

## **13. NON-METALLURGICAL USES OF BAUXITE, HYDRATE, AND ALUMINA**

Most of the alumina produced in the world is used to produce aluminum metal. However, part of the alumina hydrate and alumina produced (up to 10% as equivalent alumina) is used for non-metallurgical purposes.

There are many non-metallurgical uses for alumina hydrate and alumina:

- Major uses of alumina hydrate are for fillers, fire retardants, white pigment, activated alumina (adsorbent), catalyst substrate and aluminum based chemicals.
- Major uses of alumina are for ceramics, refractories and abrasives. The alpha crystal form of alumina has a very high melting temperature (2000°C) and is next to diamond in hardness.

Non-metallurgical bauxite is used for refractories, abrasives, proppants, and chemicals. About 5% of bauxite mined is used for non-metallurgical purposes.

The papers in this section are a summary of the typical or classical non-smelter uses for alumina as well as innovative uses for alumina such as air pollution control.

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## NON-METALLURGICAL USE OF ALUMINA AND BAUXITE

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Introduction

The CAS registry lists over 5000 aluminum containing compounds exclusive of alloys and intermetallics. With few exceptions, bauxite is the raw material for all aluminum compounds that do not occur naturally. The exceptions include nepheline and alunite in the USSR and Poland, and possibly some carbochlorination of clay in the United States.

Western world bauxite production is presently over 90 million metric tons per year. Approximately 90% is refined to aluminum hydroxide by the Bayer process [1], and about 90% of that is calcined to produce smelting grade alumina.

The largest worldwide market for a manufactured aluminum-containing compound is metal grade alumina. In 1990 that market is estimated to be over 30 million metric tons. Second, of course, is aluminum hydroxide with its applications as an additive filler or feedstock for other chemical manufacture.

In 1990 the market for  $\text{Al}(\text{OH})_3$  should approach or exceed 3.5 million metric tons. The split between additive and feedstock applications is roughly 50:50.

The non-metallurgical uses for bauxite, aluminum hydroxides, alumina and derived products include: abrasives, adhesives, cement, glass manufacture, ceramics, refractories, catalysts and catalyst support systems, fire retardant products, cosmetics, toothpaste and tooth implants, deodorants, antacids, artificial bone for body joints, mordants, dyes, detergents, zeolites, paint, titania pigment coating, paper sizing, integrated circuit manufacture, armor applications, cutting tools, fibers, sodium vapor lamps, and separation systems that remove impurities from liquids and gases.

The versatility of aluminum compounds, particularly the hydroxide and oxide, was eloquently described by Francis C. Frary in his Perkin Medal lecture of 1946, entitled "Adventures with Alumina." "Aluminum oxide and its hydrates present a variety of amazing contracts. From the hardness of sapphire to a softness similar to that of talc, from an apparent density of over 200 pounds to one of about 5 pounds per cubic foot, from high insolubility and inertness to ready solubility in acids or alkalis and marked activity, the properties can be varied over wide limits. Some forms flow and filter like sand; others are viscous, thick, unfilterable, or even thixotropic. Crystals may be of any size down to a fraction of a micron in diameter, with various allotropic forms, and there are also amorphous forms. Some are catalytically active, others inactive. But they are all converted into  $\alpha$ -alumina (corundum) of heated hot enough and long enough."

Bauxite

The term bauxite originates from the location of the deposit discovered in 1821 near the village of Les Baux in Provence, France.

Bauxite is weathered rock consisting mainly of aluminum hydroxide minerals with relatively small and variable amounts of silica, iron oxides, titanium oxide, and alumina silicate clays.

The major uses for bauxite outside of the aluminum industry are in refractories, abrasives, chemicals, aluminous cements, and miscellaneous products like proppants. Bauxites for these markets must meet more rigid compositional requirements with respect to the iron oxide, silica, and titania contents than those used for aluminum production. Refractory and abrasive grades of bauxites are calcined and chemical grades are dried before being sold. Chemical grade bauxite is consumed mainly in the production of aluminum sulfate for paper manufacture.

The chemical compositions and locations of bauxites produced for uses other than aluminum production and particular compositions required for given markets is well documented in Reference [2].

Aluminum Hydroxides

Two relatively recent publications (3,4) have dealt in detail with various aspects of the production and applications of aluminum hydroxides. Our discussion here will cover some of the commercially important areas of the industry.

Although most bauxite refining plants are geared to the production of metal grade alumina, all major alumina producers have converted part of their capacity to supply chemical grade aluminum hydroxide to take advantage of the higher prices for these grades. The production of these chemical grade hydroxides, differing in particle size, purity and other properties from the metallurgical grade, have required considerable capital investment in separate processing facilities and development activities.

The generic term alumina hydrate is used in industry to cover several different aluminum hydroxides (Figure 1). To be technically correct, these compounds are true hydroxides and do not contain water of hydration.

Aluminum hydroxide obtained from the Bayer refining plant is normally off-white; organic impurities originating from bauxite and present in the caustic liquor impart a yellowish color to the hydroxide. The soda sinter process applied to bauxite (or bauxite



residue as in the Combination process) produces a hydroxide that is completely free from organic coloring matter and is very white. Very few sinter plants are, however, in operation today because of high energy costs, and attempts have been made to satisfy the market demand for white hydroxide by various purification methods. These include reprocessing of Bayer hydroxide by dissolution in caustic and high temperature treatment (liquor burning) of the Bayer process liquor to destroy organic impurities.

Many applications of aluminum hydroxides require smaller particle sizes. These products are obtained mostly by grinding the dry hydroxide from the refining plant, followed, if necessary, by size classification. Various types of grinding equipment have been used: ball mills, vibrating mills, hammer mills, air jet micronizing systems, etc. Aluminum hydroxide is relatively easy to grind; consistency of particle size distribution is important in the production of ground hydroxides.

Direct precipitation of a finer hydroxide having the desired particle size distribution has been attempted, but is not practiced widely. Filtration, washing and drying of the fine product are more difficult requiring additional capital and operating expenses. The production of very fine hydroxide of about 1 μm particle size is, however, carried out by direct precipitation from Bayer process liquor. Precipitation is carried out under carefully controlled conditions using specially prepared seed hydroxide to yield fine, uniform hydroxide particles. Recently, some fine (<1 μm) hydroxide products obtained by attrition milling of Bayer material have appeared in the market.

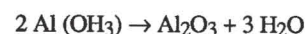
The various hydroxide grades can be surface-treated to modify dispersion behavior and slurry rheological properties. The most widely used surface coating agents are stearic acids and stearates. Various organo-functional silane compounds have been used as "coupling agents" to give improved performances in polymer filler applications of aluminum hydroxides.

Flame Retardant Filler in Plastics and Polymer Systems

Aluminum hydroxide (ATH) from the Bayer process is an inorganic mineral product that has all the requirements to be an effective filler: white or near-white color, large volume production base ensuring

dependable supply, consistency of physical and chemical properties, availability in a wide range of particle size distributions, chemical inertness, non-toxicity, and, finally, cost-effectiveness. Its wide use as a filler is, however, strongly related to its fire-retardant and smoke-suppressant properties.

The use of ATH as a fire retardant filler in plastics is extensively reported in the literature (3,4). All fire retardants work by interfering with one or more stages of the combustion process. Aluminum hydroxide operates primarily in the first two stages of the combustion process: heating and decomposition. Aluminum hydroxide decomposes above 200°C to give alumina and release water vapor by the reaction:



This reaction is strongly endothermic, absorbing approximately 280 cal/g of hydroxide. The maximum decomposition rate occurs between 300 and 350°C, which roughly corresponds to the range of decomposition temperature of most commonly used polymers. Thus, when a polymer containing aluminum hydroxide is heated, the aluminum hydroxide decomposes endothermally, acts as a heat sink, and slows the rate of temperature rise and the rate of decomposition of the polymer. As a secondary effect, the water vapor given off also serves to dilute any combustible gases evolved; thus, their ignition is more difficult.

The smoke-inhibiting activity of aluminum hydroxide fillers has been attributed to its promotion of solid-phase charring instead of soot formation. Smoke suppression is also probably related to endothermic dehydration, because heat dissipation in the condensed phase reduces pyrolysis and favors competing cross-linking reactions.

With a Mohs hardness of 2.5, aluminum hydroxide (gibbsite) is only moderately abrasive; thus, wear of the processing machinery is minimal. Because gibbsite is a crystalline product, its surface has low sorptive capacity and hence does not increase resin demand in liquid polyester, epoxy, and acrylic systems. When used as a filler in plastics exposed to electric arcing, ATH contributes to increased arc and track resistance.

Although offering these desirable features, aluminum hydroxide has some disadvantages that impose some limitations on its use as a filler. Like many other nonreinforcing mineral fillers, aluminum hydroxide generally lowers strength properties. Because it undergoes thermal decomposition, aluminum hydroxide is not suitable for processing above the temperature of about 200°C. The decomposition behavior shows rapid water release above 220°C.

Although Bayer aluminum hydroxide is slightly more expensive than other mineral fillers, its cost advantage as a fire-retardant filler has contributed to its popularity. The material is relatively low in cost compared to other flame retardants such as antimony and bromine compounds. Aluminum hydroxide is easy to handle, is nontoxic, is free of halogens, and does not produce corrosive or toxic decomposition products. Unlike many organic additives, aluminum hydroxide is not volatile, is odorless, and is chemically inert. White grades that do not discolor on aging are available.

Significant strength reduction occurs in thermoplastics as hydroxide loading is increased, and this reduction combined with the temperature constraint has been largely responsible for restricted usage in this area of applications. Efforts have been made to improve strength properties of filled plastics by the use of coupling agents such as silanes. The silane bonds the inorganic filler to the organic polymer; increased physical strength results.

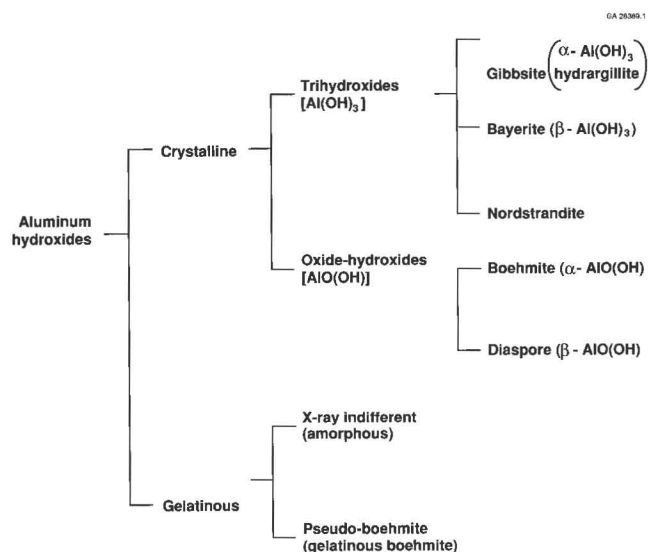


Figure 1: Classification of aluminum hydroxides.



The various polymer systems where aluminum hydroxide has been successfully employed as a filler are given in Table 1. The material became a popular filler by the late 1960s. Its use gained considerable momentum with the passing of consumer safety-oriented legislation in the United States and other countries that made it mandatory for products such as synthetic rubber carpet backings, automobile furnishings, etc., to possess a certain degree of flame retardancy. Aluminum hydroxide then began to replace calcium carbonate as a filler in these products. The next major market for aluminum hydroxide was in glass-reinforced unsaturated polyesters, and here again developments closely followed the passage of flammability regulations. Public awareness and demand for safety in plastic usage should continue to support the growing use of aluminum hydroxide fillers in the future. The estimated U.S. consumption of aluminum hydroxide as a filler in rubber and plastics was around 500,000 tons in 1988. The major market for this material continues to be the carpet industry, where it is used as a filler in latex foams and adhesives for carpet backing. Approximately 250,000 tons was used for this application in 1988. About 200,000 tons was used in plastics, a large part of which went into glass-fiber-reinforced polyester products. Vinyls, epoxies, and polyolefines consumed smaller amounts. Polyurethanes and poly(vinyl chloride) (PVC) are considered to be potentially major application areas in the future.

Table 1 Polymer Systems Using Aluminum Hydroxide as a Filler

Thermoset	Thermoplastic	Elastomeric
Epoxy	Acrylic	Neoprene
Phenolic	PVC	SBR
Polyester	Polyethylene	Natural rubber
Spray up	Polypropylene	Butyl rubber
Hand lay up		Nitrile rubber
Foam		EPDM
SMC		Silicone rubber
BMC		
Polyurethane		

Recent developments in the area of filler applications include:

- a. Variations in the morphology of aluminum hydroxide particles to enhance reinforcement properties.
- b. Surface modification to produce delayed decomposition so that the product can be used in higher temperature engineering plastics.
- c. Reduction in soda (Na<sub>2</sub>O) content for improved performance, particularly in electrical insulation applications.

Synthetic Marble/Onyx

The synthetic marble industry has seen tremendous growth since its modest beginnings in the late sixties. Aluminum hydroxide is now the preferred filler (up to 70% by weight) in these products leading to the "onyx" marble look highly desired by consumers. The pleasing visual effects of onyx synthetic marble are created by the close similarity between the refractive index of aluminum hydroxide and that of the polyester resin. The synthetic products have many advantages over natural marble: lower cost, weight, stain resistance, less brittleness, color matching, easy workability and importantly, customization of shape without joints and seams. The major applications initially were counter tops for bathrooms and kitchens, but this has now spread to very attractive furnishing of

whole bathrooms, kitchens, and other interior decor areas. The industry has developed so rapidly that special onyx grade aluminum hydroxides are now being offered by manufacturers.

These products are carefully controlled for whiteness, particle size distribution and processing behavior such as mix viscosity and gel time.

Pigment Applications

ATH is used commercially as a white pigment. High whiteness and a fine particle size (0.1-1 μm) are essential requirements for pigment-type applications. Major efforts have been made by alumina producers to penetrate the pigment area against other minerals such as chalk (calcium carbonate), clay (kaolin) and talc (magnesium silicate). Reasonable success has been achieved in the paper industry but consumption in the paint industry has not been significant.

Fine ATH has been used both as a filler and as a coating pigment for paper. The advantages of using ATH in these applications have been well documented (5). The platy structure of fine precipitated ATH is claimed to improve smoothness and gloss compared to other fillers. ATH has also been used by the paper industry for the production of non-combustible paper and carbon-less copying paper.

Aluminum hydroxide has been used in a wide range of fire retardant coatings. Although the volume of use is rather small, their value is high and progressively increasing. These include fire-retarded acrylic mastic roof coatings and coatings for construction boards and other building products.

Aluminum Hydroxide in Toothpaste

The use of aluminum hydroxide in toothpaste remains an area of slow but steady development. New developments in toothpaste formulation could result in a favorable shift towards ATH as the main component of toothpaste compared to traditional ingredients, such as chalk and dicalcium phosphate.

Toothpaste formulation is primarily aimed at removal of adhering soiling matter from teeth without damaging teeth enamel. This is achieved by incorporating a mildly abrasive powder. ATH fills this need admirably; its hardness (2-3 in the Moh scale) is lower than enamel (4 in Moh scale) and it can be produced in the required particle size of 7-10 μm found to be optimum for the desired abrasive action. Other desirable qualities include high purity to meet FDA regulations, high whiteness and neutral flavor and taste.

Over the past several years, toothpaste formulations have been increasingly designed to provide prophylactic properties for healthier teeth and gums. This has led to the addition of fluorides, tartar control agents, etc. The availability of these components even after prolonged storage has become a major consideration. Future developments will seek to ensure that the abrasive component of the toothpaste will not interfere with (and possibly enhance) the ready availability and effectiveness of these agents.

The wide range and versatility of aluminum hydroxide products and applications is represented by the above discussion. Many other applications of lesser commercial importance can be found in technical and patent literature.

Activated Alumina

The activated aluminas are used extensively in adsorbent and catalytic processes. These materials are porous, high surface area solids produced by heating aluminum hydroxide precursors. They are available with a wide variety of purity and physical properties



which have been developed for specific applications. At the present time, annual U.S. consumption of activated alumina products is on the order of 50,000 tons.

Activated alumina materials can be divided into two categories depending on the precursor alumina used in their manufacture. One large category is based on thermal decomposition of Bayer process gibbsite and these products typically contain 0.2-0.4% Na<sub>2</sub>O as an impurity. Figure 2 shows the changes which occur when gibbsite is heated [6]. Between about 200 and 400°C hydroxyl groups are driven off (as evidenced by the weight loss) leaving a porous structure with a maximum surface area of about 350 m<sup>2</sup>/g. Further increase in temperature results in a reduction of surface area and increase in skeletal density. A pattern similar to that shown in Figure 2 is also obtained on heating the other aluminum hydroxides, bayerite and nordstrandite.

A second major category of activated aluminas is based on gelatinous or pseudoboehmite precursors which are made by rapid neutralization of aluminum salt or aluminate solutions or by hydrolysis of aluminum alkoxides. These materials are typically more expensive than the gibbsite-based materials and contain less sodium and other trace impurities. They are typically used in applications where sodium is detrimental to product performance or where the thermal stability of relatively pure phase gamma alumina is important.

Figure 3 shows the relationship of the various activated alumina phases to the precursor material and temperature of heat treatment [3]. The so-called "phases" are really transitional stages of the crystal structure which undergoes continuous and irreversible rearrangement on heating. The crystal structure of these materials affects both surface area and surface chemistry of the products. These properties are of prime importance since most applications for activated alumina involve some interaction of the activated alumina surface with a process stream. The distribution of acid and base sites on the surface largely determines the effectiveness of the desired interaction.

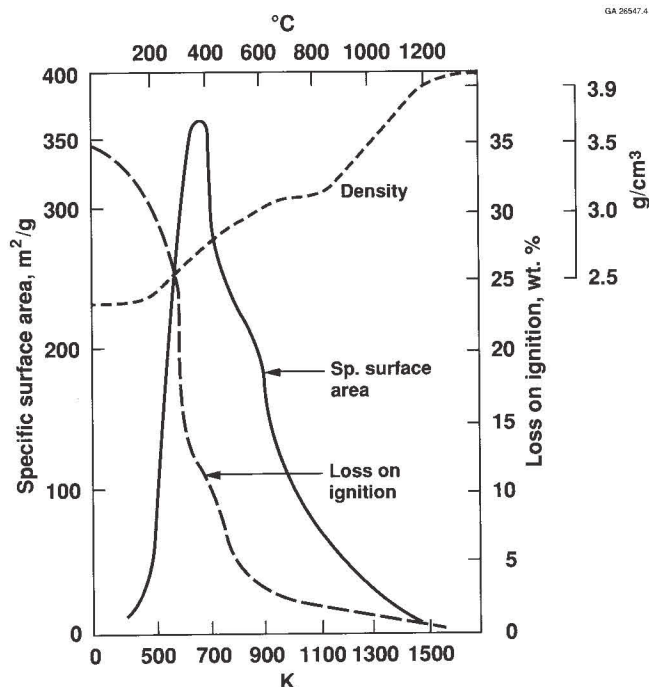


Figure 2: Properties of activated gibbsite.

Important physical properties of activated aluminas include particle shape, size, crushing strength, abrasion resistance, surface area and pore size distribution. The manufacturers of activated and catalytic aluminas have developed extensive technology to manufacture products with combinations of these properties tailored to specific applications [7].

#### Applications of Activated Alumina

Removal of water from air was one of the first commercial uses for activated alumina and it is still an important application. In practice, the air is passed through a fixed bed of alumina particles which can adsorb 10 to 15% by weight of water. The adsorption process is reversible and water can be removed from the bed by heating or by reduction in pressure. Beds of alumina can be regenerated hundreds of times with little loss of performance. The aluminas used in these operations tend to have high surface areas in the 250-350 m<sup>2</sup>/g range. Spherical particles 1/8 to 1/2 inch in diameter are widely used since this shape and size has been found to perform well in fixed bed operation. In addition to air drying, activated aluminas are used to remove water from a variety of other gases and organic liquids as shown in Table 2 [4].

Large quantities of activated aluminas are also used to remove trace impurities other than water from process streams [8]. A few examples are removal of phosphate, fluoride and arsenic from drinking water, removal of chlorides from petrochemical streams, recovery of fluorides from air in aluminum smelting operations and removal of carbonyl sulfide from propylene. Selective adsorption is becoming increasingly important due to increased energy costs and stricter environmental laws and is probably the fastest growing area of use for activated aluminas today.

In the field of catalysis, activated aluminas are widely used as the catalyst itself or as a catalyst support. The largest application where alumina serves as the catalyst is in the Claus process for recovering sulfur from natural gas and petroleum refinery operations. In one version of this process, gas streams containing SO<sub>2</sub> and H<sub>2</sub>S are passed through a bed of alumina spheres at about 300°C where they react catalytically at the alumina surface to form water and elemental sulfur. The sulfur vaporizes and is condensed downstream and recovered [9].

The largest application for activated alumina as a catalyst substrate is in hydrotreating of petroleum feedstocks [7]. The purpose of hydrotreating is to increase the H/C ratio of the petroleum and to remove undesirable contaminants which would otherwise interfere with downstream processing. Typical contaminants are organic compounds of 0.5 and N which are catalytically converted to H<sub>2</sub>O, H<sub>2</sub>S and NH<sub>3</sub> and leave with the process stream. Other impurities, especially in heavier feedstocks, are V and Ni compounds which accumulate on the catalyst, eventually deactivating it. In this application, the activated alumina is promoted with compounds of Co, Mo, W or Ni and is typically in the form of extrudates approximately 1 mm in diameter.

Automotive catalysts make use of activated alumina promoted with precious metals to oxidize hydrocarbons, carbon monoxide and nitrogen oxide to exhaust gases. In the most common type of reactor system, alumina powder is coated onto a porous ceramic honeycomb structure which provides mechanical support and a large contact area for the catalyst. Another type of system uses a bed of low density activated alumina balls as the catalyst support.

There are a number of smaller but still important applications where activated alumina is used as the catalytic substrate. These include alcohol dehydration, olefin isomerization, hydrogenation and polymerization.

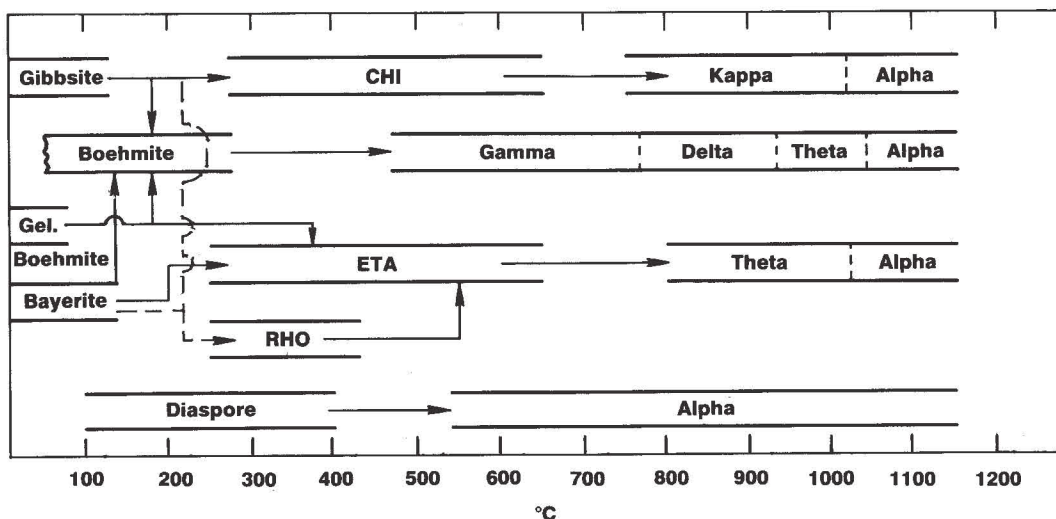


Figure 3: Transformation sequence Al(OH)<sub>3</sub> → Al<sub>2</sub>O<sub>3</sub>.

Chromatography is another field in which activated aluminas are finding application. Aluminas have long been used in the separation of organic compounds by normal phase chromatography. Recently, stable hydrophobic coatings have been developed which are allowing activated alumina to be used in reverse-phase chromatography [11]. Compared to silica, which is the dominant reverse-phase packing material, alumina has better stability at moderately high pH levels.

Specialty Calcined Aluminas

Commercial specialty calcined aluminas are produced by heating Bayer trihydroxides at about 1100° to 1450°C to obtain substantial amounts of α-Al<sub>2</sub>O<sub>3</sub>, the stable form of anhydrous alumina. The lower range of this thermal treatment is slightly above that required for metallurgical grade alumina. As a result, the surface area and resulting water adsorption values are lower. These specialty aluminas contain >70% α-Al<sub>2</sub>O<sub>3</sub> compared to only about 10 to 50% α-Al<sub>2</sub>O<sub>3</sub> for metal grade alumina.

Table 2 Variety of Gases and Organic Liquids Dried with Activated Alumina

GASES	
Acetylene	Helium
Air	Hydrogen
Ammonia	Hydrogen chloride
Argon	Hydrogen sulfide
Carbon dioxide	Methane
Chlorine	Natural gas
Cracked gas	Nitrogen
Ethane	Oxygen
Ethylene	Propane
Freon	Propylene
Furnace gas	Sulfur dioxide

LIQUIDS	
Benzene	Jet fuel
Butadiene	Kerosene
Butane	Lubricating oils
Butene	Naphtha
Butyl acetate	Nitrobenzene
Carbon tetrachloride	Pentane
Chlorobenzene	Propane
Cyclonexane	Pipe line products
Ethyl acetate	Propylene
Freon	Styrene
Gasolines	Toluene
Heptane	Transformer oil
Hexane	Vegetable oil
Hydraulic oils	Xylene

Gibbsites with various soda contents have been calcined in rotary kilns for many years and more recently in stationery or fluid-flash calciners, similar to those used for producing up to 1500 t/d metal grade alumina. However, only a few specialty calcines have sufficient commercial requirements to justify the 30-40% fuel savings afforded by the high production capacity fluid-flash calciners.

The degree of α-Al<sub>2</sub>O<sub>3</sub> crystallization is controlled during calcination by varying the temperature and duration of calcination and also by control of mineralizer additions. The halides and boron are effective mineralizers and provide significant energy savings by reducing the temperature for enhancing α-Al<sub>2</sub>O<sub>3</sub> crystal growth.

Even though about 35% water of crystallization is lost from the Gibbsite structure, very little particle shrinkage occurs during calcination. Thus, the nominally 100 to 325 mesh unground porous crystal agglomerates of calcined alumina approximate that of the hydroxide kiln feed. Calcined alumina grades may appear to be similar microscopically, but the scanning electron microscope (SEM) effectively differentiates the surfaces of the unground agglomerates. The ultimate crystals can be controlled to a median diameter as fine as 0.5 μm and as large as 15 μm. Calcined alumina physical properties begin to exhibit the effect of crystal size above about 2-3 μm. Particle density decreases, angle repose increases, attrition rate increases, and thus, bulk handling characteristics and dusting worsen with increasing crystal size.

Superground thermally reactive aluminas exhibit higher densification rates when compacted and sintered into ceramic products. Complete densification is obtained about 200°C lower than the continuously ground or coarse ground aluminas. Extensive dry batch ball milling (10 to >30 h) is required to separate the individual crystals from the alumina agglomerates.



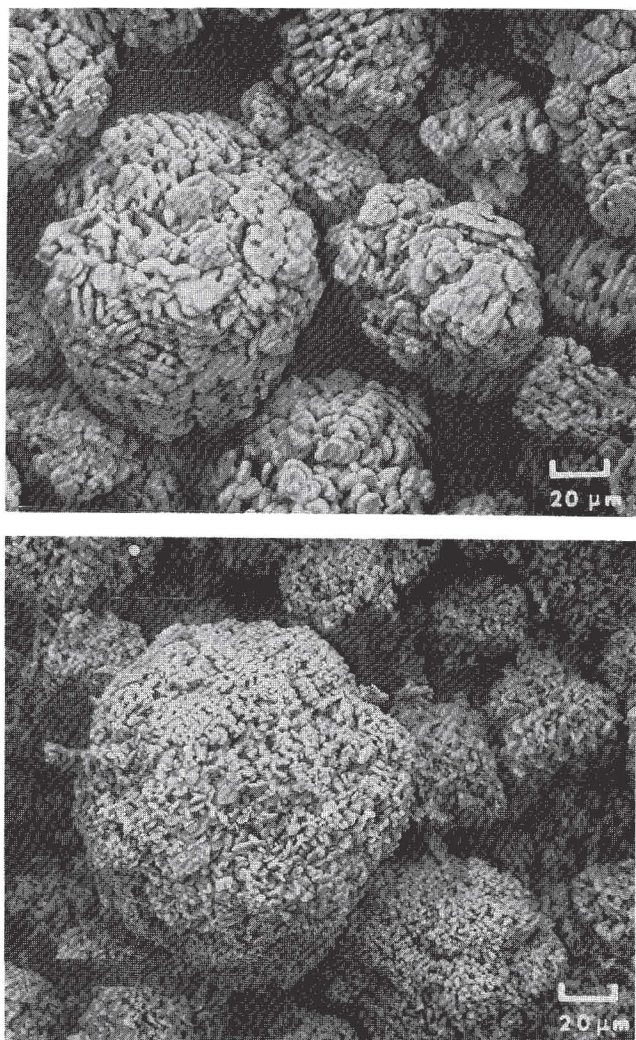


Figure 4: SEM photographs of controlled crystal size aluminas.

#### Specialty Calcined Alumina Applications

Specialty calcined Bayer aluminas are primarily categorized according to soda content and median crystal size. The degree of comminution provides further differentiation of calcined products and end-use applications. Processing costs generally increase with decreasing  $\text{Na}_2\text{O}$  content and degree of comminution. The various applications for calcined aluminas shown in Figure 5 are superimposed upon the median crystal size/ $\text{Na}_2\text{O}$  content grid with regard to alumina types used in the cited applications.

As noted, calcined aluminas are used in a wide variety of applications, including electrical, electronic and mechanical ceramics, glass, whitewares, refractories, abrasives, and polishing. Specialty calcined-alumina markets in 1988 are compared with estimates from the previous two decades in Table 3. The 1988 world non-metallurgical calcined alumina market is estimated to fall in the range 1.1 to 1.5 million metric tons.

The refractories market consumes about 50% of the non-metallurgical calcined alumina produced in the world. Iron and steel production consumes 50-60% of the world refractories. Thus, the proportion of non-metallurgical calcined alumina going into the various markets is highly influenced by the rate of world raw steel

production and the adoption of the latest iron/steel making technology. Advanced iron/steel processes require refractories made from consistent high-quality synthetic raw materials, like sintered tabular alumina, in substitution for the more variable natural raw materials. Improved predictable performance of refractories made from high-purity synthetic refractory aggregates is responsible for the large proportional increase in usage of calcined alumina by the refractories market between 1968 and 1975, even though refractory consumption per unit of steel production decreased significantly at the expense of refractories made from natural raw materials.

The use of zoned refractory linings, wherein high performance refractories are used only where needed, rather than throughout the entire vessel, is largely responsible for the proportional decline of the calcined alumina refractories market between 1975 and 1988. World raw steel production increased significantly during the past 15 years, despite a decrease in the United States raw steel production. The slower adoption of new iron/steel processes by United States compared to new Third World facilities being built and operated using the latest technology are contributing factors for declining United States output.

The shortage of Bayer alumina during 1988/89 resulting from the large increase in aluminum production caused specialty calcined alumina prices to increase significantly and initiated extensive research programs on attempting to qualify less costly substitute materials. Product substitution attempts continue in the refractories market even though prices have retreated significantly.

Future developments in alumina production will include greater emphasis on consistency, more uniform and finer crystal size, removal of alpha emitting particles and reduced impurities and improved particle density, porosity, and particle size control in tabular aluminas.

#### Tabular Alumina

Calcined Alumina is also converted to tabular alumina, a thermally stable form of  $\alpha\text{-Al}_2\text{O}_3$ . Tabular Alumina is a high-density, high-strength form of  $\alpha\text{-Al}_2\text{O}_3$  made by sintering agglomerated shapes of ground calcined alumina at 1800°-1900°C. At these temperatures the  $\alpha\text{-Al}_2\text{O}_3$  recrystallizes to form large, elongated, flat tablet-like corundum crystals, typically 50 to >400  $\mu\text{m}$  from which tabular alumina derives its name. The large tablet  $\alpha\text{-Al}_2\text{O}_3$  crystals are also characterized by the closed spherical porosity (about 5-8%) entrapped during rapid sintering of the <1  $\mu\text{m}$   $\alpha\text{-Al}_2\text{O}_3$  crystals. Open porosity is characteristically low, being <5.0% and typically 2-3%. The resulting particle density of this 99.5%  $\text{Al}_2\text{O}_3$  product is 3.40-3.65  $\text{g}/\text{cm}^3$ .

Typical impurities include about 0.5%  $\text{SiO}_2$ , 0.5%  $\text{Fe}_2\text{O}_3$  and <0.1-0.4%  $\text{Na}_2\text{O}$  with lower levels occurring in the United States-products and the higher levels in Japanese and European-products. Iron is removed from the crushed grains to minimize discoloration in ceramic and refractory products by using extensive magnetic separation.

Tabular alumina is available in the form of smooth balls (3 to 25 mm) and imperfect 19 mm spheres, which are crushed to grains and ground to obtain a wide variety of graded, granular, and powdered products with various particle size distributions ranging from a top side of 12.7 mm (0.5 in.) to -325 mesh (44  $\mu\text{m}$ ).

#### Tabular Alumina Applications

The major market for tabular aluminas is refractories. It excels in critical applications in the steel industry, including slide gate valves and nozzles, shrouds/submersion nozzles, injection lances, snorkels, impact pads and monolithic ladle linings because of its



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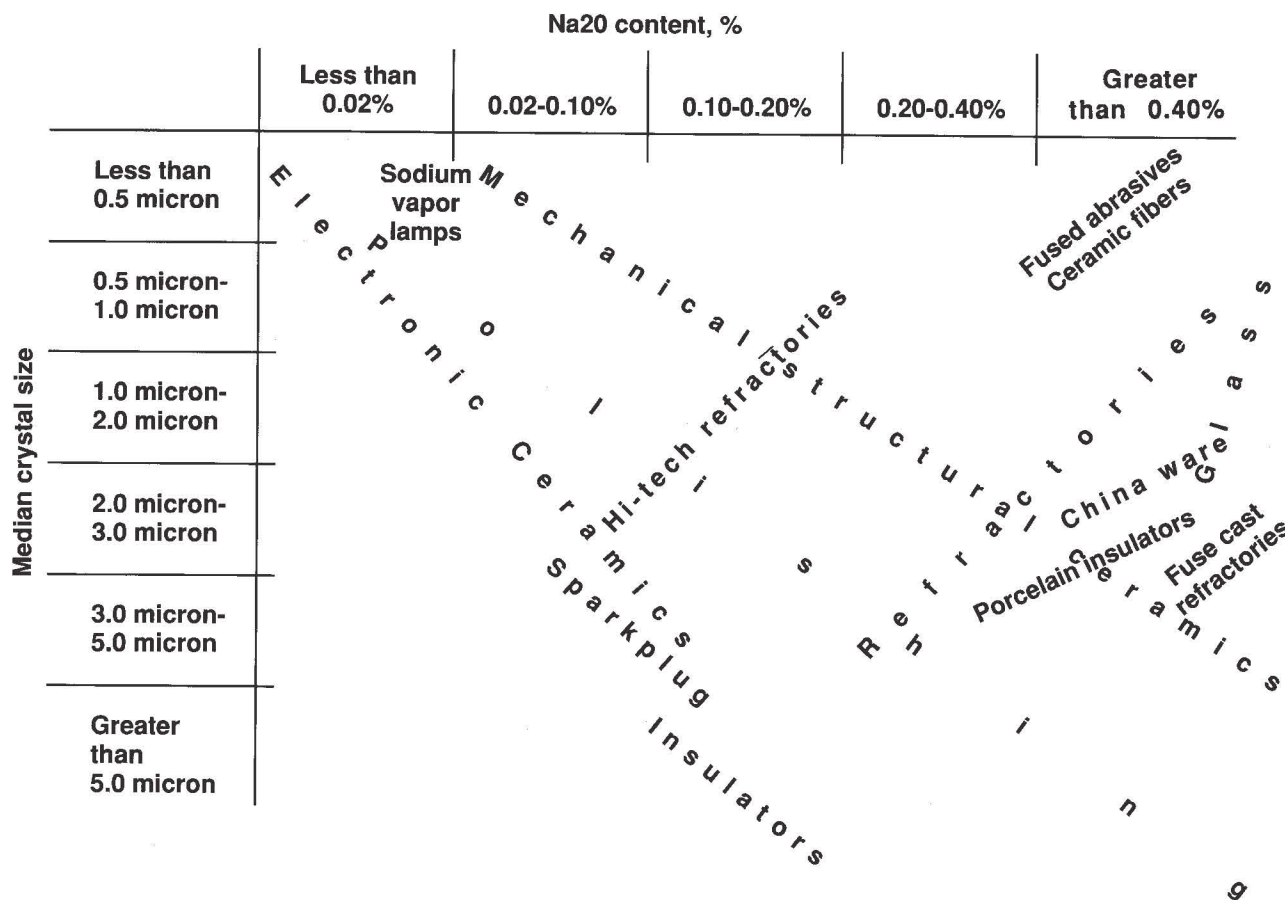


Figure 5: Specialty calcined alumina application requirements.

excellent thermal spall resistance, high temperature strength and abrasion resistance, chemical and thermal inertness and purity has also found proven application as an inert catalyst support and heat exchange media, saggars for firing electronic and technical ceramics, fillers for resins and investment casting molds.

Chemical Feedstock Applications

Feedstock applications of Al(OH)<sub>3</sub> for production of other chemicals for non-metallurgical uses are numerous. The direct application for production of refractories, calcined and activated aluminas have already been discussed. In this section, a number of economically significant compounds produced from Al(OH)<sub>3</sub> feedstock are discussed.

Aluminum sulfate, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> • 18 H<sub>2</sub>O, which is also known as alum cake, is industrially produced by reaction of Al(OH)<sub>3</sub> with sulfuric acid in agitated pressure vessels at about 170°C. The commercial product has about 10% less water of hydration than the theoretical amount. Aluminum sulfate has largely replaced alums for the major applications as a sizing agent in the paper industry and as a coagulant to clarify municipal and industrial water supplies. In terms of worldwide production, it ranks third behind alumina and aluminum hydroxide, with markets in excess of 3 million ton/year.

Aluminum chloride, hexahydrate, AlCl<sub>3</sub> • 6 H<sub>2</sub>O, is manufactured from aluminum hydroxide, Al(OH)<sub>3</sub>, and hydrochloric acid, HCl. It is used in pharmaceuticals and cosmetics as a flocculant and for

impregnating textiles. Conversion of solutions of hydrated aluminum chloride with aluminum to the aluminum chlorohydroxy complexes serves as the basis of the most widely used antiperspirant ingredients.

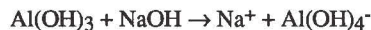
Table 3 World Non-Metallurgical Calcined Alumina Markets

Market	1968	1975	1988
Refractories (includes fused-cast and refractories made with sintered tabular and fused grains)	38	62	50
Abrasives (fused and polishing aluminas)	21	16	20
Ceramics, electronic and technical (80+% Al <sub>2</sub> O <sub>3</sub> includes spark plug insulators)	29	11	10
Whitewares (includes electrical insulators below 80% Al <sub>2</sub> O <sub>3</sub> )	6	9	15
Glass and enamels	4	1	3
Miscellaneous	2	12	2



Another cosmetic application of aluminum compounds is lakes for lipstick manufacture. A water soluble dye can become a lipstick ingredient if combined with other compounds that are colorless and insoluble. The result is called a lake, which is insoluble in both oil and water. Some dyes are laked with alumina; others are dissolved in water and treated with solutions that precipitate  $\text{Al}(\text{OH})_3$  with the dye molecules occluded in the precipitate. These lakes are mixed with castor oil, finely ground, and used as lipstick ingredients.

Sodium aluminate (theoretical formula;  $\text{NaAlO}_2$ ) is manufactured by dissolving  $\text{Al}(\text{OH})_3$  in 50% sodium hydroxide solution.



The resulting solutions contain high dissolved solids in the range of 30 wt% or more. High purity  $\text{Al}(\text{OH})_3$  and clean solutions of caustic must be used. Impurities or undissolved solids will destabilize the solution and cause unacceptable cloudiness; i.e., precipitation of  $\text{Al}(\text{OH})_3$ . Special surfactant technology is sometimes used to avoid this problem or at least extend the shelf life of the liquor.

Sodium aluminate is used in water purification, in the paper industry, for the after treatment of  $\text{TiO}_2$  pigment, and in the manufacture of aluminum-containing catalysts and zeolite. Worldwide markets are in the range of 125,000 t/yr.

A large and growing industrial use of  $\text{Al}(\text{OH})_3$  and/or sodium aluminate is the manufacture of synthetic zeolites. Zeolites are aluminosilicates with Si/Al ratios between 1 and infinity. There are 40 natural and over 100 synthetic zeolites. All the synthetic structures are made by relatively low temperature (100-150°C) high pH hydrothermal synthesis. The manufacture of industrially important zeolite A, X, and Y is generally carried out by mixing sodium aluminate (obtained by dissolving  $\text{Al}(\text{OH})_3$  in NaOH) and sodium silicate solutions to form a sodium aluminosilicate gel. Gelling under hydrothermal conditions crystallizes the final product. In special cases, a small amount of seed crystal is used to control the synthesis.

Zeolite-based materials are so versatile it is inappropriate to attempt to list all applications here. Major uses include detergent manufacture, ion-exchange resins (i.e., water softeners), catalytic

applications in the petroleum industry, separation processes (i.e., molecular sieves), and as an adsorption agent for water, carbon dioxide, mercaptans, and hydrogen sulfide.

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