ALUMINUM COMPOUNDS, SURVEY

1. Introduction

Aluminum [7429-90-5], atomic number 13, atomic weight 26.981, is, at 8.8 wt%, the third most abundant element in the earth's crust. It is usually found in silicate minerals such as feldspar [68476-25-5], clays, and mica [12001-26-2]. Aluminum also occurs in hydroxide, oxide–hydroxide, fluoride, sulfate, or phosphate compounds in a large variety of minerals and ores.

The CAS registry lists 5,037 aluminum-containing compounds exclusive of alloys and intermetallics. Some of these are listed in Table 1. Except for nepheline and alunite in the former USSR and Poland, bauxite is the raw material for all manufactured aluminum compounds. The term bauxite is used for ores that contain economically recoverable quantities of the aluminum hydroxide mineral gibbsite or the oxide–hydroxide forms boehmite and diaspore.

World bauxite production in 2000 totaled about 136×10^6 t, approximately 85% of which was refined to aluminum hydroxide by the Bayer process. Most of the hydroxide was then calcined to alumina and consumed in making aluminum metal. An additional 10% was used in nonmetallurgical applications in the form of speciality aluminum, 5% was used for nonmetallurgical bauxite applications such as abrasives, refractories, cement additives, and aluminum chemicals (1). Other uses included catalysts used in petrochemical processes and automobile catalytic converter systems (see PETROLEUM; EXHAUST CONTROL, AUTOMOTIVE); ceramics that insulate electronic components such as semiconductors and spark plugs; chemicals such as alum, aluminum halides, and zeolite; countertop materials for kitchens and baths; cultured marble; fire-retardant filler for acrylic and plastic materials used in automobile seats, carpet backing, and insulation wrap for wire and cable (see FLAME RETARDANTS); paper (qv); cosmetics (qv); toothpaste manufacture; refractory linings for furnaces and kilns; and separation systems that remove impurities from liquids and gases.

Aluminum compounds, particularly the hydroxides and oxides are very versatile. Properties range from a hardness indicative of sapphire and corundum to a softness similar to that of talc [14807-96-6] and from inertness to marked reactivity. Aluminas that flow and filter like sand may be used for chromatography (qv); others are viscous, thick, unfilterable, and even thixotropic (2).

2. Bauxite Occurence

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 but having small and variable amounts of silica [7631-86-9], the iron oxides hematite [1309-37-1], Fe_2O_3, and magnetite [1317-61-9], Fe_3O_4 , rutile or titanium oxide [1317-80-2], and alumina silicate clays. Deposits were formed over many geologic time periods in a tropical or subtropical climate having enough rainfall and circulating groundwater to

Table 1. **Aluminum Compounds Referred to in Text**

Compounds	CAS Registry Number	Molecular formula
alum	[7784-24-9]	$KAl(SO_4)_2 \cdot 12H_2O$
alumina	[1344-28-1]	Al_2O_3
aluminum bromide	[77727-15-3]	$AlBr_3$
aluminum chlorhydroxide (ACH)	[12042-91-0]	$Al_2Cl(OH)_5$
aluminum(I) chloride	[13595-81-8]	$AlCl$
aluminum(III) chloride	[7446-70-6]	$AlCl_3$
aluminumchloride hexahydrate	[7784-13-6]	$AlCl_3 \cdot 6H_2O$
aluminum(I) fluoride	[13595-82-9]	AlF
aluminum(III) fluoride	[7784-18-1]	AlF_3
aluminum hydroxide	[21645-51-2]	$Al(OH)_3$
aluminum iodide	[7784-23-8]	AlI_3
aluminum(II) oxide	[14457-64-8]	AlO
aluminum silicate	[12141-46-7]	$Al_2(SiO_3)_3$
aluminum sulfate	[10043-01-3]	$Al_2(SO_4)_3$
aluminum sulfate octadecahydrate	[7784-31-8]	$Al_2(SO_4)_3 \cdot 18H_2O$
alunite	[12588-67-9]	$K_2Al_6(SO_4)_4(OH)_{12}$
anorthite	[1302-54-1]	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
bauxite	[1318-16-7]	
boehmite	[1318-23-6]	$AlO(OH)$
calcium aluminate	[12042-78-3]	$Al_2O_3 \cdot 3CaO$
corundum	[1302-74-5]	$\alpha\text{-}Al_2O_3$
diaspore	[14457-84-2]	$\alpha\text{-}AlO(OH)$
gibbsite	[14762-49-3]	$\alpha\text{-}Al(OH)_3$
halloysite	[12244-16-5]	$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$
kaolin	[1332-58-7]	$H_2Al_2Si_2O_8 \cdot H_2O$
kaolinite	[1318-74-7]	$Al_2O_3 \cdot 2SiO^2 \cdot 2H_2O$
kyanite	[1302-76-7]	$H_6O_5Si \cdot 2Al$
montmorillonite	[1318-93-0]	
nepheline	[12251-27-3]	$NaAl(OH)SiO_3$
nepheline	[12251-28-4]	$NaAl_2(OH)_2(SiO_3)_2 \cdot H_2O$
nepheline	[14797-52-5]	AlH_4O_4Si
sapphire	[1317-82-4]	Al_2O_3
sodium aluminate	[1302-42-7]	$NaAlO_2$
triethylaluminum	[97-93-8]	$(C_2H_5)_3Al$
triisobutylaluminum	[100-99-2]	$(C_4H_9)_3Al$
zeolite A	[1318-02-1]	$Na_{12}[(Al_{12}Si_{12})O_{48}] \cdot 27H_2O$
zeolite Y		$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250H_2O$
zeolite X		$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$

dissolve constituents of the parent rock and carry them away. Weathering is intensified by good drainage and by decaying vegetation, which makes the process acidic. Table 2 gives typical compositions for bauxites found throughout the world.

Uses of bauxite other than for aluminum production are in refractories, abrasives, chemicals, and aluminous cements. Bauxites for these markets must meet more rigid compositional requirements with respect to Fe_2O_3, SiO_2, and TiO_2 content that those used for alumina production.

Table 2. **Composition of Bauxite Used for Alumina Production**

Location	Constituents, wt %				Loss on ignition (LOI), %	Mineral components
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2		
Australia						
Weipa	54.8	5.3	5.20			gibbsite, some boehmite
Gove	50	3.4–4.2	17.1	3.4	26.4	gibbsite, some boehmite
Darling Range	30–35	0.3–2.0	10–25			gibbsite, trace boehmite
Brazil						
Trombetas	55.9	4.8	9.4	1.3	28.6	gibbsite, boehmite
France	53.0	7.8	21.4	2.6	13.3	boehmite
Greece	57.6	3.0	22.8	2.75	12.17	boehmite, some diaspore
Guinea						
Boke-Sangaredi	59.1–59.6	0.7–0.9	4.9–5.9	3.3–3.5	30.6–31.0	83–86% gibbsite, 3.5–5.5% boehmite
Fria	45.5	4.0	23.6	2.5	23.9	gibbsite
Guyana	55–61	1–10	0.8–5	2–5	30–35	nearly pure gibbsite
Hungary	50–60	1–5				boehmite, some gibbsite
India						
Ranchi	51–60	0.1–5	4–10	0.3–17	22–28	gibbsite, some boehmite
East Coast province	43.7–56.5	0.5–4.2	8.6–38.4	2.1–3.5	24.6–30.5	gibbsite, boehmite
Jamaica	49.1–50.6	0.7–6.1	18.9–20	2.5–2.7	24.6–27.3	gibbsite, 7–10% boehmite
Surinam	58.5–60	3.4–4.3	2.7–4.4	2.4–2.7	30.7–31.4	nearly pure gibbsite
United States	45–50	13	8	2.5–3	25±	gibbsite, SiO_2 is mainly in kaolinite
Former USSR	45–55	2–10	5–15			boehmite; somemixed with diaspore; a few are gibbsite
Yugoslavia	56–58	3–5	20–22	2.5–2.7	13.0	boehmite, SiO_2 in kaolinite

Table 3. **World Bauxite Mine Production, Reserves, and Reserve Base, 10^3 t^a**

	Mine production			Reserve base 10^3 t^a
	2000	2001^b	Reverves	
United States	NA	NA	20,000	40,000
Australia	53,800	53,500	3,800,000	7,400,000
Brazil	14,000	14,000	3,900,000	4,900,000
China	9,000	9,200	720,000	2,000,000
Guinea	15,000	15,000	7,400,000	8,600,000
Guyana	2,400	2,000	700,000	900,000
India	7,370	8,000	770,000	1,400,000
Jamaica	11,100	13,000	2,000,000	2,500,000
Russia	4,200	4,000	200,000	250,000
Suriname	3,610	4,000	580,000	600,000
Venezuela	4,200	4,400	320,000	350,000
other countries	10,800	10,200	4,100,000	4,700,000
World total (rounded)	135,000	137,000	24,000,000	34,000,000

^{a} Ref. 3.
^{b} Estimated

The largest world bauxite producers in Australia, Brazil, Guinea, and Jamaica. They accounted for 70% of the total bauxite mined in 2000 and 2001. See Table 3 for world bauxite mine production, reserves, and reserve base (3).

Bauxite reserves are estimated to be $55-75 \times 10^9$ t, located in South America (33%), Africa (27%), Asia (17%), Oceania (13%), and elsewhere (10%) (3).

Bauxite exists in many varieties. The physical appearance ranges from earthy dark brown ferruginous material to cream or light pink-colored layers of hard, crystalline, gibbsitic bauxite. Ores composed chiefly of gibbsite, α-Al(OH)$_3$, are commonly termed trihydrate bauxites or the Surinam type; those composed of boehmite, AlO(OH), are called monohydrate bauxite, or the European type; and those composed of a mixture of gibbsite and boehmite are referred to as mixed bauxites. The term Jamaica type is applied to very fine-grained gibbsitic bauxite ore containing <10% boehmite. Diaspore, α-AlO(OH), is the major constitutent of bauxites in Greece, Romania, Russia, and China.

Iron and titanium minerals commonly found in bauxites are hematite, goethite [1310-14-1], FeO(OH), siderite [14476-16-5], FeCO$_3$, magnetite, ilmenite [12168-52-4], FeTiO$_3$, anatase [1317-70-0], TiO$_2$, and rutile. Silicon dioxide may occur as quartz [14808-60-7], but it is silica associated with the clay (qv) minerals kaolite, halloysite, or montmorillonite that is important in processing bauxite for alumina production. These aluminosilicates react during the extraction stage of alumina production to form insoluble sodium aluminum silicates resulting in losses of NaOH and Al$_2$O$_3$. The amount of this reactive silica is one of the bauxite quality and price-determining factors (4). Some ores, Brazilian Trombetas, for example, are upgraded by washing some of the fine kaolin away.

Hardness, texture, and the amount of overburden determine the methods for mining bauxite. Tropical gibbsitic bauxites are usually located so close to

the earth's surface that strip mining can be used. However, European bauxites frequently require mining to depths of several hundred meters. The Bayer process, patented in 1888 (5), involved hot leaching of bauxite withNaOH solution in pressure vessels to obtain a supersaturated sodium aluminate solution from which $Al(OH)_3$ was precipitated by seeding. This process achieved immediate industrial success, replacing the soda ash roasting of bauxite used to form leachable sodium aluminate. Development of the Bayer process also coincided with the rapid increase in demand for pure alumina to be used in metal production by the Hall-Héroult process discovered in 1886 (see ALUMINUM AND ALUMINUM ALLOYS).

3. Chemical Properties

The ground state distribution of electrons in the aluminum atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. The oxidation state of aluminum is $+3$, except at high temperatures where monovalent species such as AlCl, AlF, and Al_2O have been spectrally identified. At lower temperatures, these compounds disproportionate

$$3\,Al_2O \longrightarrow Al_2O_3 + 4\,Al$$

Aluminum, although highly electropositive, does not react with water under ordinary conditions because it is protected by a thin (2–3 nm) impervious oxide film that rapidly forms even at room temperature on nascent aluminum surfaces exposed to oxygen. If the protective film is overcome by amalgamation or scratching, water rapidly attacks to form hydrous aluminum oxide. Because of the tendency to amalgamate, aluminum and its alloys should not be used in contact with mercury or its compounds. Molten aluminum (mp 660°C) is known to react explosively with water (16). Thus the molten metal should not be allowed to touch damp tools or containers.

There is much discussion on the nature of the aluminum species present in slightly acidic and basic solutions. There is general agreement that in solutions below pH 4, the mononuclear Al^{3+} exists coordinated by six water molecules, ie, $[Al(H_2O)_6]^{3+}$. The strong positive charge of the Al^{3+} ion polarizes each water molecule and as the pH is increased, a proton is eventually released, forming the monomeric complex ion $[Al(OH)(H_2O)_5]^{2+}$. At about pH 5, this complex ion and the hexahydrated Al^{3+} are in equal abundance. The pentahydrate complex ion may dimerize by losing two water molecules

$$2\left[Al(OH)(H_2O)_5\right]^{2+} \longrightarrow \left[Al_2(OH)_2(H_2O)_8\right]^{4+} + 2\,H_2O$$
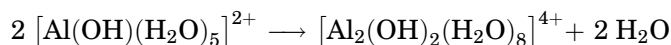
Further deprotonation, dehydration, and polymerization of monomers and dimers may yield ringlike structures of hydroxy−aluminum complexes(17). Coalescence of ring compounds into layers by further growth results in the formation of crystalline aluminum hydroxide at pH 6, the point of minimum aqueous solubility.

Highly purified aluminum, 99.999% Al, is resistant to attack by most acids but can be dissolved in aqua regia or in hydrochloric acid containing a trace of

$CuCl_2$. Addition of hydrogen peroxide [7722-84-1], H_2O_2, during dissolution in HCl speeds the process (18). Typical commercial aluminum, 99.85 to 99.95% Al, is soluble in dilute mineral acids but is passivated by concentrated nitric acid. Dissolution in acids is accompanied by evolution of hydrogen and hydration of the aluminum ion

$$2\,Al + 6\,H_3O^+ + 6\,H_2O \longrightarrow 2\,\left[Al(H_2O)_6\right]^{3+} + 3\,H_2$$
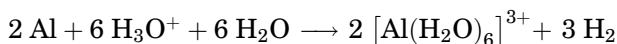
Because of its amphoteric nature, aluminum is also readily attacked by solutions of strong bases. At a pH >8.5, the solubility of aluminum increases sharply because of the formation and hydration of $Al(OH)_4^-$ ions

$$2\,Al + 2\,OH^- + 10\,H_2O \longrightarrow 2\,\left[Al(OH)_4(H_2O)_2\right]^- + 3\,H_2$$
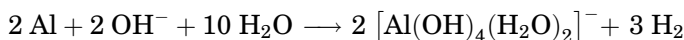
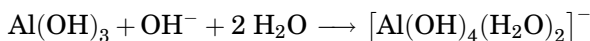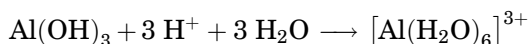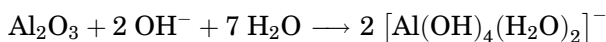In high caustic Bayer liquor, $Al(OH)_4^-$ ions exist because there is not enough water to hydrate them.

Aluminum hydroxide is capable of reacting as either an acid or a base (18).
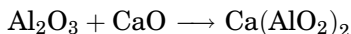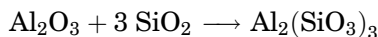
$$Al(OH)_3(s) \longrightarrow Al^{3+} + 3\,OH^-$$

$$Al(OH)_3(s) \longrightarrow AlO_2^- + H^+ + H_2O$$
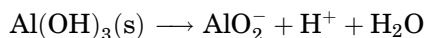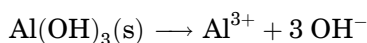
and the hydroxide is readily soluble in both acids and strong bases

$$Al(OH)_3 + 3\,H^+ + 3\,H_2O \longrightarrow \left[Al(H_2O)_6\right]^{3+}$$

$$Al(OH)_3 + OH^- + 2\,H_2O \longrightarrow \left[Al(OH)_4(H_2O)_2\right]^-$$

Calcined alumina, α-Al_2O_3, and naturally occurring corundum are practically insoluble in acids and bases, but partially calcined and low temperature amorphous oxide, such as that which forms on nacent commercial aluminum surfaces, is soluble

$$Al_2O_3 + 6\,H_3O^+ + 3\,H_2O \longrightarrow 2\,\left[Al(H_2O)_6\right]^{3+}$$

$$Al_2O_3 + 2\,OH^- + 7\,H_2O \longrightarrow 2\,\left[Al(OH)_4(H_2O)_2\right]^-$$
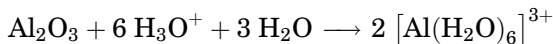
The amphoteric nature of the oxide is illustrated by its ability to form silicates and aluminates in the dry state at elevated temperatures

$$Al_2O_3 + 3\,SiO_2 \longrightarrow Al_2(SiO_3)_3$$

$$Al_2O_3 + CaO \longrightarrow Ca(AlO_2)_2$$

Aluminum also reacts vigorously with the halogens to form trihalides

$$2\,Al + 3\,X_2 \longrightarrow 2\,AlX_3$$

4. Bauxite Production

Figure 1 illustrates the Bayer process as it is practiced. The primary purpose of a Bayer plant is to process bauxite to provide pure alumina for the production of aluminum. World production of alumina totaled ca 49×10^6 t in 2000 (1). Practically all of the hydroxide used was obtained by Bayer processing and 85% of it was calcined to metallurgical grade alumina (Al_2O_3). However, about 15% of the bauxite processed serves as feedstock to the growing aluminum chemicals industry.

Bauxite grade, mineralogy, composition, uniformity and location of the ore deposit, site infrastructure, availability of low cost energy, and designer bias, as well as legislative and environmental restrictions all affect Bayer plant design.

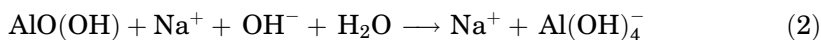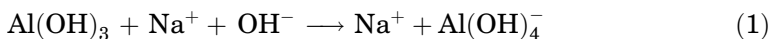**Fig. 1.**   Bayer process flow sheet.

All bauxite refineries share six common process steps: bauxite mining; raw material preparation; bauxite digestion; separation, washing, and disposal of insoluble bauxite residue; aluminum hydroxide (trihydrate) precipitation; and calcination to anhydrous alumina.

Additional operations essential to commercial bauxite processing are steam and power generation, heat recovery to minimize energy consumption, process liquor evaporation to maintain a water balance, impurity removal from process liquor streams, classification and washing of trihydrate, lime caustication of sodium carbonate to sodium hydroxide, repair and maintenance of equipment, rehabilitation of mine and residue disposal sites, and quality and process control. Each operation in the process can be carried out in a variety of ways depending upon bauxite properties and optimum economic tradeoffs.

4.1. Mining and Ore Preparation. Bauxite mining practice is dictated by the nature of the ore body. Blending operations, physical beneficiation (washing out clay slurries), and bauxite drying are used if the ore body is not uniform, contains an excessive amount of kaolin (clay) that would consume caustic, or is difficult to handle because of its moisture content (see CLAYS). Grinding is designed to produce feed material small enough to ensure easy alumina extraction yet coarse enough to avoid clarification problems with bauxite residue. Uniform, consistent, easily digested bauxite slurry is formed by blending properly ground bauxite slurry in slurry storage "surge" tanks prior to digestion.

4.2. Digestion. Digestion extracts and solubilizes the available aluminum minerals from the bauxite. Digest conditions and equipment vary widely, depending on bauxite mineralogy, ie, the solution rates of the ore, and on achieving high productivity from a given liquor flow rate. In digestion, which is performed in steel vessels, autoclaves, or tubular reactors, hot spent liquor reacts with the aluminum minerals in the bauxite to form soluble sodium aluminate. Virtually all the other constituents are rejected as undissolved solids.

$$\mathrm{Al(OH)_3 + Na^+ + OH^- \longrightarrow Na^+ + Al(OH)_4^-} \tag{1}$$

$$\mathrm{AlO(OH) + Na^+ + OH^- + H_2O \longrightarrow Na^+ + Al(OH)_4^-} \tag{2}$$

The term spent liquor is used to distinguish recycled sodium hydroxide solution containing a low amount of dissolved sodium aluminate from the "green" or "pregnant" liquor leaving digestion that has a high sodium aluminate content. Liquor concentrations are expressed as g/L of a given constituent and depending upon the refinery location, the total caustic content, including that tied up as sodium aluminate, is expressed as g/L NaOH, Na_2CO_3, or sodium oxide Na_2O.

Gibbsitic bauxite, Equation1, is the most economical to process because of gibbsite's high solubility in Bayer process liquor at moderate temperature and pressure. Liquor containing $120-135$ g/L Na_2O is used at about $140°C$. Although boehmite and diaspore have the same chemical composition (AlOOH), diaspore is denser and harder than boehmite. Boehmitic bauxite requires temperatures from $200-250°C$ and pressures of 3.45 MPa (34 atm) or higher to obtain complete extraction and form high ratio green liquors. This ratio, which ultimately determines liquor productivity, is the g/L Al_2O_3 dissolved divided by the g/L Na_2O in solution. Processing diasporic bauxite requires stronger caustic solutions,

$200-300$ g/L Na_2O, in addition to higher temperatures and pressures. Whereas some bauxites may be composed entirely of one aluminous mineral phase, others may contain all three aluminum hydroxide minerals and the mineral most difficult to extract sets the digest conditions.

Other important reactions that occur in digestion are desilication, causticization of liquor, and precipitation of impurities. The reactive silica in bauxite, for example that in kaolin, reacts with caustic to form soluble sodium silicate [1344-09-8], Na_2SiO_3

$$Al_2O_3{\cdot}2\,SiO_2{\cdot}2\,H_2O + 6\,NaOH \longrightarrow 2\,NaAlO_2 + 2\,Na_2SiO_3 + 5\,H_2O \qquad (3)$$
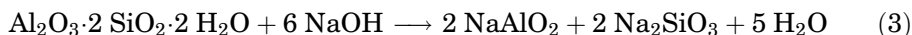
which then reacts at digest temperature to form an insoluble sodium aluminum silicate known as desilication product (DSP), the most probable formula of which is $3\,Na_2O{\cdot}3\,Al_2O_3{\cdot}6\,SiO_2{\cdot}2\,Na_2\,X{\cdot}YH_2O$, where X can be any of a number of anions, including CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-, and $Al(OH)_4^-$, all of which are present in Bayer liquors. Good desilication is effected by high temperatures and holding times and is essential for product purity.

Causticization, the reaction of hydrated lime [1305-62-0], $Ca(OH)_2$, with sodium carbonate to regenerate sodium hydroxide and precipitate calcium carbonate, is an important part of the Bayer process chemistry.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,NaOH \qquad (4)$$
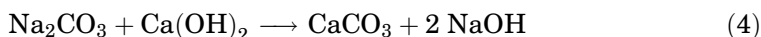
Na_2CO_3 is formed in Bayer liquors by caustic degradation of the organics (humic acids) in bauxite and by absorption of CO_2 during exposure of process liquors to the atmosphere. Although poor lime efficiency and alumina losses during digestion as calcium aluminates have led to the practice of "outside" causticization of dilute green liquor flows in the residue washing area of the plant, digestion lime additions are still made to control impurities such as phosphorous pentoxide [1314-56-3], P_2O_5.

4.3. Clarification.   Clarification is the term used to describe separation of bauxite residue solids from the supersaturated green liquor near its boiling point. Coarse particles, called sand because of the high silica content, are usually removed by cycloning followed by washing on sand classifiers prior to disposal. In most plants, the fine fraction of residue is settled in raking thickeners with the addition of flocculants to improve the clarity of thickener overflow. The concentrated thickener underflow is washed before disposal in countercurrent decantation washers (similar to the raking thickeners) or on vacuum drum-type filters, or a combination of both. Thickener overflow is filtered to remove the final traces of solids and ensure product purity. Kelly-type pressure filters are most widely used, but some plants use sand filters in which the liquor is filtered by gravity through a bed of properly sized sand. Filtered solids are removed from filter press cloth by hosing and are elutriated from the sand by backwashing.

4.4. Precipitation.   Precipitation is the heart of the Bayer plant where recovery of the $Al(OH)_3$ from process liquors occurs in high yield and product quality is controlled. The dominant use for Bayer $Al(OH)_3$ is to calcine it into smelting grade alumina.

Cooling after digestion and clarification enhances the supersaturation of dissolved $Al(OH)_3$, but the solution remains metastable and autoprecipitation, which would result in losses during clarification, still is not rapid. The liquor is usually seeded with fine gibbsite seed from previous cycles to initiate precipitation. This reaction is the reverse of Equation 1, except that seed is present so that agglomeration and creation of new particles occur simultaneously. Maintaining a seed balance around precipitation and classification is important in achieving good yield and proper particle size, ie, the number of particles created in precipitation should equal the number leaving the system as product. Thus, nucleation, agglomeration, particle growth, and particle breakage need to be balanced. Problems arise because of the lack of a complete understanding of the interaction among variables such as specific precipitation rate (SPR), residence time, liquor concentrations, inorganic and organic impurities, mixed and split seeding, active vs poisoned seed area, seed retention, temperature profiles, and the effect on yield and product quality.

Precipitation can be continuous or batch. Modern plants use the continuous system where 10 to 14 flat-bottom, internally agitated tanks, approximately 30 m in height and 10–12 m in diameter, are placed in series so that flow of the liquor−seed slurry moves by gravity through launders connecting the tank tops.

Classification.   Slurry leaving precipitation is classified into a coarse and one or more fine fractions, usually by elutriation in hydroclassifiers. Cyclones and combinations of hydroclassifiers and cyclones are gaining popularity. In smelting grade alumina plants, the coarse fraction, called primary product, is sent to calcination; the fine fractions, called secondary and tertiary seed, are recycled to be grown to product size.

4.5. Calcination.   Calcination, the final operation in production of metallurgical grade alumina, is done either in rotary kilns or fluid bed stationary calciners at about $1100°C$. Prior to calcination, the process liquor is washed from the $Al(OH)_3$ using storage tanks and horizontal vacuum filters. During heating, the trihydroxide undergoes a series of changes in composition and crystal structure but essentially no change in particle shape. The product is a white powder consisting of aggregates ranging in size from 20 μm to about 200 μm. Details of the calcination process are given in the literature (7,9,10).

4.6. Evaporation and Impurity Removal.   Evaporation over and above that obtained in the cooling areas from flashed steam is usually required to maintain a water balance by removing dilution arising from residue and $Al(OH)_3$ washing, free moisture in the ore, injected steam, purge water, and uncontrolled dilutions. Evaporation also serves to concentrate impurities in the liquor stream such as sodium oxalate [62-76-0], $Na_2C_2O_4$, a product of organics degradation, making impurity removal easier.

4.7. Energy Conservation.   Cogeneration of steam and power is usually an integral part of a Bayer plant, unless there is abundant low cost (usually hydroelectric) power available from an existing grid. The cogeneration feature enables fuel efficiencies of ≥85% compared to ca 35% in public utilities power plants where turbine exhaust steam is merely condensed and recycled rather than being used for process heating.

Minimizing energy consumption per ton of alumina while maintaining a steam-power balance is an industry-wide, ongoing effort. Reduction of steam

consumption has been limited by the cost of purchased power to compensate for loss of power generation.

In most plants heat recovery from the hot slurry leaving digestion is accomplished by flashing the slurry through a series of pressure vessels (flash tanks) to its atmospheric boiling point. The steam evolved accounts for a significant amount of the evaporation needed to maintain a water balance. It is used to heat the liquor returning to digestion before being recycled to the powerhouse boilers. Heat recovery from clarified liquor to precipitation is done in an analogous system, but because the liquor is cooled below its boiling point, flash vessels and heat exchangers must operate under vacuum.

4.8. Residue Disposal.   The major environmental problem in the Bayer process is disposal of bauxite residue which is effected by marine disposal, lagooning, use of underdrain lakes, or semidry disposal. Marine disposal in oceans or rivers, diluting the alkaline residue by large quantities of water, is environmentally unacceptable. Lagooning behind retaining dikes built around clay-sealed ground is commonly used, but there have been isolated leaks into aquifers. This has motivated installation of underdrains between the residue and clay-sealed, plastic-lined, lake bottom. This design removes the hydraulic head from the lake bottom and improves consolidation of the residue.

This is semidry disposal, sometimes referred to as dry-stacking, or the drying field method of disposal, takes advantage of the thixotropic nature of the residue. In this method, the residue is concentrated by vacuum filtration or other means to 35−50% solids. The percent solids required depends on residue rheology which varies as the source of the bauxite. Using agitation and/or additives, the viscosity of the concentrated slurry is reduced so it can be pumped to the disposal area where it flows like lava, establishing a gentle slope away from the discharge point. The slurry is called nonsegregating because neither water nor sand separate from it. In the absence of shear, the viscosity increases and flow stops. Any rainwater rapidly drains to the perimeter of the deposit. There is no free water on the surface of the impoundment, so the deposited residue dries and cracks whenever it is not raining. When the percent solids approaches 70−75%, bulldozers can work on the deposit. This method of disposal provides maximum storage for a given area and easy recovery if, in the future, any economical use for the residue is found. The disadvantages include a need for dust control and a separate cooling pond for the plant.

To return land once devoted to bauxite residue disposal to productive use, abandoned semidry disposal areas can be contoured and landscaped into surroundings capable of supporting homes and/or light industrial buildings. In the case of lagoons and lakes, the land has been returned to agricultural use. This has been accomplished, particularly in Australia, by dewatering (qv) abandoned lakes, covering them with several meters of neutral sand, and adding fertilizer to support crop growth.

4.9. Alternative Processes.   Bayer processing of bauxite is the most economical method for $Al(OH)_3$ and Al_2O_3 production; however, the lime−soda sintering process (9,11) is available to treat the high silica bauxites in the United States and nepheline in the former USSR. In the lime-soda process, leachable sodium aluminate is formed and silica is insolubilized by reaction with calcium. Research has shown that alumina production from nonbauxitic raw materials such as clay, anorthosite, alunite, coal waste, and oil shale (qv) has been

technically feasible (12–14), but these technologies cannot compete with the Bayer process economically. The one that comes closest is acid (HCl) processing of clay (see CLAYS).

5. Bauxite Economics

Alumina, Al_2O_3, production capacity, is summarized in Table 4. The smaller plants produce products solely for chemical applications; the larger refineries

Table 4. **Alumina World Production, by Country** $\times 10^3$t [a,b,c,d]

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

[a] Ref. 3, est = estimated, r = revised, – = zero
[b] Figures represent calcined alumina or the total of calcined alumina plus the calcined equivalent of hydrate when available; exceptions, if known, are noted.
[c] World totals, U.S. data and estimated data are rounded to no more than three significant digits; may not add to totals shown.
[d] Table includes data available through July 25, 2001.
[e] Reported figure.
[f] Production sharply curtailed or ceased.
[g] Data presented are for alumina used principally for specialty applications. Information on aluminum hydrate for all uses is not adequate to formulate estimates of production levels.
[h] Hydrate.

Table 5. **Bauxite Salient Statistics—United States**[a]

	1997	1998	1999	2000	2001[b]
production, bauxite, mine	NA	NA	NA	NA	NA
imports of bauxite for consumption[c]	11,300	11,600	10,400	9,030	9,500
exports of bauxite[c]	97	108	168	147	100
shipments of bauxite from government stockpile excesses[c]	1,430	3,300	4,180	1,100	200
consumption, apparent, bauxite (and alumina) (in aluminum equivalents)[d]	4,210	5,000	4,870	3,870	3,200
price, bauxite, average value U.S. imports (f.a.s.) dollars per ton	25	23	22	23	24
stocks, bauxite, industry, yearend[c]	2,260	1,860	1,440	1,300	1,200
net import reliance,[e] bauxite (and alumina) as a percentage of apparent consumption	100	100	100	100	100

[a] Ref. 1, NA = not available, also includes Virgin Islands.
[b] Estimated.
[c] Includes all forms of bauxite, expressed as dry equivalent weights.
[d] The sum of U. S. bauxite production and net import reliance.
[e] Defined as imports-exports + adjustments for Government and industry stock changes (all in aluminum equivalents). Treated as separate commodities, the net import reliance equaled 100% for bauxite and 31% for alumina in 2001. For the years 1997–2000, the net import reliance was 100% for bauxite and ranged from 33% to 37% for alumina.

are almost fully devoted to production of metallurgical grade alumina. Production facilities are located adjacent to a bauxite reserve or in countries having the largest markets for the product.

The aluminum industry is a cyclic industry responding to global economic activity. The price of metal grade alumina ranged from about \$165–440/t in 2000. Prices had started to decline in May 2000 (1). The largest cost elements in alumina production are bauxite, caustic, energy, and sustaining capital for production equipment. Some U.S. statistics for bauxite are given in Table 5 (1).

6. Commercially Significant Compounds

The aluminum containing compound having the largest worldwide market, estimated to be over 49×10^6 t in 2000, is metal grade alumina (15). Second, is aluminum hydroxide. The split between additive and feedstock applications for $Al(OH)_3$ (16) is roughly 50:50. Additive applications include those as flame retardants (qv) in products such as carpets, and to enhance the properties of paper (qv), plastic, polymer, and rubber products. Significant quantities are also used

in pharmaceuticals (qv), cosmetics (qv), adhesives (qv), polishes (qv), dentifrices (qv), and glass (qv).

Feedstock applications of $Al(OH)_3$ for production of other chemicals include almost all of the 5000 plus compounds listed in the CAS registry.

6.1. Aluminum Sulfate (Alum). Alum, a double sulfate of potassium and aluminum having twelve waters of crystallization, $KAl(SO_4)_2 \cdot 12H_2O$, is the earliest referenced aluminum containing compound. It was mentioned by Herodotus in the fifth century BC. The Egyptians used alum as a mordant and as a medicine; the Romans used it for fireproofing. Some alums contain sodium or ammonium ions in place of potassium.

Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, also known as alum cake, is industrially produced by reaction of $Al(OH)_3$ and sulfuric acid [7664-93-9], H_2SO_4, 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, The U.S. exported 7,690 t of aluminum sulfate and imported 23,500 t of aluminum sulfate in 2000 (1).

6.2. Aluminum Halides. All the halogens form covalent aluminum compounds having the formula AlX_3. The commercially most important are the anhydrous chloride and fluoride, and aluminum chloride hexahydrate.

Anhydrous aluminum chloride, $AlCl_3$, is manufactured primarily by reaction of chlorine [7782-50-5] vapor with molten aluminum and used mainly as a catalyst in organic chemistry; ie, in Friedel-Crafts reactions (qv) and in proprietary steps in the production of titanium dioxide [13463-67-7], TiO_2, pigment. Its manufacture by carbochlorination of alumina or clay is less energy-intensive and is the preferred route for a few producers (20). Aqueous $AlCl_3$ is used in water treatment (15).

Aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, manufactured from aluminum hydroxide andhydrochloric acid [7647-01-0], HCl, 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 serve as the basis of the most widely used antiperspirant ingredients (18). The U.S. exported 19,600 t of aluminum chloride and imported 1,700 t in 2000 (1).

Another cosmetic application of aluminum compounds is as lakes for lipstick manufacture (19). A water-soluble dye can become a lipstick ingredient if combined with compounds that are colorless and insoluble. The result, called a lake, is insoluble in both oil and water. Some dyes are laked with alumina; others are dissolved in water and treated with solutions that precipitate $Al(OH)_3$ with the dye molecules occluded in the precipitate. These lakes are mixed with castor oil [8001-79-4] (qv), finely ground, and used as lipstick ingredients.

Aluminum fluoride is important as an additive to the electrolyte of aluminum smelting cells. World production, is by the hydrofluoric acid [7664-39-3] HF process and the fluorosilicic acid [16961-83-4], H_2SiF_6, process. In the HF process, acid grade feldspar [7789-75-5], CaF_2, reacts in a rotary kiln with fuming sulfuric acid (oleum) [8014-95-7], $H_2SO_4 \cdot SO_3$, to produce anhydrous HF gas

and gypsum (see FLUORINE COMPOUNDS, INORGANIC, HYDROGEN)

$$CaF_2 + H_2SO_4 \longrightarrow 2\,HF + CaSO_4$$
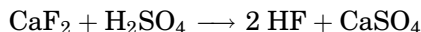
The HF is fed into the bottom stage of a three-stage fluid bed reactor and $Al(OH)_3$ is fed to the top stage where it is converted to activated alumina at $300-400°C$. In the middle stage, rising HF gas contacts downcoming alumina and forms AlF_3

$$6\,HF + Al_2O_3 \xrightarrow{400-600°C} 2\,AlF_3 + 3\,H_2O$$
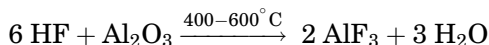
The AlF_3 goes to the bottom stage of the reactor and is removed as product.

In the fluorosilicic acid process, H_2SiF_6 solution, obtained from scrubbing stack gases from phosphate rock fertilizer plants, is reacted with $Al(OH)_3$ at about $100°C$, whereupon silica precipitates and AlF_3 is dissolved.

$$H_2SiF_6 + 2\,Al(OH)_3 \xrightarrow{100°C} 2\,AlF_3{\cdot}3H_2O(aq) + SiO_2 + H_2O$$
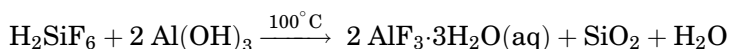
After the SiO_2 is filtered off, the aluminum fluoride is crystallized as the tri-hydrate which is then calcined at $500-550°C$ to yield anhydrous AlF_3.

6.3. Organoaluminum Compounds. Application of aluminum compounds in organic chemistry came of age in the 1950s when the direct synthesis of trialkylaluminum compounds, particularly triethylaluminum and triisobutyl-aluminum from metallic aluminum, hydrogen, and the olefins ethylene and iso-butylene, made available economic organoaluminum raw materials for a wide variety of chemical reactions (see ORGANOMETALLICS, Σ-BONDED ALKYLS AND ARYLS).

The alkyls and aryls, R_3Al (in monomer form), are colorless liquids or low melting solids easily oxidized and hydrolyzed when exposed to the atmosphere. Triethylaluminum (TEA), one of the most commercially important members of this family of chemicals, is so reactive it bursts into flame on contact with air, ie, it is pyrophoric, and it reacts violently with water. This behavior is typical and special techniques are necessary for the safe handling and use of organo-aluminum compounds.

The alkylaluminum halides, R_nAlX_{3-n}, where X is Cl, Br, I, and R is methyl, ethyl, propyl, iso-butyl, etc, in monomer form, and $n = 1$ or 2, are less easily oxidized and hydrolyzed than the trialkyls. Organoaluminum hydrides such as diisobutylaluminum hydride [1191-15-7], $(iso-C_4H_9)_2AlH$, are also available. Organoaluminum compounds are used commercially in multimillion kg/yr quantities as catalysts or starting materials for the manufacture of organic compounds such as plastics, elastomers (qv) biodegradable detergents, and organometallics containing zinc, phosphorus, or tin (8,20–22).

6.4. Sodium Aluminate. Sodium aluminate is manufactured by dissolving high purity $Al(OH)_3$ in 50% sodium hydroxide solution

$$Al(OH)_3 + NaOH \longrightarrow Na^+ + Al(OH)_4^-$$
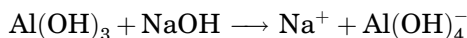
The resulting solutions contain high dissolved solids content in the range of 30 wt% or more. Special surfactant technology (23) is sometimes used to avoid precipitation of $Al(OH)_3$ or at least to extend the shelf life of the caustic liquor.

Sodium aluminate is used in water purification, in the paper industry, for the after treatment of TiO_2 pigment, and in the manufacture of aluminum containing catalysts and zeolite.

6.5. Zeolites. A large and growing industrial use of aluminum hydroxide and sodium aluminate is the manufacture of synthetic zeolites (see MOLECULAR SIEVES). 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 $(100-150^{\circ}C)$ temperature, high pH hydrothermal synthesis. For example the manufacture of the industrially important zeolites A, X, and Y is generally carried out by mixing sodium aluminate and sodium silicate solutions to form a sodium aluminosilicate gel. Gel-aging 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 extremely versatile: uses include detergent manufacture, ion-exchange resins (ie, water softeners), catalytic applications in the petroleum industry, separation processes (ie, molecular sieves), and as an adsorbent for water, carbon dioxide, mercaptans, and hydrogen sulfide.

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