ALUMINUM OXIDE (ALUMINA), CALCINED, TABULAR, AND ALUMINATE CEMENTS

1. Calcined Alumina

Calcined aluminas are generally obtained from Bayer process gibbsite [14762-49-3], α-Al(OH)$_3$(1–8), thermal decomposition of which follows the transition through the generic gamma alumina phases to α-alumina [1302-74-5] (corundum), α-Al$_2$O$_3$. Nonmineralized metal-grade or smelter-grade alumina (SGA) for

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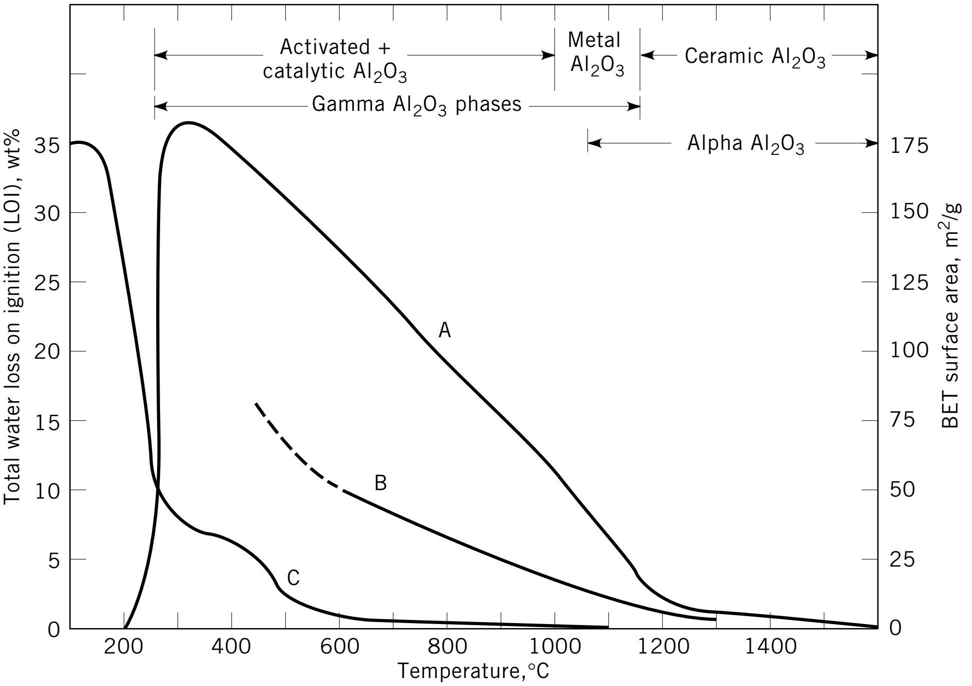

Fig. 1. Normal soda Bayer hydrate heated for one hour. A, change in surface area; B, total water, LOI plus sorbed water after exposure to 44% rh; and C, water loss on ignition when heated to 1100°C.

aluminum production is calcined at lower temperatures and usually contains about 20 to 50% α-Al_2O_3. The remainder consists of higher temperature transition aluminas, usually theta, kappa, delta, and gamma, depending upon the consolidation of the original gibbsite structure, impurities, heating rate, and furnace atmosphere. Figure 1 (9) shows the changes in gibbsite upon heating for one hour where no mineralizers are added. Loss on ignition (LOI), total water, and surface area may be used to define the degree of calcination of Bayer hydrates.

Nonmineralized SGA flows freely, and is often known as sandy alumina because it easily covers the cryolite bath of aluminum electrolysis cells (see ALUMINUM COMPOUNDS, INTRODUCTION). Properties typical of a sandy SGA are shown in Table 1. Aluminum smelting technology in the United States is primarily based upon sandy alumina. Older European smelting technology, however, is based upon a poor flowing, low bulk density, highly mineralized SGA called floury alumina, composed principally of α-Al_2O_3.

Specialty alumina derived from the Bayer process resemble SGA, except for a higher α-Al_2O_3 content, which is usually >80%, and a lower surface area, typically <20 m^2/g. The remaining material is generallysodium β-alumina (Table 2) formed as a result of the soda contamination common to the process (2–7). The mineralogical and structural properties of calcined aluminas are given in Table 2 (3).

α-Alumina, the stable form of anhydrous alumina, occurs in nature as corundum, some varieties of which are natural abrasives (qv). It is common to

Table 1. **Properties of Sandy SGA Metallurgical Alumina**[a]

Property	Value
α-Al_2O content, wt %[b]	20
specific surface area, m^2/g	50–80
particle size distribution, wt %	
+100 mesh[c]	5
+325[d]	92
−325[e]	8
bulk density, kg/L	
loose	0.95–1.00
packed	1.05–1.10
attrition index, wt %[f]	4–15
moisture at 573 K, wt %	1.0
loss on ignition, 573 to 1473 K, wt %	1.0
chemical composition, wt %	
Fe_2O_3	0.020
SiO_2	0.020
TiO_2	0.004
CaO	0.040
Na_2O	0.500

[a] Ref. 6.

[b] Determined by optical or x-ray method.

[c] Retained on 100 mesh = 149 μm Tyler screen.

[d] Retained on 325 mesh = 44 μm Tyler screen.

[e] Passes through 325 mesh = 44 μm Tyler screen.

[f] A 44 μm increase is observed by the modified Forsythe-Hertwig fluidizing test method.

igneous and metamorphic rocks and the red and blue varieties of gem quality are called ruby [12174-49-1] and sapphire [1317-82-4], respectively (6). The corundum structure consists of alternating layers of Al and O (10).

Commercial Bayer calcined aluminas, other than for aluminum production, contain substantial amounts of α-Al_2O_3. α-Al_2O_3 also results industrially from solidification of molten alumina to form artificial sapphires, abrasives, or other corundum varieties (see Gems, synthetic) or else by sintering processes (tabular aluminas). Properties include extreme hardness, resistance to wear and abrasion, chemical inertness, outstanding electrical and electronic properties, good thermal shock resistance and dimensional stability, and high mechanical strength at elevated temperatures (see Advanced ceramics; Ceramics; Glass; Enamels).

Shapes fabricated from ground, calcined α-Al_2O_3 powders have reached 98% theoretical density at temperatures below 1723 K even though α-Al_2O_3 melts at 2326 K. The fine (submicrometer) hexagonal crystals obtained during calcination permit sintering to occur at much lower temperatures after supergrinding to dislodge the individual crystals from the Bayer agglomerate. These thermally reactive, fine-crystalline, fully ground α-Al_2O_3 products have been classified as reactive aluminas by the alumina ceramic industry, because they densify at lower sintering temperatures. The increased reactivity corresponds to decreasing sintering temperatures achieved by decreasing crystal size.

Table 2. **Structural Properties of Transition Aluminas**[a]

Phase	CAS Registry Number	Formula	Crystal system	Space group	Molecules per unit cell	Unit cell length, nm			Density, g/cm^3
						a	b	c	
gamma		γ-Al_2O_3	tetragonal			0.562	0.780		3.2[b]
delta		δ-Al_2O_3	orthorhombic		12	0.425	1.275	1.021	3.2b
			tetragonal			0.796		2.34	
theta[c]		θ-Al_2O_3	monoclinic	C^3_{2h}	4	1.124	0.572	1.174	3.56
kappa		κ-Al_2O_3	hexagonal		28	0.971		1.786	3.1–3.3
			hexagonal			0.970		1.786	
			hexagonal			1.678		1.786	
α-alumina (corundum)	[1302-74-5]	α-Al_2O_3	hexagonal (rhombic)	D^6_{3d}	2	0.475		1.299	3.98
sodium β-aluminate	[1302-42-7]	$NaAlO_2$	orthorhombic	C^9_{2v}	4	0.537	0.521	0.707	2.693
			tetragonal			0.532		0.705	
sodium β-alumina	[11138-49-1]	$Na_2O{\cdot}11Al_2O_3$	hexagonal	D^4_{6h}	1	0.558		2.245	3.24
sodium β-alumina	[12005-48-0]	$Na_2O{\cdot}5Al_2O_3$	hexagonal			0.561		3.395	
potassium β-alumina	[12005-47-9]	$K_2O{\cdot}11Al_2O_3$	hexagonal	D^4_{6h}	1	0.558		2.267	3.30
magnesium β-alumina	[12428-93-2]	$MgO{\cdot}11Al_2O_3$	hexagonal	D^4_{6h}	1	0.556		2.255	
calcium β-alumina	[12005-50-4]	$CaO{\cdot}6Al_2O_3$	hexagonal	D^4_{6h}	2	0.554		2.183	
strontium β-alumina	[12254-24-9]	$SrO{\cdot}6Al_2O_3$	hexagonal	D^4_{6h}	2	0.556		2.195	
barium β-alumina	[12254-17-0]	$BaO{\cdot}6Al_2O_3$	hexagonal	D^4_{6h}	2	0.558		2.267	3.69
lithium δ-alumina	[12005-14-0]	$Li_2O{\cdot}5Al_2O_3$	cubic	O^7_h	2	0.790			3.61

[a] Ref.3.

[b] Estimated.

[c] Unit cell angle is 103°20′.

2. Preparation

Calcination of gibbsite has been done in rotary kilns for many years. Specialty calcined aluminas can also be prepared in stationary or fluid bed calciners (see Fluidization) similar to those used for producing SGA. Fluid-flash calciners producing up to 1500 t/d provide a 30–40% fuel savings compared to the rotary kiln (11). Only a few specialty calcines have sufficient commercial requirements to justify manufacture in these high production capacity fluid-flash calciners. The resulting calcined products have degrees of crystallization that vary according to the temperature, the duration of the calcination, and whether or not mineralizers are used (1–4,7,9). Mineralizer usage reduces the temperature and enhances α-Al_2O_3 crystal growth. Data for a wide variety of calcined alumina is available (1,12,13).

Rotary kiln production is preferred for coarse crystalline products which are easily attrited. Particle breakdown causes dust and materials handling problems but electrostatic precipitators are used to remove particulates from combustion products (see Powder handling). The particle size of unground calcined Bayer alumina is primarily controlled during precipitation: very little particle shrinkage occurs during calcination, even though 3 moles of water of crystallization is lost. The resulting unground porous agglomerates are nominally 100 to 325 mesh (149 to 44 μm). Scanning electron microscope (sem) data differentiates between unground Bayer agglomerates (Fig. 2) which can have crystals as fine as 0.5 μm

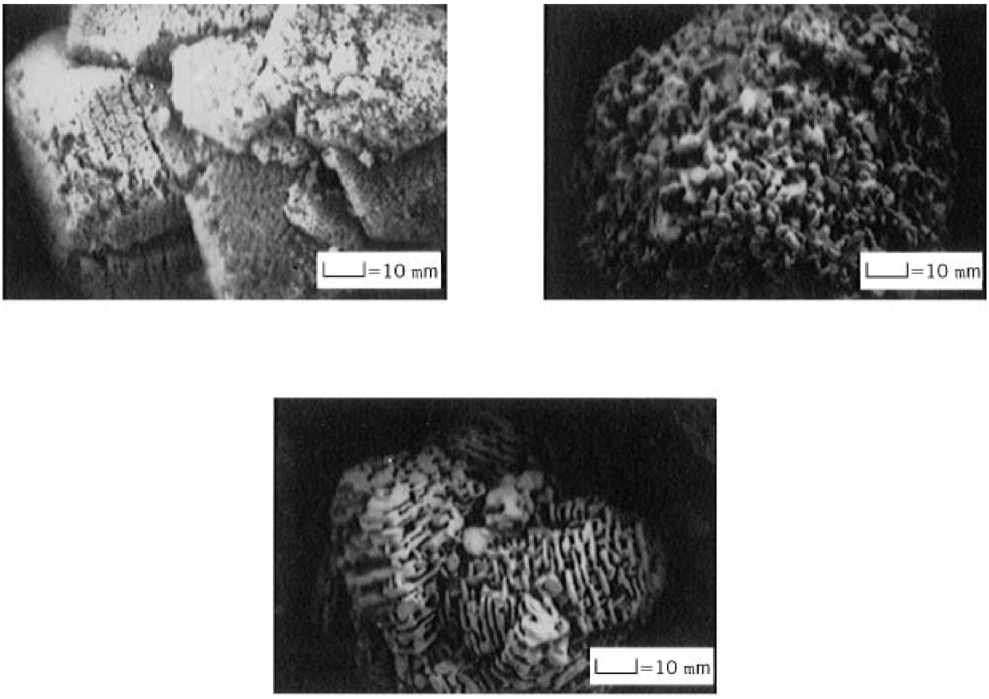

Fig. 2. Sem photographs of controlled crystal size aluminas.

and as large as 15 μm. Physical properties begin to correlate with crystal size above about 2–3 μm. As crystal size increases, bulk density decreases, angle of repose increases, attrition rate increases, and thus, bulk handling characteristics worsen.

Soft-burned calcined products having α-Al_2O_3 crystals no larger than 1 μm may include a considerable portion of transition aluminas (1–7) and exhibit specific surfaces as high as 50 m^2/g. Most special calcined products are 80–100% α-Al_2O_3 and have a specific surface area from <0.5 to ~20 m^2/g. A considerable portion of the normal 0.3–0.6% Na_2O contained in Bayer alumina is in the form of β-alumina, $Na_2O{\cdot}11Al_2O_3$.

Special calcined alumina can be broadly categorized according to soda content in addition to crystal size. Besides the normal soda products, special grades are made at the intermediate (0.15–0.25% Na_2O) and low (<0.1% Na_2O) soda levels. Extra high purity 0.5 μm calcines, typically 99.95% Al_2O_3 having less than 0.01% Na_2O, are also available in ton quantities.

2.1. Ground, Calcined, and Reactive Aluminas. Most ceramic grade aluminas are supplied dry ground to about 95% −325 mesh (44 μm) using 85–90% Al_2O_3 ceramic ball, attrition, vibro-energy, or fluid-energy milling. Particles larger than 44 μm can be removed by air classification during continuous milling to produce 99+% −325 mesh product. More fully ground, or superground, calcined aluminas having particle size distributions that approximate the natural or ultimate crystal size of the Bayer grain as calcined are often desired (8).

Thermally reactive aluminas contain submicrometer crystals. These must be separated from the Bayer agglomerate during grinding to permit dense compaction upon ceramic forming, and thus, enhance densification upon sintering at lower temperatures (14–21). Usually from 10 to greater than 30 hours dry batch ball milling is required for this separation. Such superground, thermally reactive aluminas exhibit higher densification rates when compacted and sintered into ceramic products and complete densification is obtained about 200°C lower than using the coarser, continuously ground aluminas (1).

Severe mill packing problems can occur in dry batch-milling aluminas and dry grinding aids may be used (14,15). These sorb on the surface of the aluminas, reduce the energy required to separate the individual crystals from the Bayer agglomerates and prevent mill packing by developing repelling surface charges on the alumina crystals. Mill packing tendencies also decrease with increasing mill size and ball-to charge ratio.

Reactive aluminas have enabled 85, 90, and 95% Al_2O_3 ceramics to be upgraded (16,17), because they could be sintered without fluxes in the temperature range of about 1723–2023 K, rather than 2073–2123 K. Advances in microminiaturization of components for the electronic, computer, and aerospace industries have been directly related to the development of low soda and reactive aluminas (18).

2.2. Specialty Aluminas. Process control (qv) techniques permit production of calcined specialty aluminas having controlled median particle sizes differentiated by about 0.5 μm. This broad selection enables closer shrinkage control of high tech ceramic parts. Production of pure 99.99% Al_2O_3 powder from alkoxide precursors (see ALKOXIDES, METAL), apparently in spherical form, offers the potential of satisfying the most advanced applications for calcined aluminas requiring tolerances of ±0.1% shrinkage.

The difficulty of dispersing superground aluminas which contain dense, repelletized agglomerates is illustrated in Figure 3**a**. Deflocculated 0.5 μm material is only partially dispersed when magnetically stirred, in comparison to the completely dispersed sample produced by using an ultrasonic probe. In contrast, the dispersible alumina is essentially fully dispersed as shown in Figure 3**b** (8). This product, with agglomerates mechanically disintegrated, also disperses fully

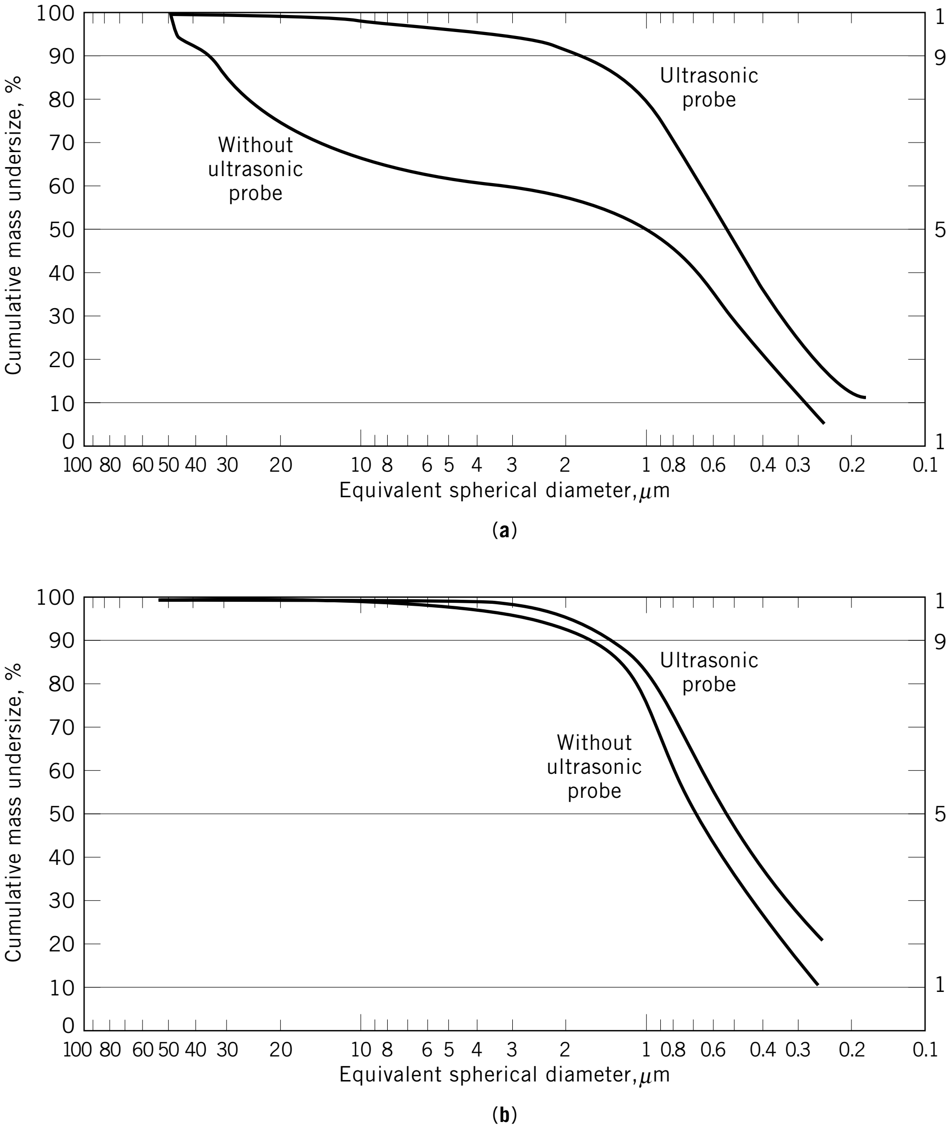

Fig. 3. Sedigraph particle size distribution for superground submicrometer alumina. (**a**) Partially dispersed; (**b**) fully dispersed.

in 3 to 5 min where low shear mixers used to homogenize refractories are employed. Improved predictability of the rheology and forming characteristics of advanced refractory mixes results.

3. Economic Aspects

Calcined alumina markets consume slightly less than 50% of the specialty alumina chemicals production (1–8,20,22–115). Worldwide usage is estimated to be

Table 3. **World Production of Alumina by Country $\times 10^3$ t**[a,b]

Country	1996	1997	1998	1999	2000[c]
Australia	13,348	13,385	13,853	14,532	15,681[e]
Azerbaijan[c]	5	10	[f]	50[d,e]	200
Bosnia and Herzegovina[c]	50	50	50	50[d]	50
Brazil	2,752	3,088	3,322	3,515[d]	3,500
Canada	1,060	1,165	1,229	1,233	1,200
China[c]	2,550	2,940	3,330	3,840	4,330[e]
France	440	454	450[c]	400[c]	400
Germany	755	738	600[c,d]	583[d]	700
Greece[c]	602[e]	602	600	600	600
Guinea[c]	640	650[e]	480	500	550
Hungary	208	76	138	145[d]	150
India[c]	1,780	1,860	1,890	1,900	2,000
Ireland	1,234	1,273	1,200[c]	1,200[c]	1,200
Italy	881	913	930	973	950
Jamaica	3,200	3,394	3,440	3,570	3,600
Japan[g]	337	368	359	335[d]	340
Kazakhstan	1,083	1,095	1,085	1,152	1,200
Romania	261	282	250	277	417[e]
Russia	2,105	2,400[c]	2,465	2,657	2,850
Serbia and Montenegro	186	160[c]	153	156	250
Slovakia[c]	100	100	100	100	100
Slovenia	88	85	70[c]	70[c]	70
Spain[h]	1,095	1,110	1,100[c]	1,200[c]	1,200
Suriname[c]	1,600	1,600	1,600	0[d]	0
Turkey	159	164	157	159[d]	155[e]
Ukraine	1,000[e]	1,080[c]	1,291	1,230	1,360
United Kingdom	99	100[c]	96	90[d]	100
United States	4,700	5,090	5,650[d]	5,140[d]	4,780[e]
Venezuela	1,701	1,730	1,553	1,335	1,400
Total	*44,000*	*46,000*	*47,400*[d]	*47,000*[d]	*49,300*

[a] From Ref. 116.

[b] Figures represent calcined alumina or the total of calcined alumina plus the calcined equivalent of hydrate when available; exceptions, if known, are noted. World totals, U.S. data, and estimated data are rounded to more than three significant digits; may not add to totals shown. Table includes data available through July 25, 2001.

[c] Estimated.

[d] Revised.

[e] Reported figure.

[f] Production shaprly curtailed or ceased.

[g] Data presented are for alumina used principally for specialty appalications. Information on aluminum hydrate for all uses is not adequate to formulate estimates of production levels.

[h] Hydrate.

for refractories (qv), for abrasives, and for ceramics (qv). Calcined aluminas are also used in the manufacture of tabular alumina and calcium aluminate cements (CAC).

World output of alumina increased 5% in 2000. Principal producing countries were Australia, the United States, China, and Jamaica. They accounted for 60% of world production. See Table 3 for world production data (116).

The United States depends on imports for one half of its metallurgical requirements despite the fact that it is one of the top four producers. Table 4 shows export/import data for the United States (117). Average annual value of U.S. imports of calcined alumina was \$226/t fas port shipment and \$238/t cif U.S. (116).

Capacities of U.S. plants are given in Table 5. Annual capacity was 6.35×10^6 t with four Bayer refineries in operation. Of the total alumina used, 90% went to primary aluminum smelters and the remainder went to nonmetallurgical uses (116).

Metallurgical-grade alumina spot prices began the year 2000 at \$375–385/t, in mid-year prices rose to \$420–440/t, and at year-end, prices dropped to \$165–175/t. The alumina market ended in 2000 in an oversupply of product. This continued into the first half of 2001 (116).

Table 4. **U.S. Imports and Exports of Alumina, t, calcined equivalent**[a,b] **(metric tons, calcined equivalent)**

Country	2001	2002 First quarter	2002 Second quarter	2002 Year to Date
Imports (for consumption)[c]				
Australia	1,810,000	421,000	451,000	872,000
Canada	83,800	23,900	21,300	45,200
India	2,830	54	21	75
Jamaica	278,000	93,300	45,900	139,000
Suriname	654,000	195,000	140,000	335,000
Other	272,000	31,200	42,600	73,800
Total	*3,100,000*	*764,000*	*701,000*	*1,460,000*
Exports[d]				
Brazil	1,420	276	331	607
Canada	1,100,000	292,000	207,000	498,000
Mexico	35,000	16,200	9,670	25,900
Other	107,000	13,400	48,500	61,900
Total	*1,250,000*	*322,000*	*265,000*	*587,000*

[a] Ref. 117. U.S. Census Bureau; data adjusted by the U.S. Geological Survey.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

[c] Includes imports of aluminum hydroxide: 159,000 tons in 2001; 31,800 tons in the first quarter, and 45,300 tons in the second quarter of 2002.

[d] Includes exports of alumina from the U.S. Virgin Islands to foreign countries. Includes exports of aluminum hydroxide: 36,600 tons in 2001; 16,500 tons in the first quarter, and 10,300 tons in the second quarter of 2002.

Table 5. **Capacities of Domestic Alumina Plants, × 10^3 t/yr**[a,b]

Company and Plant	1999	2000
Alcoa Inc.		
Point Comfort, Texas	2,300	2,300
St. Croix, VI[c]	600	600
Total	*2,900*	*2,900*
BPU Reynolds, Inc., Corpus Christi, Texas	1,600	1,600
Kaiser Aluminum & Chemical Corp., Gramercy, La.	(4/)[d]	1,250[d]
Ormet Corp., Burnside, La.	600	600
Grand total	*5,100*	*6,350*

[a] From Ref. 116, as of Dec. 31.

[b] Data are rounded to no more than three significant digits; may not add to totals shown. Capacity may vary depending on the bauxite used.

[c] Temporarily shutdown.

[d] Damaged in an explosion, partial restart in December 2000.

4. Uses

4.1. Ceramics.

Calcined aluminas are used in both electronic and structural ceramics (see ADVANCED CERAMICS). Electronic applications are dominant in the United States and Japan whereas mechanical applications are predominant in Europe (1). Specialty electronic integrated circuit packages generally use the low soda and thermally reactive aluminas.

Enamels, glass, chinaware glazes, china and hotel ware, and electrical porcelain insulators usually contain 5 to 25% alumina additions to increase strength and chip resistance, whereas electronic and mechanical alumina ceramics contain greater than 85% Al_2O_3 as calcined alumina. Coarse crystalline (2 to 10 μm) aluminas having 0.05 to 0.20% Na_2O are used in spark plug insulators which is the largest use of alumina in the electronics field. High purity 99.99% Al_2O_3 (2,3) is used to make translucent polycrystalline alumina tubes for sodium vapor lamps. Traditional glass tubes allow significant sodium diffusion at the operating temperatures of the sodium vapor lamps. All varieties of calcined aluminas are used in mechanical and technical applications. But when optimum hardness, density, and wear resistance are required, the thermally reactive aluminas are used in 95% and higher Al_2O_3 compositions. Lower price, normal soda calcined aluminas are used in compositions as low as 85% Al_2O_3 whenever lower performance can be tolerated.

Cutting tools of thermally reactive, high purity aluminas in combination withzirconia, titanium carbide ortitanium nitride, the SIALONS, and boron, nitride have high mechanical strength, fracture toughness, and cutting behavior for high speed cutting of hard steel and cast iron. High mechanical strength, fine surface finish, high density, and high purity are also the requirements for alumina ceramics used in prosthetics such as hip joints and dental implants.

Other alumina ceramic applications include ceramic armor for bulletproof vests, balls and rods for grinding media, abrasion-resistant tiles for lining coal and ash transfer lines in power stations, electrical high tension insulators, bioceramics, integrated electronic circuits, vacuum tube envelopes, r-f windows, rectifier housing, integrated circuit packages, and thick and thin film substrates.

4.2. Abrasives. Special unground calcined aluminas are used both as feedstock in the manufacture of white fused alumina and as abrasives themselves. Fused alumina production processes and applications have been documented (2,47,48). Graphite electrode, arc-resistance type furnaces are used to melt the calcined alumina in large water-cooled steel shells/pots. The optimum unground calcined alumina contains less than 1 μm crystals having a low water adsorptive capacity of about 1% LOI at 1100°C after exposure to 44% rh. This nominally 100 to 325 mesh (149 to 44 μm) free-flowing, sandy alumina provides good coverage of the fused alumina melt. Dust losses are reduced by minimizing the −325 mesh fraction. Controlled water and fluoride additions are claimed to improve whiteness or discoloration by increasing conductivity at the electrode−melt interface (114,115).

A method for using recycled aluminum oxide ceramics in industrial application has been reported (118). Alumina ceramics products which 90−97.5 wt% aluminum oxide content have been made (119).

Calcined aluminas are also used for polishing applications by mixing into polishing compounds in the form of paste or suspensions. Polishing aluminas are used to alter the surfaces of metals, plastics, glass, and stones in the manufacture of cutlery, automobiles, computers, furniture, eyewear, semiconductors, and jewelry. Polishing aluminas are also used to coat surfaces, such as video tapes (1).

4.3. Refractories. Calcined alumina is used in the bond matrix to improve the refractoriness, high temperature strength/creep resistance, and abrasion/corrosion resistance of refractories (1,2,4,7). The normal, coarse (2 to 5 μm median) crystalline, nominally 100% α-Al_2O_3, calcined aluminas ground to 95% −325 mesh are used to extend the particle size distribution of refractory mixes, for alumina enrichment, and for reaction with chemical binders and/or clays for reaction bonding. One or more of the calcined aluminas are utilized in amounts to 10% for special refractories requiring optimum density (4,55).

Unground calcined aluminas are also used as feedstock in the production of fused refractory fibers, bubbles, aggregate, and fused-cast alumina refractories. Abrasive grade calcined alumina is satisfactory for production of all, except for the fused-cast refractories which require a hard-burned Bayer alumina calcined to a low (less than 0.2% ignition loss after exposure to 44% rh) water adsorptive capacity to minimize porosity. Low sulfur requirements for both abrasive and fusion-cast grades of calcined alumina limit the type of fuels that can be used for calcining. The alumina bubbles and $Al_2O_3{\cdot}SiO_2$ ceramic fibers are used to produce insulating refractories having high porosity and low density structures. A process for producing aluminum oxide fibers has been patented (120).

Refractories made using aluminas are used in the iron and steel, chemical and petroleum, ceramics and glass manufacture, minerals processing (cement, lime, etc), public utilities, waste incineration, and power generation industries.

Porous high-alumina fused cost refractory having corrosion resistance and methods of production are discussed in Ref. 121. Aluminum oxide is also used in semiconductors (122–124).

5. Tabular Alumina

Tabular alumina is a high density, high strength form of α-Al_2O_3 made by sintering an agglomerated shape of ground, calcined alumina. It is available in the form of smooth balls having diameters from 3 to 25 mm and imperfect 19 mm diameter spheres, which are crushed, screened, and ground to obtain a wide variety of graded, granular, and powdered products having various particle size distributions ranging from a top size of 12.7 mm to −325 mesh (44 µm).

Tabular alumina is a recrystallized, sintered α-Al_2O_3 that gets its name from the large, elongated, flat, tablet like corundum crystals, typically 50 to greater than 400 µm, that develop upon rapid heating of briquettes or balls. It is also characterized by closed spherical porosity (about 5–8%) entrapped in the large crystals during rapid sintering of the less than 1 µm α-Al_2O_3 crystals. Open porosity is characteristically low, being less than 5% and typically 2 to 3% (55).

Tabular alumina processing is similar to that required for making sintered alumina ceramics. Ground calcined alumina is shaped by agglomerating, extruding or pressing, and sometimes using organic binders. The compacted pieces are recrystallized upon sintering at 1873–2123 K, producing a 3.40–3.65 t/m^3 bulk-specific gravity product (99.5% Al_2O_3) having closed spherical porosity, typical of a fully sintered ceramic with secondary crystallization. Impurities typically include about 0.05% SiO_2, 0.05% Fe_2O_3, and less than 0.1–0.4% Na_2O. The lower soda levels are evident in the U.S. products; the higher level in Japanese and European products. Extensive magnetic separation is required to remove iron from the crushed grain to minimize discoloration in ceramic and refractory products. Some processes have been patented (55).

Not all sintered aluminas are tabular Al_2O_3, primarily because sintering aids, such as MgO compounds, are used to achieve densification at lower temperatures and the resultant α-Al_2O_3 crystal size is not large enough to warrant the distinction of tabular Al_2O_3. Such dense sintered alumina grain exhibits poor thermal shock characteristics in comparison with tabular alumina.

6. Uses

The large α-Al_2O_3 crystals containing closed round pores make tabular alumina an excellent refractory raw material. Advantages include: high refractoriness; high fusion point; good abrasion resistance; excellent hot load strength; low creep; good resistance to chemical attack; high density; low permeability; low reheat shrinkage; good thermal shock resistance; and high purity, minimizing system contamination.

Tabular alumina is the ideal base material for high alumina brick and monolith liners in the metal, ceramic, and petrochemical industries. Applications in the steel industry include alumina slide-grade valves, nozzles, shrouds, weir plates, impact pads, runners, troughs, torpedo car linings, tap holes, high alumina brick, ladle linings, snorkles, and lances. Tabular alumina is universally accepted as the most effective alumina aggregate for manufacture of mullite-bonded and carbon-bonded alumina slide-gate plates used to control the flow of steel from 250 tons and larger ladles.

Tabular alumina also offers advantages over other materials as an aggregate in castables made from calcium aluminate cement as the binder and in phosphate-bonded monolithic furnace linings in all thermal processing industries. Other applications include their use in electrical insulators, electronic components, and kiln furniture. Applications other than refractories and high Al_2O_3 ceramics include molten metal filter media (125), ground filler for epoxy and polyester resins (see FILLERS), inert supporting beds for adsorbents or catalysts, and heat exchange media, among others.

7. Aluminate Cement

Refined calcined alumina is commonly used in combination with high purity limestone [1317-65-3] to produce high purity calcium aluminate cement (CAC). The manufacture, properties, and applications of CAC from bauxite limestone, as well as high purity CAC, has been described (104). High purity CAC sinters readily in gas-fired rotary kiln calcinations at 1600–1700 K. CAC reactions are considered practically complete when content of free CaO is less than 0.15% and loss on ignition is less than 0.5% at 1373 K.

Table 6. **Characteristics of Calcium Aluminate Cement (CAC) Mineral Constituents**[a]

Mineral[b]	Chemical composition, wt % CaO	Chemical composition, wt % Al_2O_3	Melting point, K	Molecular weight	Density, g/cm^3	Crystal system
C	99.8		2843	56.1	3.25–3.38	cubic
$C_{12}A_7$	48.6	51.4	1633–1663	1387	2.69	cubic
CA	35.4	64.6	1873 2023–2038	158	2.98	monoclinic (triclinic)
CA_2	21.7	78.3	decomposes	260	2.91	monoclinic
C_2S[c]	65.1		2339	172	3.27	monoclinic
C_4AF[d]	46.2	20.9	1688	486	3.77	orthorhombic
C_2AS[e]	40.9	37.2	1863	274	3.04	tetragonal
CA_6	8.4	91.6	2103	668	3.38	hexagonal
α-A		99.8	2324[a]	102	3.98	hexagonal

[a] Ref. 2.
[b] $A = Al_2O_3$, $C = CaO$, $F = Fe_2O_3$, and $S = SiO_2$.
[c] Contains 34.9% SiO_2.
[d] Contains 32.9% Fe_2O_3.
[e] Contains 21.9% SiO_2.

Table 6 lists the characteristics of CAC mineral constituents that can occur in CAC of varying purities. The primary hydraulic setting cement phase in all CAC grades is CA [12042-68-1], $CaO{\cdot}Al_2O_3$; the main secondary phase in 70% Al_2O_3 CAC is CA_2, [12004-88-5], $CaO{\cdot}2Al_2O_3$. CA_2 and $C_{12}A_7$ [12005-57-1], $12CaO{\cdot}7Al_2O_3$, occur in minor amounts in the 80% Al_2O_3 CAC products. The $C_{12}A_7$ phase reacts rapidly with water to initiate hydraulic bonding and early strength development for rapid mold removal when manufacturing precast shapes. A significant advantage of CAC over Portland cement is its rapid strength development, developing in 24 hours of moist curing, the same proportional strength as Portland cement after 28 days. CA_6 [12005-50-4], $CaO{\cdot}6Al_2O_3$, is the only nonhydrating CAC phase.

Emplaced CAC concrete should be moist cured at temperatures greater than 294 K to avoid explosive steam spalling upon heating after the curing cycle. Below 294 K, an alumina gel forms reducing the permeability of the refractory lining. Low permeability has resulted in severe explosions during heatup of thick (>10 mm) linings. At temperatures above 300 K, the gel crystallizes into $Al(OH)_3$ resulting in increased permeability.

CAC castables have rather short working times for placement in comparison to Portland cement concretes. Thus, preconditioning, mixing, and placement of CAC refractory concrete at lower (about 285–290 K) temperatures is favored. This provides sufficiently long placement times to minimize formation defects, which enlarge on drying and firing restricting strength development. Immediately after placement, the temperature of the lining should be increased to above 300 K while being covered with polyethylene plastic sheet or a curing compound to prevent water loss during the moist curing. Hydraulic, dried, and fired strengths increase in proportion to the moist curing time used, but strength development becomes asymptotic after 48–96 hours.

8. Uses

High purity CA cements are primarily used as binders for high strength refractory castables to form linings up to about 1.0 m thick, as, for example, in iron blast furnaces. Since the 1970s, large monolithic precast CAC castable shapes have found increased usage in a variety of specialty fired shapes that are too expensive to be inventoried.

The high purity CAC finds extensive use as an efficient binder for other aggregates such as fire clays, kaolin, and alusite, kyanite, pyrophyllite, sillimanite, mullite, and refractory grade bauxite, having the added advantage of increasing the refractoriness of some of these aggregates. The many applications cited for tabular alumina in refractories are also common for high purity CAC.

High purity CAC is also used as a steel slag conditioner during ladle refining of steel. CAC clinker in the unground form is added to the steel ladle either prior to or after filling the ladle with steel to form a clean slag, after first removing most of the dirty slag used to protect the steel from oxidation in the transfer ladles. The nominal 50 to 65% Al_2O_3 CAC clinker melts rapidly to provide a protective insulating layer over the molten steel, prevent oxidation, entrap and remove sulfur and metal oxide inclusions from the steel during mixing.

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