleyite. This led to

Zircon Sand / Flour / Opacifier Prices 2000

Shipping Terms	Pricing	May 2000	April 2001
Sand fob[a] Australia	US$/t bulk	430 – 480	330 – 360
fob South Africa	US$/t bulk	320 – 350	350 – 390
fob US	US$/t bulk	340 – 370	350 – 390
Flour (95% below 45 micron) fob Europe	US$/t bagged	390 – 430	440 – 460
fob Asia	US$/t bagged	420 – 460	450 – 470
Micronised (d_{50} 5 micron) fob Europe	US$/t bagged	600 – 650	560 – 580
fob Asia	US$/t bagged	600 – 650	610 – 620

a: fob = Free on Board

developing tightness in the supply of replacement zirconias, and new investment in plant around the world.

Baddeleyite, with ZrO_2 and HfO_2 typically 99%, continues to be mined in commercial quantities in the Northern Province of South Africa and in the Kola Peninsula in the northwestern part of Russia, close to the Finnish border. In Phalaborwa, South Africa, two operators are involved in baddeleyite extraction: Palabora Mining Co. (PMC), with largest shareholder Rio Tinto with headquarters in London, recovers the mineral as a by-product of its open-pit copper mine and the state-owned Phosphate Development Corp. (Foskor) produces the mineral from phosphate rock processing derived from Foskor's own mine and from PMC.

PMC continued to be the world's largest producer of baddeleyite in 2000. With much reduced quantities of feed being available, Foskor agreed to sell its baddeleyite output to PMC for onward processing. This, together with improvements in PMC's operating performance, led to an increase in PMC output.

Around 80,000 t of ore are processed daily by PMC to produce a diverse product mix of copper, magnetite, precious metal slimes and baddeleyite. After copper is removed by flotation, the heavy mineral stream is beneficated by gravity separation, then fed to a magnetic separation/acid leaching plant. This produces both refractory and ceramic pigment grades of zirconium ore. Some of this is further converted to zirconium (ortho) sulphate (Grade 4) by reaction with sulphuric acid, this being a by-product of the copper smelting operation.

PMC saw a 14 % rise in baddeleyite output to 8,526 t (1999:7,486 t). Feed from the open pit continued to show a reduction in ZrO_2 grade due to geology and open-pit geometry. This was offset by feedstocks purchased from Foskor. Foskor decided to sell this material since quantities had fallen such that operating costs of its recovery plant became uneconomic. PMC's increased output eased the refractory (Grade 1) product supply and allowed a 44% increase in ceramic pigment (Grade 5) quality to 2,497 t.

Contaminant levels in all feeds increased the technical demands on production staff. This required skilful handling of feed balance, processing conditions and close co-operation of works personnel.

PMC's underground project neared completion with test quantities of ore being recovered and processed. Full production is still on target for 2002, when the open-pit operations will be scaled down. PMC saw a further reduction in headcount in preparation for a more streamlined, capital-intensive operation, and to mirror a leaner Rio Tinto organisation.

Foskor's baddeleyite output also fell due to lower $Zr0_2$ grade in phosphate feed. Foskor, through it's Zirconia business unit (ZBU) saw further major gains in 2000 with increased acceptance of its synthetic refractory and synthetic pigment grades, and all product being sold by year end.

Foskor commissioned a further furnace in 2000 to boost output to 4,500-5,000 t, and is shortly to add one more; such is the demand from all markets. Its fumed silica by-product also performed well leading to a very successful year for Foskor's ZBU. In contrast, Foskor's main business in phosphates saw a more difficult year.

Downstream organisation/relationships for both PMC and Foskor changed in 2000/early 2001. PMC's subsidiaries in UK, and Singapore all had name changes. Mandoval Ltd., based in Guildford, UK, became Palabora Europe Ltd and focused operations on vermiculite also mined at Phalaborwa. Mandoval's minerals and chemicals department (Minchem) was sold off by way of management buy out and formed into a new company called Minchem Ltd. based in Aldershot, UK.

Minchem Ltd. began operations on September 1, 2000, and all previous Minchem department staff transferred. A sole agency agreement between Mandoval's sister company Zirconia Sales (UK) Ltd. (still based in Guildford) and Minchem Ltd. also commenced on September 1. This arrangement ensured that sales management, marketing and technical back up for PMC's Zirconium products would continue, since the relevant staff also formed the Minchem department. Thus, PMC achieved a win-win situation whereby its desire to reduce the UK head count led to benefits for PMC (lower costs) and benefits for its outgoing staff (continuing employment). Minchem Ltd. continues to represent all principals previously handled through Mandoval Ltd.

In the US, PMC's subsidiary office Amverco and sister company Zirconia Sales (America) Inc. based in Kennesaw, Georgia, remain unchanged in name.

PMC sales into the Far East particularly, Japan and Taiwan were co-ordinated through Rio Tinto's Singapore office - and renamed Palabora Singapore Ltd. Foskor also altered its downstream representation with changes in the UK - this leading to more direct sales from the Phalaborwa base.

In the southwest part of the Kola Peninsula, some 20 km from the Finnish-Russian border lies the Kovdor mining district. Here, A O Kovdorsky GOK recovers iron ore, apatite and baddeleyite from a complex ore body. From first production, around 1975, baddeleyite output has risen to meet depleting reserves in South Africa. Kovdor is the only known economic deposit of baddeleyite other than the Phalaborwa complex.

A comprehensive investment programme has led to quantity and quality improvements with output up to 6,500 t. In 2000, some 5,500 - 6,000 t of 98.2% ZrO_2 was sold mainly to abrasive and refractory markets in Japan.

Recoveries in the plant are based on feed from the open pit as well as tailings accumulated during the first 20 years of operation. Development of this plant and operation has been a very considerable feat of engineering and personnel expertise.

Quality issues in both South African and Russian baddeleyite such as higher silica ($Si0_2$) levels and other impurities have led to replacement in refractory markets by synthetic zirconias derived from fusing sand. Suppliers here include Norton US, Washington Mills US, Unitec Ceramics UK, Foskor South Africa and AFM Australia.

Daiichi Kigenso Kagaku Kogyo Co. Ltd. (DKK) in Japan operates its IDU fusion plant on Shikoku Island, this based on baddeleyite feed. Similarly, the Nako AS plant in Narvik, Norway, is designed to use Russian baddeleyite feedstock. Plans to reopen this plant continue to be discussed.

Further expansion of fused zirconia plants were announced by Unitec UK and Chinese output also increased. AFM has yet to make a decision on its proposed new furnace due to shareholder disputes.

Usage of baddeleyite in all markets continues to require significant technical juggling of batch chemistry with required end-product specifications. Naturally occurring baddeleyite generally offers lower costs than synthetically sourced zirconias and it is mainly these lower prices that secure product sales in current markets. Radioactive issues are still debated both on baddeleyite and zircon sand, in particular their status as a NORM (Naturally Occurring Radioactive Material). The situation remains unclear, with suppliers and users unsure if licensing will be needed.

During 2000, markets continued to change with shortages in supply being felt in several

Main Ports cif EC/US/Japan (US$/t)	
*Monoclinic Zirconias**	
Refractory/Abrasive Grade	2,300 – 2,700
Ceramic Pigment Grade	2,700 – 4,500
Stabilised Zirconias	
Refractory Grade	3,600 – 4,200

*Baddeleyite price levels in the lower half

sectors. Worldwide, steel output rose despite difficulties in the US and Japan, and this led to increased demand for baddeleyite and fused zirconias.

This combined with a developing shortage of zircon sand led to considerable shortfalls between supply and demand. Glass production also saw increases, which again put pressure on all zirconia feedstocks. Abrasives demand also grew.

Ceramic pigment applications further developed, particularly in strong colours such as blues and yellows, which added to raw material shortages.

These imbalances in supply/demand pushed prices upward in baddeleyite and fused zirconias (including stabilised grades). Typical levels (April 2001) were:

Zirconium Metal Oxide and Chemicals

The range of zirconium products offered continued to diversify in 2000, and new applications added to the wide range of uses. The key markets for zirconium metal, oxides and chemicals are shown in Figures 2 and 3.

Metallic zirconium is made in alloyed or unalloyed forms, some with hafnium removed. Its extreme resistance to temperature and corrosion makes it ideal for applications in engineering - particularly the fabrication of chemical plant. Hafnium- free zirconium continues to be a critical part of nuclear fuel rod claddings and core components, and products are sold into new reactor construction as well as operational maintenance replacements. Non-nuclear applications have grown such that producers are contemplating expanding manufacturing plants.

Zirconium oxide in natural and synthetic forms is available in a range of chemical purities and particle size distributions. Figure 2 summarises markets for baddeleyite / synthetic zirconias.

In 2000, usage of zirconium chemicals increased in almost all markets with major gains in onward processing for catalyst, paint drier (siccative) and medical products.

The major players are zirconium acetate (ZAC), basic carbonate (ZBC) ammonium zirconium carbonate (AZC), zirconium oxychloride (ZOC), acid sulphate (ZOS/ZST) and basic sulphate (ZBS).

Markets for Baddeleyite/Synthetic Zirconia (t)

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

Major zirconium (Zr) and Hafnium (Hf) Chemical Production and Applications

Product	Abbreviation	Formula	Capacity (t/y)	Application
Zr metal	Zr	Zr	10,000	Chemical processing plant nuclear fuel rod/core components, explosives, alloys, pyrotechnics
Zr oxychloride	ZOC	$ZrOCl_2{\cdot}8H_20$	35,000	Manufacture of other Zr chemicals, titania coating, antiperspirant, oil field acidising agent
Zr sulphate	Acid/ZST/ Orthosulphate	$Zr(SO_4)_2{\cdot}4H_2O$	6,000	Manufacture of other Zr orthosulphate chemicals, titania coating, leather tanning reagent
Zr basic sulphate	ZBS	$Zr_5O_8(SO_4)_2$ x H_2O	10,000	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)
Ammonium Zr carbonate	AZC	$(NH_4)_3ZrOH(CO_3)_32H_2O$	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 repellent 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 (Zr silicate)[a]		$ZrO_2{\cdot}SiO_2$	978,000	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 diboride		HfB_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: Not available.
Note: a: Zircon is included in this table for comparison. It is generally considered a mineral, not as a processed zirconium chemical.

Production worldwide increased with new plants in China and extensions to existing plants in the US, China, South Africa and Japan. Despite increasing zircon sand feed prices, increasing freight costs and stronger markets, intense competition meant that final selling prices continued to fall. Some overstocking also contributed here. It is anticipated that this trend cannot continue throughout 2001 due to falling profit levels and anxiety amongst producers in securing reasonable quality zircon sand feedstocks.

ZOC is the largest tonnage reactive chemical made, and output in 2000 was stepped up by several producers in China, to meet demand for this and other downstream compounds such as ZBS+ZBC. ZOC continued to replace ZOS/ZST in pigment coating applications due to its lower cost and higher water solubility. Its corrosive classification necessitated more careful shipment and handling but this was no real hardship to an industry used to acid solutions. The selection of either ZOC or ZOS/ZST in coating depends on plant design.

Zirconium Sulphate Tetrahydrate (ZST/Grade 4) produced by PMC using direct reaction of sulphuric acid on baddeleyite/zirconium ore rather than zircon sand continued at a similar level (1,769 t) to 1999.

Chinese output of ZOS continued to grow although slower markets in leather tanning particularly into 2001 due to foot and mouth disease in the UK led to some surpluses.

PMC's ZBS plant utilising feed from sister company RBM continued to make progress with a new furnace and other chemical plant scheduled for 2001. This plant now produces the highest specification material for demanding uses in Japan and US. Chinese ZBS is also sold to export markets.

Sepr, a member of the French Saint Gobain Group pushed ahead with its Shanghai based ZBC plant. Shenyang Astron Mining Industry Ltd, based in Shenyang China but actually an Australian-listed company, further developed its range of products. The new ZBC plant in Yingkou, near Dalian, China, saw sales grow to markets in Europe, Japan and the US. This plant, built alongside Astron's single crystal manufacturing operation, will see further expansion in 2001. Also based in China, Yixing Xinxing Zirconium Co. Ltd, which is the largest zirconium chemical producer, opened its group office, Asia Zirconium Ltd, in Hong Kong.

Millennium Performance Chemicals plants in Rockingham, Australia, and Thann et Mulhouse, France, continued to restructure on markets in catalysts, pigments and advanced ceramics.

Japan saw significant growth in plant expansion. Daiichi Kigenso Kagaku Kogyo Co. Ltd (DKK), having already filled capacity of its new Gohtsu site, is adding additional plant to satisfy high technology sales to catalyst and related markets. Similarly, both Tosoh Corp. and Sumitomo Osaka Cement Co. Ltd (SOC) decided on additional lines to meet demand in electronics/fine ceramics, particularly optical fibre connectors for North America.

In the US, Mississippi-based Southern Ionics Inc. expanded production, and AZC producer Hopton Technical of Albany was purchased by Eka, part of Akzo Group. Wah Chang (part of Allegheny Technologies), also based in Albany, saw a full order book and plans new reactor installation.

MEL UK (and sister company MEI, US) continued to refocus on advanced technology markets.

The shortages of low impurity zircon sand feedstocks may bring higher costs and therefore higher prices into 2001. Certainly it is becoming increasingly important for major producers to have long term sand contracts.

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 chemical similarity to zirconium is only removed when necessary. All hafnium compounds are derived from zircon sand during the manufacture of hafnium-free nuclear grade zirconium metal.

Hafnium is used in similar ways to zirconium (as metal/alloy in plate, strip, sheet, foil, rod, wire and tube), as an oxide.

Hafnium's ability to absorb neutrons (the opposite of zirconium) makes it an ideal material for use in control rods in nuclear reactors. Aerospace and surgical implants markets continue to grow.

The major producer, US-based Wah Chang, saw demand outstrip supply with resulting price increases.

