# ZIRCONIUM AND HAFNIUM

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The principal economic source of zirconium is the zirconium silicate mineral, zircon (ZrSiO<sub>4</sub>). The mineral baddeleyite, a natural form of zirconia (ZrO<sub>2</sub>), is secondary to zircon in its economic significance. Zircon is the primary source of all hafnium. Zirconium and hafnium are contained in zircon at a ratio of about 50 to 1. Zircon is a coproduct or byproduct of the mining and processing of heavy-mineral sands for the titanium minerals, ilmenite and rutile, or tin minerals. The major end uses of zircon are refractories, foundry sands (including investment casting), and ceramic opacification. Zircon is also marketed as a natural gemstone, and its oxide is processed to produce cubic zirconia, a diamond and colored gemstone simulant. Zirconium is used in nuclear fuel cladding, chemical piping in corrosive environments, heat exchangers, and various specialty alloys. The major end uses of hafnium are in nuclear control rods, nickel-base superalloys, nozzles for plasma arc metal cutting, and high-temperature ceramics.

World production of zirconium mineral concentrates was estimated to have increased 11% in 1999. Data on U.S. production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data. Domestic production of zircon increased as a recently opened mining operation in Virginia continued to scale-up production. In 1999, production of milled zircon was essentially unchanged from the previous years' level. According to U.S. Customs trade statistics, the United States was a net exporter of zirconium ore and concentrates. U.S. imports of zirconium ore and concentrates decreased 36%, and domestic exports of zirconium ore and concentrates increased 70%.

With the exception of prices and referenced data, all survey data in this report have been rounded to no more than three significant digits. Totals and percentages were calculated from unrounded numbers.

#### **Production**

Data for zirconium and hafnium materials are developed by the U.S. Geological Survey from one voluntary survey of domestic operations. Of the 49 operations surveyed, 30 responded. Data for nonrespondents were estimated on the basis of prior-year levels. Data on domestic production and consumption of zircon concentrates were withheld to avoid disclosing company proprietary data.

Domestic production of milled zircon and zirconium oxide declined very slightly from their 1998 levels (table 1).

Zircon is normally produced as a byproduct of the mining and processing of heavy-mineral sands for the titanium minerals ilmenite and rutile. In 1999, U.S. mine producers of zircon were Iluka Resources Inc. (previously RGC (USA) Mineral Sands, Inc.), a subsidiary of the Australian company, Iluka Resources Limited, and E.I. du Pont de Nemours and Co. (DuPont). DuPont produced zircon from its Highland and Maxville heavy-mineral sands deposits near Starke, FL. Iluka produced zircon from its heavy-mineral sand operations at Green Cove Springs, FL, and Stony Creek, VA. It was estimated that the United States controlled about 19% of world's zircon production in 1999 (Minerals Sands Report, 2000e). U.S. producers of zirconium and hafnium metal were Oremet-Wah Chang, a subsidiary of Allegheny-Teledyne Corporation, Albany, OR, and Western Zirconium, a subsidiary of Westinghouse Electric Company, Ogden, UT. Primary zirconium chemicals were produced by Oremet-Wah Chang and Magnesium Elektron Inc., Flemington, NJ. Secondary zirconium chemicals were produced by about 10 companies, and zirconia was produced from zircon sand at plants in Alabama, New Hampshire, New York, Ohio, and Oregon.

Iluka, which completed construction of zircon production facilities at Stony Creek, VA, in late 1997, continued to improve production output in 1999. Zircon production capacity at Stony Creek is 30,000 metric tons per year. Iluka also announced plans to invest A\$250 million in its worldwide heavy-mineral sands business. Of the total, Iluka apportioned \$100 million to double capacity at its mines in Florida and Virginia (Industrial Minerals, 1999e).

Altair International Inc. announced that its two heavymineral sand deposits near Camden, TN, contain an estimated 490 million metric tons (540 million short tons) grading 3.6% heavy minerals. MD Mineral Technologies was selected by Altair to design and engineer a wet concentrator process and pilot plant (Altair International Inc., Design firm selected for Altair's Camden pilot project, accessed March 7, 2000, at URL http://www.altairint.com/News/1999/1999.html).

# Consumption

Approximately 95% of all zirconium consumed is in the form of zircon, zirconium oxide, or other zirconium chemicals. The remainder is consumed as zirconium metal and zirconium-containing alloys.

Zircon, used for facings on foundry molds, increases resistance to metal penetration and gives a uniform finish to castings. Milled or ground zircon is used in refractory paints for coating the surfaces of molds. Zircon in the form of refractory bricks and blocks is used in furnaces and hearths for containing molten metals. Glass tank furnaces use fused cast and bonded alumina-zirconia-silica-base refractories.

Baddeleyite is used principally in the manufacture of aluminazirconia abrasives, as well as in ceramic colors and refractories.

Stabilized zirconium oxide exhibits high light reflectivity and good thermal stability and is primarily used as an opacifier and pigment in glazes and colors for pottery and other ceramic products. Yttria-stabilized zirconia (YSZ) is used in the manufacture of oxygen sensors that control combustion in furnaces and automobile engines. YSZ is also used in the manufacture of a diverse array of products including high-temperature, high-strength structural ceramics, heat- and break-resistant shirt buttons, golf shoe cleats, golf putters, fiber optic connector components, coatings for the hot sections of jet engines, and cubic zirconia, a gemstone simulant for diamonds and colored gemstones.

Because of its low thermal neutron absorption cross section, hafnium-free zirconium is used as cladding for nuclear fuel rods. Commercial-grade zirconium, unlike nuclear grade, contains hafnium and is used in the chemical process industries because of its excellent corrosion resistance.

Hafnium is used in nuclear control rods because of its high thermal neutron absorption cross section. However, the largest end use for hafnium metal is as an alloy addition in superalloys.

#### **Prices**

In 1999, the increased availability of zirconium-base concentrates resulted in a decrease in price. The average value of imported ore and concentrates decreased 12% from \$355 per ton in 1998 to \$311 per ton in 1999. Domestic prices of standard- and premium-grade zircon declined as a result of excess supply. Published prices for imported grades of zircon were lower than those of 1998. Published prices for zirconium, hafnium, and zirconium oxide products were unchanged or slightly higher (table 2).

## Foreign Trade

According to the Bureau of the Census trade statistics, the United States was a net exporter of zirconium ore and concentrates in 1999. U.S. exports of zirconium ore and concentrates were 69,500 tons, a 70% increase from that of 1998 (table 3). U.S. exports of unwrought zirconium metal, waste, and scrap were 156 tons, a 3% decrease in tonnage compared with those of 1998. U.S. exports classified as "other zirconium metal, waste, and scrap" were 846 tons.

U.S. imports of zirconium ore and concentrates were 57,600 tons, a decrease of 31,900 tons from those in 1998 (table 4). Australia and South Africa supplied about 92% of the imports of ores and concentrates. The United States was a net importer of zirconium and hafnium metal in 1999. Imports of unwrought zirconium metal and waste and scrap were 859 tons, a 4% decrease compared with those of 1998. The leading import sources of unwrought zirconium were, in descending order of quantity, France, Germany, and Canada. Domestic imports of ferrozirconium alloys were 99.6 tons in 1999. Imports originated entirely from Brazil. U.S. imports of unwrought hafnium metal and waste and scrap were 9.38 tons, an 18% increase compared with those of 1998.

#### **World Review**

Excluding U.S. production, world production of zirconium mineral concentrates in 1999 is estimated to be 941,000 tons, a modest increase compared with that of 1998 (table 5). Australia and South Africa supplied about 85% of all production outside the United States. World reserves of zircon are estimated to be 36 million tons of ZrO<sub>2</sub>, while identified world resources of zircon were 65 million tons of ZrO<sub>2</sub>. During 1999, the zirconium industry continued to be active in the exploration and development of mineral deposits on a global basis, particularly in Australia, Kenya, Mozambique, South Africa, and the United States.

Australia.—Australia was one of the two largest producers of zircon concentrates in the world (table 5). In 1999, major producers of zircon concentrates were Iluka Resources Limited (formerly RGC Ltd. and Westralian Sands Ltd.), Tiwest Joint Venture, Cable Sands Ltd. (CSL), and Consolidated Rutile Ltd. (CRL). Australian zircon production in tons for 1999, was as follows: Iluka, 211,000; Tiwest Joint Venture, 60,000; CSL, 37,000; CRL, 41,000; Broken Hill Proprietary Company Limited (BHP), 1,000; and New South Wales producers, 7,000. Total production in 1999 of 360,000 tons was a 6% decrease from the 1998 level (Mineral Sands Report, 2000a).

Worldwide production from Iluka was 300,600 tons of zircon in 1999. A total of 211,500 tons was produced from Iluka's five mines in Western Australia, which includes the South Mine and West Mine near Eneabba, and the Yoganup, Yoganup Extended, and Busselton mines in the southwestern region. The West Mine ceased operations in November 1999 as a result of the depletion of its reserves. A new operation, the North Capel Mine, was commissioned in late December (Iluka Resources Limited, 1999, accessed March 10, 2000, at URL http://www.iluka.com/profile\_au\_2.asp).

Alkane Exploration NL announced the completion of an initial feasibility study of the Dubbo zirconium-bearing deposit in New South Wales by DEMA Pty. Ltd. The multimineral deposit is based on the Toongi alkaline intrusive that contains hafnium, lanthanides, niobium, tantalum, yttrium, and zirconium. Based on a planned 200,000-ton-per-year sulfuric acid leach process, annual capacities at the plant were expected to produce 3,650 tons zirconium oxide (and hafnium oxide), 1,130 tons of yttrium-lanthanide concentrate, and 875 tons of tantalum-niobium pentoxide concentrate (Industrial Minerals, 1999a).

A new heavy-mineral sands deposit was discovered in the Victoria section of the Murray Basin by Basin Minerals NL. Basin Minerals' Douglas deposit showed a width ranging from a few meters to over 1,000 meters, a length of tens of kilometers, and a thickness of 10 to 20 meters (Industrial Minerals, 1999b).

BHP lifted its *force majeure* at its Beenup heavy-mineral sands mine in January. The *force majeure* had been in effect since May 1998 when the company experienced problems with the dredge and high slime content in the tailings. Production reportedly reached 30,000 tons per month at the beginning of 1999 (Industrial Minerals, 1999c). By the end of the first quarter, however, production problems could not be resolved

and the Beenup operation was closed (Industrial Minerals, 1999d).

Tiwest Joint Venture, an Australian collaboration of Kerr McGee Corp. (USA) and Ticor Ltd. (previously Minproc Holdings Ltd.) produced zircon from its Cooljarloo Mine in Western Australia. In 1999, Tiwest produced 548,498 tons of heavy-mineral concentrates, an increase from the 418,000 tons produced in 1998. Zircon production, however, decreased to 60,188 tons from the 1998 level of 64,000 tons (Minerals Sands Report, 2000d).

RZM Pty. Ltd. announced it had acquired full ownership of the Wemen heavy-mineral sands project in the Muray Basin by buying out Western Metals Limited's 30% share for A\$5 million. Following the purchase, RZM entered into a 50-50 joint venture with the Australian company, Sons of Gwalia, for the Murray Basin mineral resources and its heavy-mineral sands processing equipment and operations at Tomago, New South Wales (Mineral Sands Report, 2000c).

Mineral Deposits Limited (MDL) (previously BHP Titanium Minerals Pty. Ltd.) suspended operations in April at its Viney Creek Mine in New South Wales because of poor mineral sands market conditions. MDL continued to operate its Fullerton operation in New South Wales and shipped the wet mill concentrate to MDL's Hawks Nest dry mill for separation (Mineral Sands Report, 1999).

*Finland.*—The merger of two leading European sanitaryware producers was announced in July. Finnish corporation Sanitec Ltd. Oy, a subsidiary of Metra Corp. announced its offer to purchase Dutch corporation NV Koninklijke Sphinx Gustavsberg. The companies are major consumers of zircon for opacification of ceramic sanitaryware for bathrooms and kitchens. Combined sales of both companies was **i** 850 million (US\$892 million) (Industrial Minerals, 19991).

India.—The Government of India was seeking a joint-venture partner for a heavy-mineral sands deposit. The venture will be implemented by Mineral Sands India Private Ltd. (MSIL), which is 26% owned by mineral sands producer Indian Rare Earths Ltd. The MSIL deposit has a planned capacity of 270,000 tons of ilmenite, 135,000 tons of synthetic rutile, 36,000 tons of sillimanite, 12,600 tons of zircon, and 4,500 tons of leucoxene (Industrial Minerals, 1999f).

Japan.—A controlling interest in abrasives producer Japan Abrasives Co. Ltd. was purchased by French conglomerate Saint-Gobain. Saint-Gobain acquired a 55% interest for \$27 million. Japan Abrasives produced fused alumina and fused zirconia for abrasive and refractory markets worldwide. The Sakai City abrasives plant was expected to be operated under Saint-Gobain's Specialty Ceramic Grains Division (Industrial Minerals, 1999k).

Rasa Corporation became the exclusive distributor of mineral sands for Iluka Resources Limited, the company formed from the merger of the Australian mineral sands firms RGC Ltd. and Westralian Sands Ltd. RGC's long-time Japanese distributor, Iwatani International Corporation, ceased distribution at mid-June. Iwatani has since signed an agreement with Richards Bay Minerals (RBM) of South Africa to exclusively trade their mineral sands products in Japan (see South Africa) (Industrial Minerals, 1999g).

*Kenya.*—Tiomin Resources Inc. announced the appointment of Barclays Capital, part of Barclays PLC group in the United Kingdom, as the financial advisor for its Kwale heavy-mineral sands project (Industrial Minerals, 1999m). Tiomin's Kwale deposit includes zircon resources of 600,000 tons contained in 200 million tons of ore. A prefeasibility study indicated an annual dry mill capacity of 33,000 tons of zircon.

Tiomin secured funding for a feasibility study of its Kwale heavy-mineral sands project from Aur Resources Inc. Aur Resources has provided a \$2 million loan for the study to be repaid within 2 years. Tiomin has also offered Aur Resources a 26-month option to purchase its Panamanian subsidiary's Cerro Colorado porphyry copper deposit (Industrial Minerals, 1999n).

South Africa.—Anglovaal Mining Ltd. sold its interest in Rhino Minerals Pty. Ltd. to Mircal South Africa Pty. Ltd. for an undisclosed price. The sale excluded Rhino's 50% interest in Nyala Minerals Pty. Ltd., an alumina and zirconia crushing, grinding, and sizing facility supplying the ceramic and refractory industries (Industrial Minerals, 1999j). In Europe, Rhino Minerals BV moved its office to a new location in Amsterdam, Netherlands (Industrial Minerals, 1999i).

RBM announced it would distribute its zircon sold to Japan through Itawani. RBM had previously distributed its zircon through Sumitomo Corp. (Industrial Minerals, 1999h).

RBM operated its Tisand and Zulti North heavy-mineral sands operations in 1999. Zircon production was estimated at 230,000 tons. RBM's additional reserves are in the Zulti South deposit that is estimated to average 2.6% ilmenite, 0.13% rutile, and 0.34% zircon. RBM's current reserves are expected to keep its mines operating until 2025 (Mineral Sands Report, 2000b).

*United Kingdom.*—Mandovaal Ltd. and Zirconia Sales (UK) Limited of the United Kingdom, a subsidiary of the Rio Tinto Group, has moved its offices to Surrey Research Park in Guilford, United Kingdom (Industrial Minerals, 1999o).

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### GENERAL SOURCES OF INFORMATION

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<sup>&</sup>lt;sup>1</sup>Prior to January 1996, published by the U.S. Bureau of Mines.

# TABLE 1 SALIENT U.S. ZIRCONIUM STATISTICS 1/

#### (Metric tons)

	1995	1996	1997	1998	1999
Zircon:					
Production:					
Concentrates	W	W	W	W	W
Milled zircon	56,000	55,300	55,700	55,700	55,600
Exports	40,300	35,000	44,300	41,000	69,500
Imports for consumption 2/	93,600	92,500	62,400	89,500	57,600
Consumption, apparent 2/	W	W	W	W	W
Stocks, December 31: Dealers and consumers 3/	33,400	34,300	29,300	32,000	24,700
Zirconium oxide:					
Production 4/	14,200	15,000	15,900	17,300	17,100
Exports 5/	1,680	1,480	1,970	1,540	1,680
Imports for consumption 5/	4,370	5,240	4,220	3,900	3,140
Consumption, apparent	W	W	W	W	W
Stocks, December 31: Producer 4/	W	822	982	985	W

- W Withheld to avoid disclosing company proprietary data.
- 1/ Data are rounded to no more than three significant digits.
- 2/ Includes insignificant amounts of baddeleyite.
- 3/ Excludes foundries.
- 4/ Excludes intermediate oxides associated with metal production.
- 5/ Includes germanium oxides and zirconium dioxides.

 ${\it TABLE~2} \\ {\it PUBLISHED~YEAREND~PRICES~OF~ZIRCONIUM~AND~HAFNIUM~MATERIALS} \\$ 

1998	1999
\$320.00	425.00
280.00	267.00
390.00	490.00
360.00-410.00	320.00-360.00
360.00-395.00	320.00-360.00
330.00-375.00	320.00-360.00
1.00	1.23
1.45	1.36
3.00-6.60	3.00-6.60
3.50-8.00	3.66-7.50
3.35-4.00	4.00
3.35-4.00	4.00
3.60	4.20
75.00-150.00	75.00-150.00
9.00-12.00	9.00-12.00
20.00-50.00	20.00-50.00
75.00-95.00	75.00-95.00
	\$320.00 280.00 390.00 360.00-410.00 360.00-395.00 330.00-375.00  1.00 1.45  3.00-6.60 3.50-8.00 3.35-4.00 3.35-4.00 3.60  75.00-150.00 9.00-12.00 20.00-50.00

<sup>1/</sup> Domestic average price.

- 2/ Industrial Minerals (London), no. 375, December 1998, p. 79, and no. 387, December 1999, p. 71.
- 3/ American Vermiculite Corp. baddeleyite price lists.
- 4/ Chemical Marketing Reporter, v. 254, no. 26, December 28, 1998, p. 29; and v. 256, no. 26, December 27, 1999, p. 25.
- $5/\ American\ Metal\ Market,\ v.\ 106,\ no.\ 247,\ December\ 28,\ 1998,\ p.\ 16;\ and\ v.\ 107,\ no.\ 251,\ December\ 31,\ 1999,\ p.\ 6.$

 ${\bf TABLE~3} \\ {\bf U.S.~EXPORTS~OF~ZIRCONIUM,~BY~CLASS~AND~COUNTRY~1/}$ 

		1998		1999		
	Quantity	Value	Quantity	Value		
Class and country	(metric tons)	(thousands)	(metric tons)	(thousands)		
Ore and concentrates:						
Argentina	449	\$333	652	\$412		
Belgium	450	231	3,390	1,020		
Brazil	2,590	1,340	1,030	542		
Canada	7,060	3,300	4,240	1,980		
China	3,120	1,550	2,960	1,240		
Colombia	2,320	1,890	2,240	1,440		
Dominican Republic	278	263	254	209		
Ecuador		147	532	336		
France		649	2,100	1,210		
Germany	1,440	1,300	4,370	1,730		
Hong Kong	48	33	104	65		
Indonesia	39	28	117	65		
Ireland	129	140	427	306		
Italy	6,400	2,560	16,900	5,140		
Japan	1,210	298	993	400		
Korea, Republic of	243	71	16	12		
Malaysia		60	59	32		
Mexico	6,700	3,210	3,920	1,520		
Netherlands			16,500	4,830		
Pakistan	273	216	670	422		
Philippines	234	173	276	164		
Spain	2,270	761				
Sweden		35	34	22		
Taiwan	68	68	187	115		
United Kingdom	2,880	2,110	5,160	2,570		
Venezuela	1,200	941	1,350	849		
Other	341	375	1,010	714		
Total	41,000	22,100	69,500	27,300		
Unwrought zirconium and waste and scrap:						
Canada		471	11	544		
Japan		1,040	56	959		
Nepal		61				
Netherlands		181	2	43		
United Kingdom		1,170	64	1,020		
Other		536 r	/ 23	592		
Total	160 r/	3,450 r	/ 156	3,160		
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r/ Revised. -- Zero.

Source: Bureau of the Census.

 $<sup>1/\,\</sup>text{Data}$  are rounded to no more than three significant digits; may not add to totals shown.

 ${\bf TABLE~4} \\ {\bf U.S.~IMPORTS~FOR~CONSUMPTION~OF~ZIRCONIUM~AND~HAFNIUM,~BY~CLASS~AND~COUNTRY~1/}$ 

	1998		1999		
	Quantity	Value	Quantity	Value	
Class, harmonized code, and country	(metric tons)	(thousands)	(metric tons)	(thousands)	
Zirconium ore and concentrates:					
(2615.10.0000)					
Australia	29,900	11,700	23,800	6,770	
Austria			38	13	
Canada	24	40	27	42	
China	117	175			
Germany			107	143	
Italy	1,570	1,180	3,560	2,540	
Japan			38	28	
Netherlands	587	507	448	403	
Russia			26	66	
South Africa	57,300	18,100	29,400	7,440	
Ukraine			80	38	
United Kingdom			102	416	
Other	6 r	/ 58 r/	(2/)	8	
Total	89,500	31,800	57,600	17,900	
Zirconium, unwrought and waste and scrap:					
(8109.10.3000, 8109.10.6000, 8109.90.0000)					
Canada	15	1,460	53	1,990	
China	35	412	31	514	
France	566	28,000	596	25,100	
Germany	151	14,000	118	18,000	
Japan	23	1,030	32	479	
Sweden	19	1,360			
United Kingdom	58	1,050			
Other	27 r	/ 549 r/	29	610	
Total	894	47,900	859	46,700	
Hafnium, unwrought and waste and scrap:					
(8112.91.2000)					
Belgium			1	191	
Canada			1	245	
France	9	1,500	6	1,060	
Germany	1	265	(2/)	238	
Japan	(2/)	2			
Russia			1	30	
United Kingdom	1	96			
Total	11	1,870 r/	9	1,770	

r/ Revised. -- Zero.

Source: Bureau of the Census.

 $<sup>1/\,\</sup>text{Data}$  are rounded to no more than three significant digits; may not add to totals shown.

<sup>2/</sup> Less than 1/2 unit.

# TABLE 5 ZIRCONIUM MINERAL CONCENTRATES: WORLD PRODUCTION, BY COUNTRY 1/ 2/

### (Metric tons)

Country	1995	1996	1997	1998	1999 e/
Australia	518,000	502,000	424,000	404,000	400,000
Brazil 3/	16,343	15,560	19,252 r/	19,300 r/	19,500
China e/	15,000	15,000	15,000	15,000	15,000
India e/	18,000	19,000	19,000	19,000	19,000
Indonesia	2,000 e/	2,000 e/	105 r/	231 r/	250
Malaysia	3,790	4,511	4,050	4,000 e/	2,500
Russia 4/	2,652	5,080	5,745	6,293	6,800
South Africa e/ 5/	260,000	260,000	265,300 6/	300,000 r/	400,000
Sri Lanka	21,971	15,863	12,450	12,500 e/	13,000
Thailand		5		e/	
Ukraine e/	60,000	55,000	65,000	65,000	65,000
United States	W	W	W	W	W
Total	918,000	894,000	830,000 r/	845,000 r/	941,000

- e/Estimated. r/Revised. W Withheld to avoid disclosing company proprietary data; not included in total. -- Zero.
- 1/ World totals and estimated data are rounded to no more than three significant digits.
- 2/ Includes data available through May 11, 2000.
- 3/ Includes production of baddeleyite-caldasite.
- 4/ Production of baddeleyite concentrate averaging 98% ZrO2.
- 5/ Includes production of byproduct zircon from titanium sands mining and 15,000 to 20,000 tons per year baddeleyite from Palabora Mining Co. Ltd.
- 6/ Reported figure.