# **Alumina**

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# HISTORICAL CONTEXT

In 1988, the Bayer process celebrated its 100-year anniversary since its invention by the Austrian chemist Karl Josef Bayer. In the intervening years, significant events have shaped the present alumina industry (Gerard and Stroup 1962; Cundiff 1985; Hudson 1987; Donaldson and Raahauge 2013).

More energy-efficient digestion designs have evolved, with a shift toward indirect slurry heating technologies in preference to either indirect liquor heating or direct steam injection. The introduction and use of synthetic flocculants, combined with improved thickener designs, has reduced the size of settler and washer tanks, decreased losses of soda and alumina, and increased the solids concentration of the bauxite residue. Improved bauxite residue management guidelines on dry mud stacking emerged from 1986 onward. A tragic accident with a breached dam in Hungary in 2010 highlighted the importance of adhering to these criteria. Many refineries converted their precipitation process from floury to sandy alumina during the 1980s and 1990s. Sandy alumina has a coarser particle size distribution and higher specific surface area (SSA) for fluoride capture at the smelters. Increasing oil prices made rotary kilns obsolete, and they were replaced by stationary calciners, with an almost 30% reduced fuel consumption.

Economy of scale is the major driver for justifying new refineries outside China. China, however, has emerged as the major alumina-producing country in the world, increasing production from approximately 4 Mt (million metric tons) in 2000 to more than 70 Mt in 2017. Growth was predominantly achieved through replication of standardized process trains, with 0.3- to 0.5-Mt capacity each only achieving 65%–70% capacity utilization. In the same period, production in the rest of the world increased from approximately 48 to about 56 Mt, mainly through installation of new process trains of 0.7- to 2.0-Mt capacity each. Closures of poorly performing assets in this period were partially offset by debottlenecking existing refineries.

Total world bauxite demand in 2013 was estimated at 325 Mt, with China accounting for about 135 Mt. Decreasing the ratio of alumina to silica (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) in Chinese bauxite increased the imported bauxite price to about US\$50–60/t CIF (cost, insurance, and freight) in 2015. This led to investigation of new bauxite beneficiation technologies, with flotation introduced commercially in China. The alumina price decoupled from the traditional percent linkage to the 3-month London Metal Exchange price of primary aluminum and was replaced with its own Alumina Price Index (API). The API reflects alumina cost price fundamentals.

Despite the increasing deficit of alumina on an estimated world demand of 126 Mt/yr alumina in 2017, price volatility remains an issue. For example, a high of US\$600/t fob (free on board) in Australia in 2005/2006 to a low of US\$200/t in early 2016 has been seen. Such price volatility makes investment in new alumina refineries very risky in the near term.

# **Alumina Uses and Properties**

Annual production of aluminum hydroxide globally in 2017 was 189 Mt. Of this, about 178 Mt was converted to aluminum oxide for conversion to aluminum metal (termed smeltergrade alumina [SGA]); the remaining approximately 11 Mt of aluminum hydroxide is termed nonmetallurgical-grade alumina or chemical-grade alumina (CGA). This CGA market is comprised almost equally between uses of the aluminum hydroxide and specialty aluminum oxides. Aluminum hydroxide is used to make water-treatment chemicals, such as aluminum sulfate, polyaluminum chloride, and sodium aluminate. It is also used as fire retardant and to make pseudoboehmites for catalysts, for titanium dioxide coatings, for zeolite production, or as feedstock for speciality aluminum oxides and aluminum hydroxides. The specialty aluminum oxides include calcined alumina, activated alumina, fused alumina, and tabular alumina. Specialty calcined alumina is used in refractories, engineering ceramics, electronics, electrical insulators, spark

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plugs, wear parts, whitewares, and polishing; many of these applications require a high alpha-alumina content and are normally still made using rotary kiln calcination. The specialty applications are driven by the characteristics of aluminum oxide, which impart good temperature resistance, hardness and abrasive properties, chemical resistance, thermal shock resistance, electrical resistance, and transparency to radiofrequency radiation. As well as the alpha-alumina content, the other critical requirements for specialty aluminum oxides are controlled soda content, particle size, particle size distribution, and morphology.

Activated alumina may be obtained either by low-temperature (LT) calcination of aluminum hydroxide at 200°–400°C or flash activation at approximately 1,100°C. The material has a high SSA—up to 350 m²/g—and the pore size distribution can be carefully controlled. Major applications include acting as a desiccant, a Claus catalyst, catalyst removal agent in polyethylene production, a fluoride and arsenic removal agent for water, and a catalyst bed support.

Fused alumina is manufactured by electrofusing calcined aluminum oxide to more than 2,000°C in a furnace and then allowing the fused melt to slowly cool. After cooling, it is crushed and graded to different grain sizes and primarily used for the manufacture of abrasives; minor amounts are used in refractories.

Tabular alumina is manufactured from calcined alumina by initially pelletizing finely milled calcined alumina into spheres ~15–30 mm in size. The spheres are then sintered in a shaft kiln at about 1,900°C. The spheres are sometimes used as produced, or more frequently, they are crushed and separated into various size fractions. The main use is in high-alumina refractories for many industries with secondary uses in the filtration of molten aluminum metal used for can stock, as a support medium in desiccant beds, heat exchangers (HEs),

Table 1 Chemical composition of typical raw bauxites

Bauxite-Grade Applications	Major Oxides, %			
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
Metallurgical	31–52	1.5–15	5–30	1–6
Cement	45-55	Max. 6	20-30	3
Abrasive	Min. 55	Max. 5	Max. 6	Min. 2.5
Chemical	Min. 55-58	Max. 5-12	Max. 2	0–6
Refractory	Min. 59-61	Max. 0.5-5.5	Max. 2	Max. 2.5

Source: Mahadevan 2015

or catalysts. The name *tabular* derives from the large tablet-shaped alumina crystals that typically measure 50–200 μm with a density of at least 3.45 g/cm<sup>3</sup> (Sleppy et al. 1991).

# **Bauxite Uses and Composition**

Aluminum represents about 8% of the earth's crust by mass but is never found isolated as the metal. Bauxite of various chemical compositions is used in different industries (Table 1) but not in quantities comparable to bauxite used for production of metallurgical-grade alumina or SGA. The bauxite application as a ceramic proppant in the hydraulic fracturing industry, however, is quickly growing (estimated to be about 12% per year), reaching 65 Mt/yr by 2017 (O'Driscoll 2013).

Bauxite is the ore with the highest content of alumina of the raw material considered for making alumina (Table 2), which is subsequently reduced to primary aluminum. The major mineral is gibbsite, Al(OH)<sub>3</sub>, also named alumina trihydrate (ATH) Al<sub>2</sub>O<sub>3</sub>3H<sub>2</sub>O. The other common minerals are boehmite and diaspore, AlO(OH), also named alumina monohydrate (AMH), Al<sub>2</sub>O<sub>3</sub>H<sub>2</sub>O.

#### **BAUXITE AND SMELTER-GRADE ALUMINA**

The Bayer process using bauxite as raw material is the most economical process currently known to be applicable to ores containing hydrated alumina minerals for the production of SGA and thus the focus of the remainder of this alumina section.

# Bauxite Origin, Mineralogy, and Composition

Bauxite is named after the deposit found in Les Baux, France, in 1821, which was discovered by geologist Pierre Berthier. Figure 1 shows bauxite reserves in selected countries.

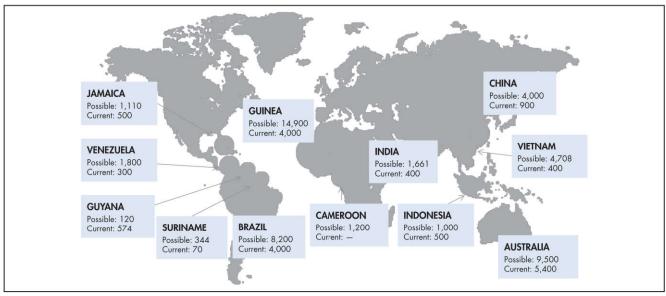
There are two basic types of bauxite—lateritic and karst—referring to their geological formation over thousands of years (Komolossy 2010). Lateritic bauxites are mostly found in or close to the tropics and account for approximately 90% of total bauxite deposits of about 67 Mt (Best 2013). Lateritic bauxite is formed as a residue after weathering/acid leaching away of silicates from the original alumina-silicate formation, leaving behind aluminum hydroxides. Many elements and minerals can be found in tropical bauxite (Authier-Matin et al. 2001; Table 3).

Karst-type bauxite is residual sediment accumulated on karstified carbonate rocks. This type of bauxite accounts for about 10% of total bauxite deposits and can be found in

Table 2 Mineralogy of aluminous ores

Ore/Rock	Mineral	Formula	Al <sub>2</sub> O <sub>3</sub> in Mineral, %	Al <sub>2</sub> O <sub>3</sub> in Ore, %
Bauxite	Gibbsite	AI(OH) <sub>3</sub>	65	
	Boehmite	AlO(OH)	85	35-67
_	Diaspore	AlO(OH)	85	
Clay	Kaolin	Al <sub>2</sub> O <sub>3</sub> 2SiO <sub>2</sub> 2H <sub>2</sub> O	40	20–35
Anorthosite	Albite	Na <sub>2</sub> O Al <sub>2</sub> O <sub>3</sub> 6SiO <sub>2</sub>	20	
	Anorthite	CaO Al <sub>2</sub> O <sub>3</sub> 2SiO <sub>2</sub>	37	22-30
Nepheline syenite	Nepheline	(Na,K)·(Al,Si) <sub>2</sub> O <sub>4</sub>	36	
- 10	Feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	18.4	20-25
Alunite	Alunite	$K_2SO_4Al_2(SO_4)_34Al(OH)_3$	37	6–15
Shale	Clay + illite	(OH) <sub>4</sub> K <sub>2</sub> (Si <sub>6</sub> Al <sub>2</sub> )(Mg, Fe)O <sub>20</sub>	38.5	15–30
Aluminous phosphate	Wavellite	Al <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>3</sub> 5H <sub>2</sub> O	37	
1000 (100)	Millisite	$(NaK)CaAl_{6}(PO_{4})_{4}(OH)_{9}$	37	5-15

Source: Milne 1982



Source: Wood and Harbor Intelligence 2014

Figure 1 Bauxite reserves per million metric tons

Table 3 Mineralogical composition of tropical bauxite

Element	Mineral	Chemical Composition
Major		
Aluminum	Gibbsite	Al(OH) <sub>3</sub> or Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O
Silicon	Boehmite	AlO(OH) or Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O
Iron	Quartz	SiO <sub>2</sub>
Titanium	Kaolinite/halloysite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> or Al <sub>2</sub> O <sub>3</sub> 2SiO <sub>2</sub> 2H <sub>2</sub> O
	Hematite	Fe <sub>2</sub> O <sub>3</sub>
	Aluminian goethite	(Fe,Al)O(OH) or (Fe,Al) <sub>2</sub> O <sub>3</sub> H <sub>2</sub> O
	Anatase	TiO <sub>2</sub>
	Rutile	TiO <sub>2</sub>
Minor		
Carbon	Organic carbon	Humic materials
Phosphorus	Wavellite	$Al_3(PO_4)_2(OH)_35H_2O$
Calcium	Crandallite-H	$CaAl_3(PO_4)(PO_3OH)(OH)_6$
Potassium	Calcite	CaCO <sub>3</sub>
Manganese	Crandallite-H	$CaAl_3(PO_4)(PO_3OH)(OH)_6$
Magnesium	Illite	$KAl_2(Si_3AlO_{10})(OH)_2$
Sodium	Lithophorite	(Al, Li)MnO <sub>2</sub> (OH) <sub>2</sub>
Strontium	Magnesite	MgCO <sub>3</sub>
Sulfur	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Zinc*	Dawsonite	NaAlCO <sub>3</sub> (OH) <sub>2</sub>
Chromium*	Celestite	SrSO <sub>4</sub>
Vanadium*	Woodhouseite	$CaAl_3(PO_4)(SO_4)(OH)_6$
Zirconium	Pyrite	FeS <sub>2</sub>
	Gahnite	$ZnAl_2O_4$
	Chromite	FeCr <sub>2</sub> O <sub>8</sub>
	Schubnelite	Fe <sub>2</sub> (V <sub>2</sub> O <sub>5</sub> )2H <sub>2</sub> O
	Zircon	ZrSiO <sub>4</sub>

Source: Authier-Matin et al. 2001. Copyright 2001 by The Minerals, Metals & Materials Society. Used with permission.

Jamaica, Russia, China, and Mediterranean countries, where diaspore is the main Al<sub>2</sub>O<sub>3</sub> mineral (Komolossy 2010).

# **Smelter-Grade Alumina Requirements**

Alumina is a commodity traded on world markets with changing specifications over time (Table 4). Many smelters may buy on long-term contracts or buy from the spot market. To

minimize transportation cost, refineries are finding it economical to trade alumina with each other. As the smelters have continually improved in energy efficiency, environmental performance, and increased pot size and life, the quality requirements of the alumina have changed. The types of aluminum alloys now produced and the use of recycled aluminum has added to lower levels of impurities being required in the product. SGA is needed that has the required transport characteristics of flowability and attrition resistance (S.J. Lindsay 2014; Archer 1983); that is, it is not dusty and is able to absorb hydrogen fluorides from the off-gases passing through the dry scrubbers (high surface area) without breaking down (attrition resistance). Further, a particle sizing is required such that the alumina will disperse freely in the pots and enable complete dissolution of the alumina (Homsi 2001; Welch and Kuschel 2007). The chemical requirements of SGA address the application as raw material for primary aluminum production.

# **Chemical Requirements**

The chemical requirements of SGA are shown in Table 5 (middle column) compared with bauxite composition (right-hand column). A high level of *soda* is tolerated as the electrolyte is cryolite. Too high a soda content, however, means excess bath (electrolyte) is produced, so there is an upper limit that decreases as pot life is increased (J.B. Lindsay 2012). Lime is added to the bath and thus calcium is not such a critical component in SGA. Neither the soda nor the calcium end up in the metal. The Bayer process can generally meet the required impurity-level specifications, provided the pregnant liquor is filtered to remove residual particulates prior to precipitation. Historically, silica was an issue with especially low-reactive silica bauxites and for certain refineries because of their design and processing conditions. It was often necessary to add reactive silica (with consequently higher caustic consumption) or redigest some of the precipitated gibbsite to meet product specifications. With the introduction of predesilication, not only can silica in liquor (and consequently product alumina) be controlled to the required level, but it is

<sup>\*</sup> At least some of the zinc, chromium, and vanadium have been established to be present in alumina goethian lattice.

Table 4 Smelter-grade alumina properties over time

SGA Property	Unit	Floury Alumina	Sandy Alumina	Typical 2015
Purity	wt %	>99.3	>99.3	99.3–99.7
Loss on ignition, 300°–1,000°C	wt %	0.1-0.3	0.4-0.8	<1.0
Gibbsite	wt %	No data	No data	<0.5
Bulk density, loose	g/L	800	950	950-1,000
Angle of repose	degree	45	30–32	30–32
Particle size distribution >100 mesh/150 µm <325 mesh/45 µm Superfines <20 µm	wt % wt % wt %	No data 45–60 No data	No data 5–10 1.3	5–10 Maximum 10 1–2
Specific surface area, BET (Brunauer–Emmett–Teller)	m <sup>2</sup> /g	5	50–80	60–80
Alpha content	%	85–96	10–30	<5-10
Attrition index*	wt %	No data	13–23	<20
Flow funnel test*	second	No data	No data	85–95
Dust index*	kg/t	No data	1.03-1.37	0.5-1.3

<sup>\*</sup>Not in all certificates of analyses; see text for references and additional comments.

Table 5 Typical chemical compositions of smelter-grade alumina and tropical bauxite\*

Constituent	In SGA, wt % oxide	In Bauxite, wt %
Al <sub>2</sub> O <sub>3</sub> * as gibbsite Al <sub>2</sub> O <sub>3</sub> as boehmite	<0.5% No data	30–60 <0.2–20
$Al_2O_3$	99.3-99.7	35–67
Fe <sub>2</sub> O <sub>3</sub>	0.005-0.020	1–30
SiO <sub>2</sub> clay	No data	0.3-6
SiO <sub>2</sub> quartz	0.005-0.025	0.2-10
Na <sub>2</sub> O	0.30-0.50	No data
CaO	<0.005-0.040	0.1-2
TiO <sub>2</sub>	0.001-0.008	<0.5-10
ZnO	<0.001-0.010	0.002-0.10
P <sub>2</sub> O <sub>5</sub>	<0.0001-0.0015	0.02-1.0
V <sub>2</sub> O <sub>5</sub>	<0.001-0.003	0.01-0.10
Ga <sub>2</sub> O <sub>3</sub>	0.005-0.0015	0.004-0.013
Cr <sub>2</sub> O <sub>3</sub>	No data	0.003-0.30
BeO	<1 ppm	No data
MnO	< 0.001	No data
K <sub>2</sub> O	<0.002	No data
SO <sub>3</sub> /S	<0.05-0.20	0.02-0.10
F	No data	0.01-0.10
Hg (ppm)	No data	50-1.000
Organic carbon (as C)	No data	0.02-0.40

Source: Authier-Matin et al. 2001; S.J. Lindsay 2005b; B.J. Welch (personal communication)

also possible to process lower-reactive silica bauxites while still maintaining the required quality. *Iron*, present as iron oxide in the bauxite, is sparingly soluble in Bayer liquor. Any iron that is dissolved in the liquor precipitates and ends up in the alumina. Iron can be an issue for high-temperature (HT) digestion refineries and those refineries processing low-iron bauxite. In some instances, it has required low-iron bauxite to be blended with high-iron bauxite to control the iron in alumina. There are other ways that iron can be controlled, and generally, the smelter requirements can be met.

Titanium also behaves like iron, but it can be removed from Bayer liquor prior to precipitation using lime. Lime is also used for phosphate control, but that is often as much for processing issues within the refinery rather than product quality. Gallium cannot be controlled, as it reacts similarly to aluminum, and thus refineries processing high-gallium bauxite produce high-gallium alumina. The gallium in the liquor can be, and at some refineries is, extracted for gallium production. The large amount of gallium in Bayer liquor is far greater than the world's current requirement, and generally, it is not profitable to extract it. Beryllium is a worker exposure concern at smelters in the United States and Quebec and is currently a watch list item for alumina producers (S.J. Lindsay 2005a).

#### **Physical Requirements**

The physical characteristics required for SGA are shown in Table 6 together with the reasons for their importance. The modern Bayer refinery can readily meet the particle size requirements that are predominantly related to the handling properties (flowability) of the alumina and its impact on anode effect and current efficiency in the smelters (Lindsay 2014). Content of fines (<325 mesh) and superfines (<20 µm) is of special importance in this respect, but also because of its perceived impact on dustiness (Perra 1984; Hsieh 1987; Authier-Matin 1989). Fines and superfines are produced in precipitation (Audet et al. 2012) and from the breakdown of the alumina particle in stationary calciners (Klett et al. 2010; Raahauge and Devarajan 2015), as well as in certain types of dry scrubbers at the smelters (Taylor 2005; S.J. Lindsay 2011). Transportation of SGA has also added to the need for attritionresistant particles (Wind et al. 2012; Saatci et al. 2004) that do not easily break down. Laser sizers, the flow funnel (Hsieh 1987), and attrition tests (Forsyth and Hertwig 1949) are major enablers to characterize these properties. A marked improvement in alumina properties by reducing the fines content of the alumina and making a more robust particle (Sang 1987; Bhasin and Schenk 1992) has reduced many of the issues at the smelters and enabled the cells to be run at ever higher efficiencies.

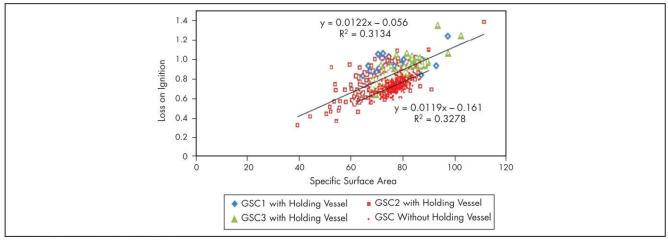
The Alumina Quality Workshops held in Australia since 1993 (S.J. Lindsay 2005a) bring smelting and alumina refiners

<sup>\*</sup>Typically, alpha-Al<sub>2</sub>O<sub>3</sub> content ranges from 2% to 30%.

Table 6 Smelter-grade alumina properties and their importance

SGA Property	Role/Importance of Property in Smelter
Purity	Na and Ca for AIF <sub>3</sub> consumption, other metallic impurities
Loss on ignition	0°–300°C adsorbed readily; releases volatiles (can form <i>volca</i> os for point feeders) 300°–1,000°C predominantly Al-O-H compounds that are major contributors to hydrogen fluoride (HF) evolution
Bulk density	Accuracy of correlation between volumetric feed and assumed mass
Angle of repose	Covering quality if using only Al <sub>2</sub> O <sub>3</sub> , flow properties, ability to fill storage vessels, actual volumetric feed transfer
Particle size distribution	Consistency of properties, tendency to release dust (fines), cell performance perception of impact on solubility (coarse)
Specific surface area, BET (Brunauer–Emmett–Teller)	Potential capacity for HF gas absorption
Alpha content	Measure of conversion of the calcined Al(OH) <sub>3</sub> (trh yd ate) to the most stable alumina phase, a secondary measure of surface area for a given calcination method; crusting tendency
Attrition index	Tendency for the polygranular alumina to disintegrate to a finer particle size range
Flow funnel test	The flowability of alumina
Dust index	Qualitative assessment of ability to become suspended in the cell environment and be transported away
990 DATE MANUAL OF TRANSPORT OF 1997	AND

Source: Welch and Kuschel 2007. Copyright 2007 by The Minerals, Metals & Materials Society. Used with permission.



Source: Raahauge and Devarajan 2015

Figure 2 Properties of smelter-grade alumina from gas suspension calciner (GSC)

together and facilitate the understanding of refinery issues and smelter requirements. The major issue now is that small amounts of superfines ( $<20~\mu m$ ) are sufficiently deleterious, as they can segregate in bins and then have a significant effect on handling and dusting. Some of those superfines come from the refinery, and some are produced at the smelter.

The use of dry scrubbers at the smelters to clean the offgases has necessitated producing a high SSA SGA product for hydrogen fluoride (HF) capture (S.J. Lindsay 2009). To produce the SSA required, calciners at the refineries are operated at an overall lower temperature. This results in a higher loss on ignition (LOI) as the two properties are interlinked, which is illustrated in Figure 2 showing LOI versus SSA from a gas suspension calciner (GSC) without and with a fluidized holding vessel. With current calcination technology, it is difficult to produce higher SSA without increasing the LOI content.

#### Measurements of Smelter-Grade Alumina Properties

There are agreed-on methods for measuring the various alumina properties, for example, Standards Australia. Chemical analysis uses either inductively coupled plasma spectrometry or X-ray fluorescence (XRF) (Figure 3). Particle size

analysis uses sieve shaker screens (down to and including 325-mesh/45-µm sieve) although most sizing for control utilizes lasers. There are agreed-on standard tests for flowability and attrition resistance but, to date, none for dusting (Kimmerle 1999).

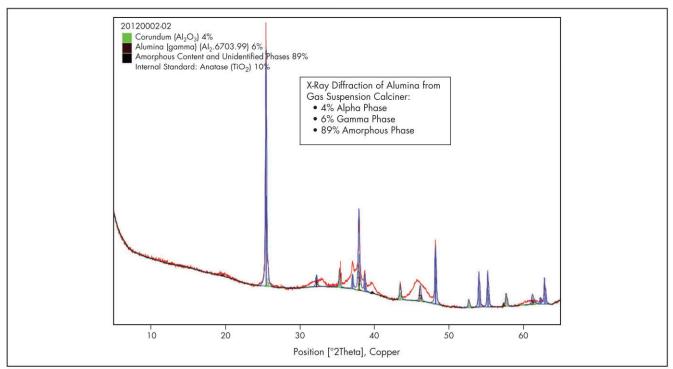
# BAUXITE, THE BAYER PROCESS FLOW SHEET, AND UNIT OPERATIONS

Bauxite is widely traded, which will continue, but currently, there is no single international approach to determine the price.

# **Commercial Bauxite Assessment**

The key Bayer plant processing parameters are extractable alumina, mud factor, chemical caustic consumption, lime consumption, and goethite-to-hematite ratio, as well as total organic content.

Over the years, several assessment methods have been employed of varying accuracy, performance time, and cost (Hill and Robson 1981). Prior to 1990, mostly wet chemical analytical methods were used, while the tendency today is toward using advanced analytical techniques such as X-ray diffraction, XRF, and thermogravimetric analysis in



Source: Raahauge and Devarajan 2015

Figure 3 Chemical analysis of SGA from GSC by X-ray diffraction

combination with mathematical models (Ferret 2014). New bauxite deposits are analyzed based on representative composite samples obtained from detailed drilling programs and feasibility studies carried out to decide if a deposit represents a valuable asset with respect to investing in a new alumina refinery (Wehrli and Jiang 2010).

#### Other Raw Materials and Fuels

The main reagent and consumable is *caustic soda* reacting with silica minerals in the bauxite (primarily kaolin) and precipitate as desilication products (DSPs). The high-strength caustic can be used to remove alumina scales from tanks and piping, before adding that liquor to the process as caustic makeup.

Refinery boilers are fueled with coal, heavy fuel oil, or natural gas, which produce steam and power. Calciners are fueled by heavy fuel oil or natural gas to maintain the purity of the alumina. In China, sinter kilns are fueled by coal, and most calciners are fueled by coal gas derived from coal gasification.

# Mining and Beneficiation

Nowadays the utilized bauxite deposits are nearly all-surface or near-surface deposits, and open cut mining is used, making mining very easy. The average thickness of bauxite deposits ranges from 2 to 20 m with a production average of 5 m (Wagner 2013). There is rarely any need to use blasting unless a hard cap has formed in the upper layer. The overburden thickness, which has to be removed before excavating the bauxite, can vary from 0.4 to 12 m with an average of 2 m (Wagner 2013).

Some deposits can be quite deep (e.g., in Brazil), requiring high stripping ratios that significantly increase the mining cost. For surface bauxites, the mining costs per metric ton of

alumina are low and not a major contributor to the cost of the alumina; however, those costs increase sharply for the deeper deposits. Several of these deposits—about 50%—contain a high level of clay minerals that need to be washed from the bauxite to reduce reactive silica, increase alumina content, and improve the handling characteristics. The clay has a severe impact on both the mining and transport of the material to the washing stage because of its sticky nature.

For those bauxites requiring washing, the washing operation is relatively straightforward, which, at most, requires some crushers to generally break up the material. The washer/scrubber stage is followed by further size classification with material <1 mm in size usually being discarded to tailings ponds with >80% clay. Grade control is relatively clearcut for recoverable alumina and reactive silica, although in some areas, the organics content in the bauxite also needs to be considered. No milling is required, and consequently there is not a large power requirement for the mining/washing operations readily done at the mine site. For some operations, the tailings are filtered, and the filtered mud is deposited to the tailings area with such areas rehabilitated. Given that many of these deposits are in equatorial and tropical areas, there are water containment issues.

China has very rapidly developed to become the largest alumina producer in the world, consuming approximately 130 Mt/yr bauxite, of which about 50% is imported (Jiang et al. 2016). The reason for the relatively high import of bauxite is that most Chinese bauxite deposits are diasporic with a decreasing alumina-to-silica (A/S) ratio over time, resulting in an increasing bauxite-to-alumina ratio and increased soda consumption. For high-silica bauxites with A/S = 3 to 5, froth flotation techniques have been developed and introduced into the flotation Bayer process. In China, flotation technology is also

being developed for desulfurization of bauxite, and reverse flotation has been tested in Brazil at Companhia Brasileria de Aluminio's plant at Mirai, Minas Gerais (Chaves 2010). Because many of the high-quality, easily accessible bauxite deposits have been exploited for years, more sophisticated bauxite beneficiation technologies are emerging. Subject to grain size and iron content, jigs for coarse or spiral classifiers for fines classification in combination with drum separators or wet high-intensity magnetic separators may enter future bauxite beneficiation flow sheets (Bautenbach 2008). Thermal activation of boehmitic bauxite for removing organics (Hollit et al. 2002) and roasting high-silica bauxites (Smith and Xu 2010) have been tested but have still not reached industrial-scale application.

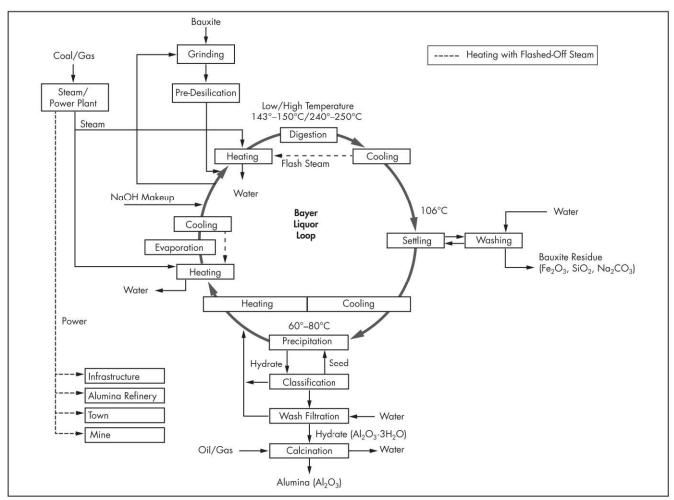
Transport of the bauxite to the refinery can be a significant cost, as many refineries are situated some distance from the mines. Each ton of bauxite is transported 54 km on average from the mine to the local refinery stockpile or shipping point (Wagner 2013). Some examples are the Worsley refinery in Western Australia receiving bauxite from its Mount Saddleback mining hub on a 51-km-long conveyor line (Cochrane et al. 2011). In some cases, a slurry pipeline is the most economical solution, for example, the 245-km-long, 13.5-Mt/yr Mineração Bauxita Paragominas pipeline in

Brazil (Grandhi et al. 2008). The average energy consumption ranges from 40 to 470 mJ/t dry bauxite mined with an average of 153 mJ/t, encouraging mine operators to adopt energy-efficient strategies and reduce emissions (Wagner 2013). Bauxite bought commercially is invariably significantly higher in cost than for a refinery-owned mine and, together with transport costs, can be a major part of alumina cost.

# Introduction to the Bayer Process and Terminology

A typical schematic block flow sheet of the alumina refinery Bayer process for LT and HT digestion of bauxite is shown in Figure 4, naming the various unit operations in the process. The *Bayer liquor loop* or *Bayer wheel* comprises a circulating caustic liquor flow with dissolved alumina (Al<sub>2</sub>O<sub>3</sub>) measured in grams per liter (g/L). The following liquor definitions apply:

- **Spent liquor.** This occurs after precipitation and before digestion. Spent liquor is the most common name for this part of the Bayer process liquor loop.
- **Test tank liquor.** This is the spent liquor just before digestion. Liquor analysis is used to calculate the bauxite quantity to be charged to the process. *Digester blow-off* is cooled by flashing before settling.



Source: P.J.C. ter Weer 2014

Figure 4 Bayer process block flow sheet

- **Pregnant liquor.** This occurs after digestion/settling and before precipitation; also named *green liquor*. Pregnant liquor is polished by filtration to remove solids before precipitation of Al(OH)<sub>3</sub>.
- Caustic concentration. The caustic concentration of the circulating liquor is determined by thermotitration and is expressed in various ways, originating in the old North American and European practices of Bayer process design and operation. The following conversions apply:

$$Na_2CO_3 (g/L) = (106/80) \times NaOH (g/L)$$
  
=  $(106/62) \times Na_2O (g/L)$  (EQ 1)

**Total caustic (TC).** TC or C includes sodium present as  $[OH^-] + [Al(OH)_4^-]$  and is expressed as g/L sodium carbonate  $(Na_2CO_3)$ .

**Total alkali (TA).** TA includes sodium present as  $[OH^-]$  +  $[Al(OH)_4^-]$  +  $[CO^{3-}]$  and is expressed as  $g/L Na_2CO_3$ .

**Total soda.** This is measured by atomic absorption, including carbonate ions  $(CO_3^{2-})$  and sodium with other anionic impurities  $(C_2O_4^{2-}, Cl^-, SO_4^{2-}, \text{etc.})$  of which sodium oxalate  $(Na_2C_2O_4)$  plays an important role.

The alumina-to-caustic (A/C) ratio is also expressed in various ways:

$$A/C = Al_2O_3 (g/L)/Na_2CO_3$$
, caustic (g/L) (EQ 2)

RP = 
$$Al_2O_3$$
 (g/L)/Na<sub>2</sub>O, caustic (g/L)  
=  $(106/62) \times A/C$  (EQ 3)

MR = Na<sub>2</sub>O, caustic (mole/L)/Al<sub>2</sub>O<sub>3</sub> (mole/L)  
= 
$$(102/106)/(A/C) = (102/62)/RP$$
 (EQ 4)

where

RP = ratio ponderel MR = mol ratio

The circulating liquor density ranges from 1.25 g/mL up to as high as 1.35 g/mL, with an average of 1.30 g/mL or 1,300 g/L. The liquor density, D, can be estimated from the following formula (as corrected by Raahauge; Ikkatai and Okada 1963):

$$\begin{split} D\ (g/cm^3) &= 1.027 + 0.8985 \cdot 10^{-3} \cdot [Na_2O] \\ &- 0.25 \cdot 10^{-6} \cdot [Na_2O]^2 - 0.395 \cdot 10^{-3} \cdot T \\ &- 0.2 \cdot 10^{-5} \cdot T^2 + 0.49 \cdot 10^{-3} \cdot [Al_2O_3] \end{split} \tag{EQ 5}$$

The "red side" flow-sheet variations depend on the type of bauxite used, whereas the "white side" flow-sheet variations with precipitation are almost standard, regardless of the type of bauxite. The overall refinery production and economics are very dependent on the liquor productivity or yield of alumina expressed as g/L Al<sub>2</sub>O<sub>3</sub> and calculated as follows:

yield = 
$$C_{in} \cdot [(A/C)_{in} - (A/C)_{out}]$$
 (EQ 6)

The green liquor  $(A/C)_{in}$  ratio from digestion is typically in the range of 0.72 to 0.77. The yield of alumina ranges from 50 to 90 g/L  $Al_2O_3$  with an average of 70 g/L  $Al_2O_3$ .

Using the preceding average numbers, the circulating liquor equals 18.6 g liquor/g Al<sub>2</sub>O<sub>3</sub> produced or 18.6 t liquor/t Al<sub>2</sub>O<sub>3</sub> or 14.3 m<sup>3</sup>/t Al<sub>2</sub>O<sub>3</sub> produced.

The alumina production is given by the following equation:

Because of the closed-loop liquor circulation, impurities build up in the liquor. The effect of the impurities is to increase the end ratio (A/C)<sub>out</sub> and thus decrease the yield and productivity (Lectard and Nicolas 1983). Keeping the level of impurities in the liquor circuit under control is a key enabler to maximize the yield/productivity of a modern Bayer refinery.

All refineries have carbonate removal systems. Some remove sulfate and others remove oxalate and other organics from the liquor. The equipment used is bauxite specific. Some refineries use salting out for carbonate and oxalate removal. utilizing evaporators (falling film). Others remove or control carbonate by side stream causticizing. Lime is added to wash liquor, reacting with the liquor in a series of agitated tanks, returning the causticized liquor to the washing operation. Some refineries precipitate sodium oxalate from the spent liquor and filter the slurry, and then treat the filter cake to recover the caustic by various methods and equipment. Organics removal is required at some refineries, subject to organic content in the bauxite and years of refinery operation in order to maintain yield/productivity. As a rule of thumb, more than 10 g/L total organic carbon is critical. Total organic removal can be achieved by liquor burning. Using a rotary kiln or GSC with associated equipment is one option, where stack gases are generated that must be thoroughly controlled and cleaned (Pulpeiro et al. 1998, 2000). Wet oxidation is another option, which is less efficient with respect to oxalate removal, but more cost-effective (Costine et al. 2010; Clegg 2005).

#### **Bayer Process Unit Operations**

The weathered nature of the tropical bauxite means that there are no physiochemical accessibility issues related to digesting the gibbsite.

#### Comminution

The bauxite is typically ground from F80 = 10–25 mm to P80 = 200–400 µm (Filidore and Hadawy 2010), with Bond work indices ranging from 1 to 34 kW·h/t. Some bauxites (notably Jamaican bauxites) almost disintegrate down to slime-sized material that results in flowability issues. Normally the percent solids in the mill can be of the order of 50% without any issues, but for Jamaican bauxite, this reduces to 30% because of the high viscosity of the slurry. The particles are generally a finely interdispersed mixture of gibbsite, iron oxides, and clay. Grinding is done to reduce the size such that the slurry can be readily pumped through the digesters and quartz separated as sand particles afterward. Only in a few instances, such as with diasporic bauxite, is there a need to specifically grind the bauxite to a very fine size for extraction. All bauxite grinding is done in spent liquor at around  $70^{\circ}$ C.

Rod, ball, rod-ball mills, and some semiautogenous mills are used with systems being open or closed circuits. Where closed-circuit milling is practiced, this is often associated with hard components in the bauxite, and then classification by DSM (sieve bend) screens is used.

# Pre- and Post-Desilication Chemistry

The ground bauxite is fed to slurry storage tanks that are also used for pre-desilication prior to digestion. Most refineries use pre-desilication, but at least one refinery has used post-desilication (Harato et al. 1996) to reduce the soda consumption almost 50% compared to a conventional pre-desilication process. Post-desilication is not further discussed (Banovolgyi and Siklosi 1998; Songqing 2008).

The ultimate objective of pre-desilication is to reduce the silica present in the liquor by dissolving and precipitating reactive silica as DSPs. The dynamic desilication process is illustrated in Figure 5. The process involves kaolinite (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O), which is reactive silica that reacts readily with sodium hydroxide (NaOH) and dissolves in the liquor at approximately 100°C (Roach and White 1988). Silica as quartz needs temperatures higher than 200°C to be significantly attacked by caustic (Oku and Yamada 1971).

Following the dissolution of kaolinite (Equation 8), more complex reactions take place by seeded precipitation forming various compositions of DSP (Equation 9) (Authier-Matin et al. 2001), where *X* may be a mix of ½CO<sub>3</sub><sup>2-</sup>, ½SO<sub>4</sub><sup>2-</sup>, 2AlO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, and so forth (Milne 1982).

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O(s) + 6NaOH(aq) \rightarrow$$

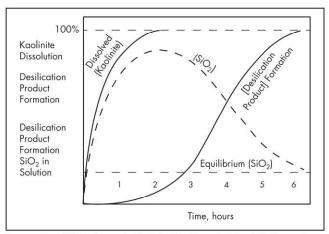
$$2NaAlO_2(aq) + 2Na_2SiO_3(aq) + 5H_2O$$
(EQ 8)

$$\begin{array}{l} 6 \text{NaAIO}_2(\text{aq}) + 6 \text{Na}_2 \text{SiO}_3(\text{aq}) + \text{Na}_2 X(\text{aq}) + 12 \text{H}_2 \text{O} \rightarrow \\ 3 (\text{Na}_2 \text{O} \cdot \text{Al}_2 \text{O}_3 \cdot 2 \text{SiO}_2 \cdot \text{nH}_2 \text{O})(\text{s}) \\ + \text{Na}_2 X + 12 \text{NaOH} \end{array} \tag{EQ 9}$$

#### **Pre-Desilication Unit Operations**

On its way to the storage tanks, the slurry is heated, normally close to 100°C, to dissolve all the clay and form the DSP. These large tanks are agitated by rakes, and there are often three or four in series to reduce short-circuiting and give the residence time required (normally 6–24 hours) (Thomas and Pei 2007; Zirnsak et al. 1999).

The solids density of slurry is normally of the order of 50%, resulting in a plug-flow-type passage of the tanks with limited back-mixing (Oku and Yamada 1971). Exactly how much desilication is required is bauxite specific and also depends on digestion conditions, but modern Bayer refineries have little trouble controlling the silica to meet customer specifications.



Source: Kotte 1981. Copyright 1981 by The Minerals, Metals & Materials Society. Used with permission.

Figure 5 Typical desilication process

#### **Digestion Chemistry**

The digestion process is to dissolve all the hydrated alumina in the bauxite and react all the clay minerals that then precipitate as DSP and thus desilicate the liquor. The digestion process is conducted at different temperatures, pressures, and caustic concentrations depending on the mineralogy of the bauxite.

Bauxite containing mainly trihydrated alumina (ATH), with traces of monohydrated alumina (AMH), as boehmite, can be digested at atmospheric pressure and moderate temperatures (100°–107°C) with caustic concentration between 150 and 250 g/L (Grubbs 1987; Bitsch and Lamerant 1995), compared to standard Bayer digestion of gibbsite (140°–145°C) at less than 10 atm. The chemical reaction dissolving the gibbsite is shown in the following equation:

$$2Al(OH)_3(s) + 2NaOH(1) \rightarrow 2NaAl(OH)_4(1)$$
 (EQ 10)

The boehmite  $(230^{\circ}-245^{\circ}C)$  and diaspore  $(230^{\circ}-280^{\circ}C)$  with the addition of calcium oxide (CaO) need higher digestion temperatures and pressures up to 80 atm (Figure 6), with caustic concentrations of 180-200 g/L  $Na_2CO_3$  and 230-350 g/L  $Na_2CO_3$ , respectively, to dissolve together with other impurities such as quartz, goethite, and anatase:

$$AlOOH(s) + NaOH(l) + H_2O \rightarrow NaAl(OH)_4(l)$$
 (EQ 11)

$$SiO_2(s) + 2NaOH(1) \rightarrow Na_2SiO_3(1) + H_2O$$
 (EQ 12)

$$2\text{FeOOH(s)} \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}$$
 (EQ 13)

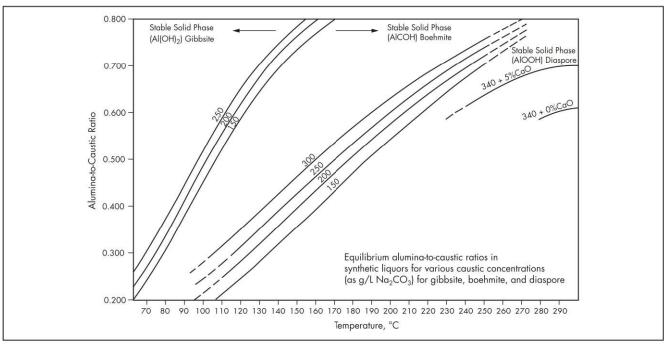
$$TiO_2(s) + 2NaOH(l) \rightarrow Na_2TiO_3(l) + H_2O$$
 (EQ 14)

During HT digestion with optimized lime addition, many complex DSPs are formed and precipitated (Jiang et al. 2016).

# Digestion Flow Sheet and Equipment

The bauxite slurry from pre-desilication and spent liquor is heated and sent to the digesters. This is either done as two separate streams or in some refineries by mixing the bauxite slurry and spent liquor streams before pumping the mixed streams through the slurry heaters. The slurry or liquor heaters can be shell and multitube HEs or jacketed pipe heaters (JPHs) with the slurry or liquor passing inside the pipes in either case. In dual- or two-stream plants, the spent liquor is normally heated by flash and live steam to a higher temperature than the digester temperature and then mixed with the slurry either in the digester or earlier in a contact live steam heater (LSH) (Figure 7A), where steam is added directly to achieve digestion temperature.

As live steam adds dilution, the trend is to minimize direct live steam uses and heat the slurry mixed with spent liquor as a single stream. Since 2002, JPHs have gained a foothold in HT digestion (Songqing and Zhonglin 2004; Kelly et al. 2006). The latest refineries built outside China are using a single stream with JPH (Haneman and Rae 2015; Figure 8). Several stages are required to maximize energy efficiency, matching the flash vessel stages so that export of excess live steam is minimized or avoided (Kelly et al. 2006). Some refineries use internal heating coils in the digesters after the heaters. A very attractive and energy-efficient system for diasporic bauxite is to use molten salt as the final heating stage to avoid final steam heating. This was used in the VAW (Vereinigte Aluminium-Werke) tube digesters (Bielfeldt and Winkhaus 1981) in Germany. Subsequently, this technology has been vastly improved in Chinese refineries where it has been a



Source: Kotte 1981. Copyright 1981 by The Minerals, Metals & Materials Society. Used with permission.

Figure 6 Equilibrium A/C ratio in synthetic caustic liquors

major enabler in terms of energy reduction in processing such bauxites (Songqing and Zhonglin 2004).

The digesters are a series of tanks: self-agitated (without internals) or with mechanical agitators. Vertical autoclaves or horizontal tube digesters are used today. Autoclaves are economically used for HT digestion of bauxites that require more than 5–10 minutes of retention time. Normally, there are three to five autoclaves arranged in series to minimize short-circuiting and achieve the residence time required. For HT plants needing long digestion times, there can be up to 10 autoclave units. The slurry feed may be as high as 20% solids, but that becomes less than 10% at the final digester. For pumping, positive displacement pumps are used because of the higher pressure in HT refineries processing boehmitic or diasporic bauxite.

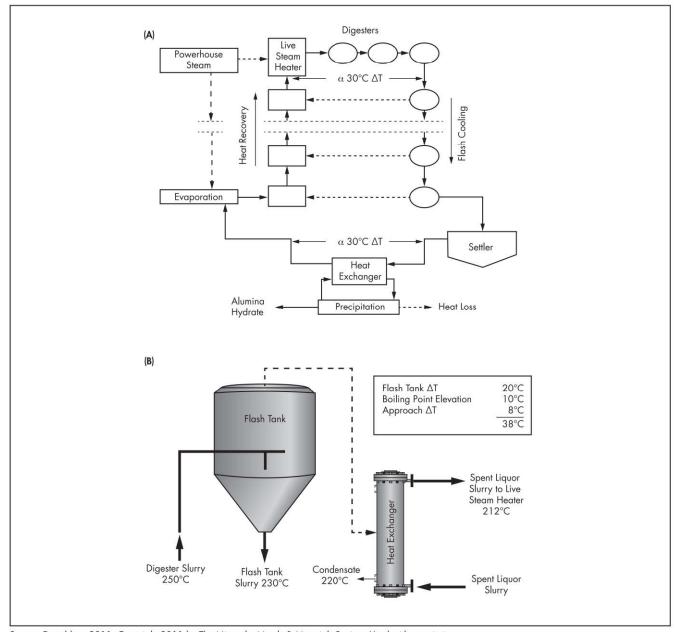
The digested slurry is let down to atmospheric pressure through a series of flash tank/HE stages, about 3-4 for LT digestion and 10-12 for HT digestion. Letting down the slurry in incremental stages is required to (1) provide steam at varying pressures and temperatures to heat the incoming bauxite/ slurry/spent liquor to maximize heat transfer efficiency and (2) reduce wear and carryover through the flash vessels. In HT plants, with evaporation economy of about 7 t water/t steam compared to only about 3-4 t water/t steam (Donaldson 2011), enough flashing steam is recovered to almost eliminate evaporation at the expense of installing more flashing stages. The final flash vessel is essentially a vented tank with little steam exiting, as any steam exiting is a direct energy waste. The last flash stage(s) may be connected to a water-cooled condenser instead of a liquor heater. Heat exchange between the spent liquor heating side of the process and the digested slurry cooling side is critical to ensure minimum energy usage. Multistages are used to maximize heat recovery. Because of the evaporation requirement to remove dilution from the main liquor circuit, most heat interchange is through flashing of the

hot liquor/slurry. This includes some vacuum stages in the lower temperature end to produce steam, which is used to heat the incoming cool liquor. At some of the lowest temperatures, plate heat exchangers (PHEs) are used, but there can be scaling and other issues associated with such equipment. Much of the inefficiency in the heat recovery system comes from scaling of heater tubes by DSP. This may become much less of an issue by using a chemical additive to control the growth of such DSP, which has shown great potential (Spitzer et al. 2005). Another major inefficiency is that the shell side of the HEs can scale up from carryover in the flash tanks. The shell side is very difficult to clean. Heat exchange is still the major energy inefficiency in the Bayer process and will continue to improve with development of chemicals and design to reduce the impact of scaling. Double digestion in combination with a pressure decanter is an alternative to tube digestion for bauxite containing ≥5% boehmite (Kumar et al. 2008).

#### Solid-Liquid Separation and Clarification

Cooled slurry from the digestion area is fed to the settler/ washer thickener train for separation of the solids from the pregnant liquor, washing the solids almost caustic free in a countercurrent thickening process (Laros and Baczek 2009). In the initial thickener (typically called a *clarifier*, *decanter*, or *settler*), it is important to achieve an overflow with high clarity (typically <0.1 g/L solids content) and an underflow slurry with maximum solids concentration (typically >30%). Both requirements are achieved by carefully selecting the most suitable flocculants or combination of flocculants, in combination with a proper feed-well design. The overflow liquor from the settler is sent to a security filtration area, whereas the mud from the underflow is fed to the washer train.

The washer train is a series of thickeners (commonly termed *washer*) arranged in a countercurrent decantation scheme for removing caustic liquor from the mud and

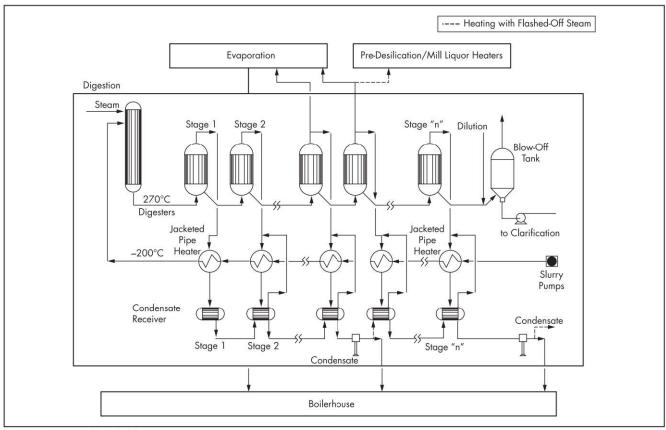


Source: Donaldson 2011. Copyright 2011 by The Minerals, Metals & Materials Society. Used with permission.

Figure 7 Temperature difference across digestion and precipitation

recovering aluminate liquor. This is achieved by the addition of caustic-free hot condensate to the feed of the final washer stage together with the underflow mud from the upstream washer. The same process is repeated several times (typically four to five times), depending on the underflow solids concentration, which can reach up to 65% and higher. When the final washing stage is followed by a filtration stage, the number of washers can be further reduced. For washer services, underflow solids concentration becomes the most important criteria because the increase in underflow solids concentration is key to reducing the number of washing stages. The mud discharged with the underflow of the last washer is either directly pumped to the mud disposal area or fed to an additional filtration stage using red mud drum filters or filter presses.

For several decades, the predominant continuous thickener design used in alumina refineries was the flat bottom/large diameter/outward raking concept, using starch as an additive to promote solids settling and overflow clarification. Today, with the development of modern synthetic flocculants and new feed-well designs, this approach has changed significantly. The use of synthetic flocculants allows achievement of higher settling rates in combination with higher underflow solids concentrations, resulting in thickener designs with greatly reduced tank diameter. By selecting suitable tank parameters, including tank height, thickener rake, and rake drive design, such thickeners produce mud at the high viscosity suitable for paste disposal (common supplier terms are Hi-Rate Thickener or Deep Cone Thickener). Mainly for washer services,



Source: Haneman and Rae 2015

Figure 8 Ma'aden single-stream hybrid digestion flow sheet

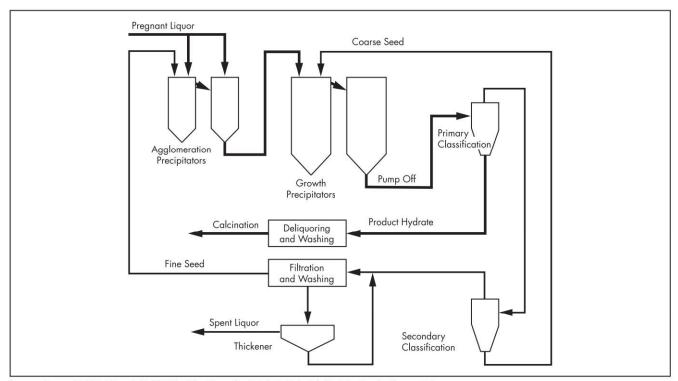
autodilution feed-well designs are provided, suitable for adjusting the feed solids concentration at a level of minimum flocculent consumption and optimum thickener performance. Modern rake designs are designed for high raking torques and to promote underflow density. Rake lifting devices are provided for improving scale removal during tank cleaning.

De-scaling is an important issue to be considered in thickener tank designs, because depending on the tank designation, the tank has to be taken out of service more or less frequently for removal of scales growing on surfaces in contact with the liquor. Scale removal is carried out by chemical cleaning using concentrated caustic liquor or mechanical cleaning based on hydroblasting technology with blasting pressures in the range of 1,500 bar and higher. Tank design is playing a major role in accelerating scale removal during mechanical cleaning.

Many settler/washer thickener designs installed in alumina refineries require the installation of an upfront sand removal system to avoid raking problems. Removal of sand (>150 µm particles) is typically provided by a combination of hydrocyclones followed by a series of rake or screw classifiers in a countercurrent arrangement to wash the sand free of caustic. Because of the higher mud underflow solids concentrations that are achieved in modern thickener designs, those thickeners are tolerating higher sand loads and typically no longer warrant sand removal systems.

A key feature of any settler/washer is a properly designed mud-level transmitter measuring the vertical solids profile inside the thickener tank. The measurement is used to control the mud bed height by controlling the underflow pump rotational speed. The mud-level instrument can also be used to control the flocculent dosage based on the solids inventory in the supernatant.

The clarified aluminate liquor discharged with the overflow of the settler is fed to the security filtration area for further reduction of the solids concentration (<20 mg/L) to avoid quality losses of the hydrated alumina produced in the precipitation area. For decades, horizontal leaf pressure filters (e.g., Kelly filters) have been the standard type of technology for security filtration and are still operated in large numbers in alumina refineries around the globe. These filters have to be drained and opened after each filtration cycle for removal of the accumulated solids and cloth wash. A limited number of refineries used sand filters for security filtration to overcome some of the issues of horizontal leaf filters. The sand filter concept, however, was limited to only a few plants and is no longer considered in modern flow sheets. The predominant contemporary technology is the vertical leaf pressure filter technology, operating with liquor backflush for filter cake removal. This concept allows operating the filter for a large number of cycles with intermittent caustic and sometimes also condensate cleaning to remove nonreacted flocculants, oxalate, and precipitated scale from the filter media. The backflush vertical leaf-type pressure filter typically needs to be opened for changing the filter bags only. Both pressure filter concepts, however, require the addition of tricalcium aluminate (made by reacting milk of lime with aluminate liquor) as a filter aid to support the removal of the fine particles  $(1-2 \mu m)$  that are carried over with the settler overflow. Several vertical pressure



Source: Howard 1988. Copyright 1988 by The Minerals, Metals & Materials Society. Used with permission.

Figure 9 Swiss aluminum precipitation flow sheet

filters are operated in parallel to achieve the desired plant filtration capacity. Standby filters need to be provided for cases when filters are taken out of service for changing filter bags.

#### **Hydrate Precipitation Chemistry**

The polished liquor is sent to hydrate precipitation after being cooled through further heat exchange. The chemistry is the reverse of the ATH digestion:

$$2NaAl(OH)_4(1) \rightarrow 2Al(OH)_3(s) + 2NaOH(1)$$
 (EQ 15)

Although the chemistry appears simple, the design, operation, and control of the population balance of the precipitation process is rather complicated:

- Agglomeration of fine seed particles reduce the number of particles in suspension.
- Formation of new nuclei/crystals and breakage of weak agglomerates increase the number of particles in suspension.
- Agglomerated particles grow to final particle size distribution and process yield.

The driving force and linear growth rate of  $Al(OH)_3$  precipitation from the caustic solution depends on seed surface area, temperature, the degree of supersaturation  $(A-A_{eq})$ , and the caustic concentration C(g/L) of the liquor phase:

$$G \propto \text{Sa Exp}(-E/RT) (A/C - A_{eq}/C)^{g/C^{1/g}}$$
 (EQ 16)

where

 $G = linear growth rate of Al(OH)_3 \mu m/h$ 

Sa = seed area of solid Al(OH)<sub>3</sub> in liquor,  $m^2/L$ 

E = activation energy, kJ/mole

R = universal gas constant, kJ/mole/Kelvin

T = absolute temperature, Kelvin

A = dissolved alumina concentration, g/L

A<sub>eq</sub> = equilibrium concentration, g/L

The equilibrium concentration of dissolved Al(OH)<sub>3</sub> can be predicted (Roesenberg and Healy 1996; McCoy and Dewey 1982). The rate of agglomeration and nucleation is also proportional to the seed area (Sa) of the particle population in the liquor. Because both the rate of precipitation and equilibrium concentration of alumina increase with liquor temperature, there will be an optimum temperature profile across the precipitation flow sheet to maximize the yield of alumina (Chaubal 1990). Therefore inter-tank slurry coolers are installed between the growth tanks (Audet et al. 2012) to control the supersaturation profile.

#### **Precipitation Flow Sheet and Unit Operations**

The agglomeration process is critical to understand. Favorable conditions are low to medium charge of fine seed and high initial ratio. Fine seed hydrate from the second classification stage is added to facilitate agglomeration of fine seed particles into coarser particles (Anjier and Roberson 1985) (Figure 9). The agglomeration process is completed after 4–6 hours of retention time (Tschamper 1981).

The slurry with the agglomerated hydrate particles from the agglomeration tank is mixed with coarse hydrate seed particles from the first classification stage and added to the first precipitation growth tank. Published growth tank conditions are shown in Tables 7 and 8. The residence time required to maximize the yield is of the order of 30–40 hours. Nowadays, the precipitators are mechanically agitated.

The optimum precipitation conditions with respect to achieving high yield or liquor productivity and a strong product have been suggested (Sang 1989) as shown in Figure 10. The *floury* precipitation process employed prior to the 1980s achieved a high yield but did not produce particles suitable for modern smelters. At that time, the objective of the successful conversion from floury to sandy alumina (Tschamper 1981; Minai et al. 1978) was to maintain the high yield of the European floury alumina process while producing a coarser and stronger hydrate particle suitable for calcination in stationary calciners. As an example, those objectives were met by the Gove alumina refinery in Australia (Bhasin and Schenk 1992):

Liquor productivity: 70–80 g/L Al<sub>2</sub>O<sub>3</sub>
Hydrate: 6–7 wt % <45 μm or 325 mesh</li>

Alumina attrition index: 13%–15% on a 45-μm sieve

Impurities, however, also impact the yield or liquor productivity and in a declining direction. Both mineral (sodium chloride [NaCl], sodium sulfate [Na<sub>2</sub>SO<sub>4</sub>], SiO<sub>2</sub>) and organic compounds increase the end point A/C ratio, and thus decrease the yield (Lectard and Nicolas 1983).

Precipitation is one of the most critical areas in the Bayer process, as the amount of alumina removed from the liquor directly relates to the productivity of the circuit and the quality of the final calcined product with respect to purity, particle size, and toughness or attrition resistance. Design and operation of the hydrate precipitation area is driven by economics, including the resulting liquor productivity or yield (P-H. ter Weer 2014; Thomas and Iroside 2015).

The tankage requirement and the large recycle requirement means that the precipitation area in the Bayer process is a highly capital-intensive area.

Table 7 Agglomeration conditions

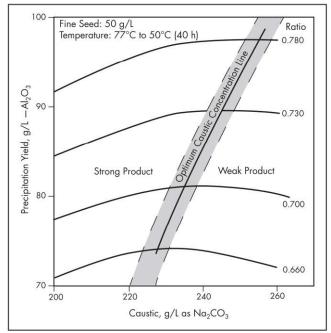
Agglomeration Parameters	Initial A/C Ratio	Temperature, °C	Seed Charge, g/L
Alcoa Chemie	0.65–0.70	65–80	15–70
Kaiser Alumina	0.575-0.700	75–85	70-140
Sumitomo	0.534*	65-80	30-150
Swiss Aluminium	No data	46-77	7-25*

Source: Anjier and Roberson 1985. Copyright 1985 by The Minerals, Metals & Materials Society. Used with permission.

**Table 8 Growth conditions** 

Growth Parameters	Initial A/C Ratio	Temperature, °C	Seed Charge, g/L
Alcoa Chemie	0.490	70	300-900*
Pechiney	0.590-0.620	50-75	700-2,000
Kaiser Aluminum	0.575-0.700	75-85	120-300
Norsk Hydro	0.600-0.650	60–75	500-600*
Sumitomo	0.400-0.480	45-65	400-1,500*
Swiss Aluminium	No data	46-77	130-400

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Source: Sang 1989. Copyright 1989 by The Minerals, Metals & Materials Society. Used with permission.

Figure 10 Yield versus caustic concentration and initial ratio

# Hydrate Classification

At the end of precipitation, the slurry is classified in hydrocyclones. The amount of seed area has to be carefully controlled; otherwise, too many fines will be produced, and a weak agglomerated product will be achieved rather than the desired tough product. The primary hydrocyclone is used to remove product size material with an average particle size of approximately 100 µm. The overflow, returned as coarse and fine seed, is split to improve the strength of the product by classification in a secondary hydrocyclone. The fine seed from the overflow of the secondary hydrocyclone is concentrated in a fine seed thickener. The fine and coarse seed slurry is accompanied by a significant amount of liquor, hence the seed is often filtered to prevent dilution of the incoming liquor. There are also precipitation circuits with a single stage of hydrocyclone classification, which produce a coarser fine seed for the agglomeration process (Audet et al. 2012). This results in a weaker alumina particle with lower bound soda in the alumina (Raahauge and Devarajan 2015).

# Scaling Chemistry

Bayer liquor is supersaturated with respect to many components of the liquor, and one thing it does is form scale. No part of the refinery circuit is immune to scaling, and it requires a large amount of resources to ensure that such scaling does not result in significant production losses. In particular, valves can readily scale and thus become an issue when used for isolation, which extends maintenance shutdowns. When shutdowns for scale removal are frequent, spare equipment is used. Scale removal is accomplished via chemical and mechanical cleaning.

The scale that forms is generally categorized as either *growth* scales or *settled* scales. The former are invariably hard and grow at predictable rates; the latter, which primarily

<sup>\*</sup> Al<sub>2</sub>O<sub>3</sub> supersaturation (g/L/m<sup>2</sup>) seed surface.

<sup>\*</sup>Solids retention precipitators.

occur in slurry lines and tanks, result in slurry particles being cemented together.

Settled/emented scales can grow very rapidly and unpredictably, both in rate and location. Throughout the long history of the Bayer process, various ways and means to minimize the negative impact of scale on productivity, energy efficiency, and safety have been a major focus, and that focus continues. There are two major types of growth scale.

Gibbsite scales form after the pregnant liquor has been clarified. Such scales can be removed in most locations using caustic wash systems utilizing fresh caustic with the resulting wash liquor added to the process liquor stream.

DSP scales form in the spent liquor heaters. These are normally removed using an acid cleaning system. A recent breakthrough was the production of a scale inhibitor reagent for such DSP scales. This can almost eliminate the growth of DSP in two-stream digester flow sheets (Spitzer et al. 2005). The solid in the slurry in single-stream digester flow sheets will absorb the reagent and render it ineffective.

#### Heat Interchange and Evaporation

Solids streams exiting the Bayer process are washed for economic, environmental, and product-quality reasons. These washing operations result in water addition to the Bayer circuit, and water is also added via rainfall, instrument purge water, pump gland water, bauxite moisture content, steam injection heating, and/or other chemical additives.

To remain in balance, all of the added water must be removed from the Bayer circuit. Part of this removal requirement is met by flash evaporation in digestion. A small amount leaves with the washed bauxite residue and washed gibbsite feeding calcination. The remainder of the water balance requirement is met by spent liquor evaporators. The heating  $\Delta T_h$  (30°C in LSH in Figure 7A) is dictated by the heat recovery efficiency from the digester slurry, bauxite type, and boiling point elevation (Dewey 1981) and approach as shown in Figure 7B (Donaldson 2011). The cooling  $\Delta T_c$  (HE) is dictated by the precipitation temperature profile controlling the supersaturation as discussed earlier.

Pregnant liquor typically leaves the red area at around 105°C and returns as spent liquor at around 50°-60°C. Heat interchange between these two streams helps reduce overall energy consumption. Two different types of heat exchange systems are typically used for this purpose: vacuum flash cooling or PHEs. Vacuum flash systems typically consist of three to five flash stages feeding vapor to shell-and-tube spent liquor heaters. Condensate collected from the heaters is generally of good quality and may be used for product washing, instrument/ gland water, or boiler feed water. PHE systems exchange heat between pregnant and spent liquor in one or more plate packs. The final stage of either system may be water-cooled rather than exchanging the heat with spent liquor, in order to provide better temperature control and/or to achieve lower pregnant liquor exit temperature. Both vacuum and plate systems accumulate gibbsite scale and require periodic chemical cleaning with hot caustic solution and occasional acid and/or mechanical cleaning if other scales or deposits build up. Vacuum flash systems can generally operate for longer periods before cleaning is required. The vacuum flash alternative generally requires higher capital cost and has a slightly unfavorable impact on alumina supersaturation for precipitation. However, its positive impact on water balance may reduce evaporation plant capital and operating costs.

Two main technologies are employed for evaporation: multi-effect and multi-flash; some configurations may employ a combination thereof.

#### Water Balance and Energy Consumption

Energy consumption varies widely throughout the alumina industry, ranging from 7 to 32 GJ/t alumina, but both refineries with LT (gibbsitic bauxite) and HT (boehmitic bauxite) digestion plants can be <10 GJ/t in total energy consumption (Hendricks 2010). Energy consumption for the Bayer circuit (excluding calcination) is predominantly used for digestion and evaporation.

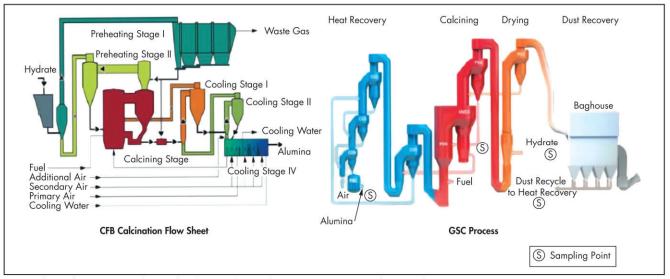
Calcination accounts for about 2.79–3.0 GJ/t alumina (Monteiro et al. 2011). An efficient refinery water balance will lead to reduced evaporation requirements and hence reduced energy consumption. Drivers for this improvement include

- Refinery layouts to minimize rainfall capture to the Bayer circuit,
- Design and operation to reduce need for hose-up operations,
- · Reduction of moisture in bauxite and other feedstocks,
- Selection of digestion and/or heat interchange options that maximize water removal,
- Employing high-efficiency mud-washing processes such as pressure filtration/washing,
- Selection of instruments with low water addition rates, and
- Selection of pump seal technologies with low water addition rates.

Optimization of a new or existing refinery involves tradeoff considerations between capital cost, operating philosophy, and operating cost.

#### Cogeneration and Power Consumption

The Bayer circuit, particularly if processing gibbsitic bauxites, is a large consumer of medium-pressure steam. This makes it well suited to cogeneration of electricity using steam turbines. Steam is produced at a higher temperature and pressure than that required by the Bayer process, then passed through a steam turbine to generate electricity and reduce pressure to the required level used by the Bayer process. A refinery processing gibbsitic bauxite may be able to generate close to 100% of its internal electrical requirements by this means. The quantity of electricity generated by the steam turbines is typically around 80% of the incremental fuel consumption (relative to operation of the refinery without a steam turbine). This is nearly double the efficiency of conventional (non-cogeneration) electricity generation and so is generally an attractive option. If natural gas is available and attractively priced, a gas turbine cogeneration configuration may be employed. Electricity is generated in the gas turbine, and the waste heat from the gas turbine feeds a heat recovery steam generator (HRSG), which supplies steam to the Bayer circuit. In this configuration, the electricity generation can be significantly higher than the refinery's electrical requirements. A steam turbine can be used in combination with the HRSG to further boost the electricity generation. Selection of the appropriate cogeneration configuration for a refinery must take into account a range of economic, logistic, and commercial considerations.



Source: Klett et al. 2010. Copyright 2010 by The Minerals, Metals & Materials Society. Used with permission.

Source: Raahauge and Devarajan 2015

Figure 11 Circulating fluid bed and gas suspension calciner technologies

#### **Materials of Construction**

Most plant equipment is exposed to caustic soda solutions at moderate temperatures and pressures. Experience has shown that appropriately selected carbon steel is adequate for these services. Areas exposed to a combination of high temperatures, high velocities, high caustic concentration, vibration, and/or frequent chemical cleaning may give unsatisfactory service life in carbon steel and may warrant application of duplex alloys or nickel lining. Equipment for preparing and circulating acid cleaning typically employs chemical-resistant linings or uses more exotic alloy materials. Pumps and control valves exposed to slurry service are vulnerable to erosion and may employ high chrome-iron liners and/or have their design customized to reduce local velocities. In the calcination area, refractory steels are employed for anchoring the refractory materials used for thermal insulation and protection of vessels and ducts against high-process stream temperatures.

#### **Process Control and Simulation**

Modern refineries employ a high level of automatic control. Control hierarchy typically consists of large numbers of individual control loops, some of which may be integrated and optimized by supervisory controls. The supervisory controls may range from simple cascade controllers to sophisticated fuzzy-logic and/or model-based controllers. A key prerequisite for good process control is reliable instrumentation. This remains a significant challenge in the Bayer refinery because of the high tendency for scale growth. Solid strategies to address this challenge include customized instrument design, flushing systems, duty/standby configurations, and preventive instrument maintenance. A heat and mass balance simulation for the Bayer circuit is an important tool for design, operation, and optimization. There are several commercial simulation platforms that contain chemical and process database information to support modeling of the Bayer circuit. Alternatively, some operating companies develop in-house simulations using their own software platform. A dynamic simulation of part or all of the refinery can be used as the back end for a training simulator to train control room operators. The simulation can also be used to develop and test process control strategies, or as part of a model-based control scheme.

#### Calcination

The product hydrate from precipitation is filtered and washed, normally on pan filters (Petersen et al. 2009), with the final wash step aided by steam and sometimes dewatering aids. Being quite coarse (50–150  $\mu m$ ), the hydrate is readily filtered to low moisture contents (6%) and then fed to the calciner to dehydrate and convert into alumina at temperatures around 1,000°C. Initially, such calcination was done in rotary kilns. Since the 1950s, fluid-flash and circulating fluid bed (CFB) stationary calciners with several heat recovery stages were developed (Fish 1974; Williams and Schmidt 2012) and designed to be significantly more energy efficient than rotary kilns. Since then, there has been significant further development of this concept originating from GSC technology used in the cement industry.

There are many flow-sheet commonalities between the CFB and GSC technologies for alumina (Figure 11), such as

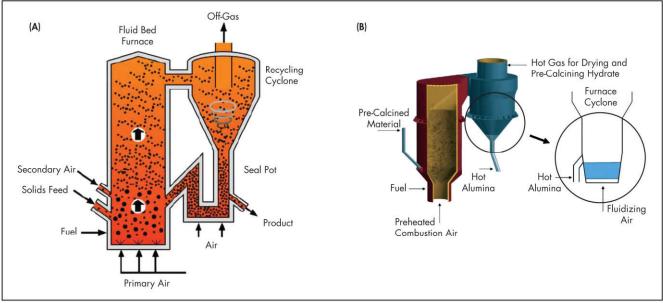
- Feeding moist hydrate into venturi dryers,
- Direct drying and preheating/calcination of feed hydrate by hot combustion products,
- · Calcination to alumina in direct-fired HT furnace/reactors,
- Preheating air for combustion by direct heat exchange with hot alumina in staged cyclone/fluid bed-type HEs,
- Indirect and final cooling of alumina with air and/or water in fluid bed coolers, and
- Dedusting of the exhaust gas in electrostatic precipitators or fabric filter/baghouses.

The major differences between the CFB and GSC furnace technologies are summarized in Table 9 and shown in Figure 12. The CFB furnace is a multipass calcination process operated at a pressure exceeding atmospheric pressure. The GSC furnace is a low-velocity (5–7 m/s) single-pass calcination process operated below atmospheric pressure. The operation of the GSC furnace is inherently safe with respect to avoiding emission of hot alumina from holes/openings generated by internal wear of the refractory-lined calciner vessels and/or ducts over time.

Table 9 Typical stationary calciner furnace operating parameters

Circulating Fluid Bed Furnace		Gas Suspens	Gas Suspension Calciner Furnace		
Holding Vessel	Not Applicable	Holding Vessel	No	Yes	
Nominal capacity, t/d	3,500	Nominal capacity, t/d	4,500	3,500	
Temperature, °C	950	Temperature, °C	1,050	<960	
Pressure, kPa (absolute)	>101.3	Pressure, kPa (absolute)	<101.3	<101.3	
Retention time, minutes	3–5	Retention time, seconds	10-12	≥200	

Source: Raahauge and Devarajan 2015



Source: Klett et al. 2010. Copyright 2010 by The Minerals, Metals & Materials Society. Used with permission.

Source: Raahauge and Devarajan 2015

Figure 12 (A) Circulating fluid bed furnace and (B) gas suspension calciner furnace with and without holding vessel

A major calciner design requirement has been the need for stationary calciners to minimize the breaking of particles (Klett et al. 2010; Raahauge and Devarajan 2015) during calcination to meet the smelter requirement of maximum 10% <45  $\mu$ m or 325 mesh and minimize generation of superfine (<20  $\mu$ m) particles.

Smelters use the alumina for dry-scrubbing HF in the exhaust gases (S.J. Lindsay 2009). The calcination temperature is therefore regulated to meet the SSA (m²/g) requirement of SGA. There is much current research on the pore size distribution of SGA (Agbenyegah et al. 2014) and its impact on HF absorption efficiency.

Modern stationary calciners are fuel efficient, running on either gas or heavy fuel oil, with the latter causing acid dew-point issues to be considered in the design (Wind and Raahauge 2009; Missalla et al. 2011).

The thermal energy requirement in calcination is about 30% of the total energy requirement of a modern refinery, corresponding to less than 2,750 MJ lower heat value (LHV)/t alumina in GSC units. Energy is supplied from the combustion of fossil fuel releasing significant amounts of CO<sub>2</sub>.

The rapid expansion of the Chinese alumina capacity in recent years is mostly based on coal as an energy source. The GSC technology in China uses coal gas as fuel, making this technology the most frequently applied calcination technology worldwide.

#### **Environmental Control in Stationary Calciners**

The electrostatic precipitators and/or baghouses collect fine particles from the stack gases. Compared to electrostatic precipitators, dust emission from baghouses do not increase in cases of a power failure because they offer an absolute barrier against the dust emission. Modern stationary calciners operate with relatively low exit stack temperatures in the range of 150° to 180°C. This allows dedusting the exhaust gases using baghouses rather than electrostatic precipitators as introduced to the 4,500-t/d GSCs replacing the old rotary kilns at Queensland Alumina (Fenger et al. 2004).

The collected dust particles can be added back to the calcination process, or to the alumina product, often with significant impact on the flow properties and dusting of the resulting SGA. In addition, gibbsite in the dust increases HF generation in the smelters. Limited emissions of nitrogen oxides, CO, and sulfur oxides within local national standards are normally not a problem.

## Composition, Management, and Uses of Bauxite Residue

**Composition.** The residual material remaining at the end of the Bayer process is termed *bauxite residue* or *red mud*. The

mineralogical and chemical composition of this residue can be varied and is dependent on the nature of the bauxite used and the extraction conditions. It is mainly composed of metallic oxides that have not been attacked by the caustic soda; the main components typically lie within the following ranges:

- Fe<sub>2</sub>O<sub>3</sub>, 5%–60%
- Al<sub>2</sub>O<sub>3</sub>, 5%–30%
- TiO<sub>2</sub>, 0.3%–15%
- CaO, 2%-14%
- SiO<sub>2</sub>, 3%-50%
- Na<sub>2</sub>O, 1%–10%

Small amounts of a wide range of other components may also be present, normally as metallic oxides, for example, arsenic, beryllium, cadmium, chromium, copper, gallium, lead, manganese, mercury, nickel, potassium, scandium, thorium, uranium, vanadium, zinc, zirconium, and rare earth elements (REEs). Nonmetallic elements that may occur in the bauxite residue are phosphorus, carbon, and sulfur. Sodium may be present in a sparingly soluble form as DSP or in a soluble form predominantly as a mixture of sodium aluminate and sodium carbonate.

The DSP  $(3\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_2\cdot2\text{SiO}_2\cdot0-2\text{H}_2\text{O}\cdot2\text{Na}X)$  where X could be  $\text{CO}_3^{2-}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , or  $\text{Al}(\text{OH})_4^-$ ) arises from the reaction between sodium aluminate and soluble sodium silicates. Small quantities of the soluble sodium compounds resulting from the sodium hydroxide used in the extraction process will remain depending on the dewatering and washing systems used.

All Bayer alumina refineries try to maximize the recovery of the valuable caustic soda from the residues to reuse it during the extraction process. A variety of organic compounds can also be present, arising from vegetable and organic matter in the bauxite/overburden or the use of crystal growth modifiers or flocculants. Compounds present include carbohydrates, alcohols, phenols, and the sodium salts of polybasic and hydroxyacids such as humic, fulvic, succinic, and acetic or oxalic acids.

Quantities. The global average for the production of bauxite residue per metric ton of alumina is between 1 and 1.5 t. Based on the annual production of SGA and CGA in 2017 of 126 Mt, it is estimated that some 160 Mt of bauxite residue is produced annually. This is generated at some 80 active Bayer plants of which approximately 30 are in China; in addition, there are at least another 50 closed legacy sites. Thus the combined stockpile of bauxite residue at active and legacy sites is estimated at 3,000 Mt.

Disposal and storage. The early history of bauxite residue disposal and storage involved using estuaries or land impoundment areas adjacent to the factory. Disposal into rivers, estuaries, or the sea was common for many years, but this has now ceased. Storage of bauxite residue as a dilute slurry (typically 20% solids) in old mines, impounded areas, or dammed valleys was widely practiced until the mid-1980s, but since then, there has been a growing trend to higher solids storage methods. Almost all modern plants use dry stacking technology to produce higher solids and more compact residue. More recently, to produce an even higher solids residue, filter presses have become increasingly common.

Uses. In one of Bayer's early patents in the 1890s, he described the benefits of recovering the iron values of the bauxite residue. Since that period, there has been an enormous amount of work within the alumina producers, research

institutes, universities, and by entrepreneurs to extract value from the bauxite residue. Despite all this work, the estimated total usage is between 3 and 4 Mt/yr. The following is a list of the most successful large-scale uses:

- Cement (500,000–1,500,000 t)
- Raw material/additive in iron and steel production (200,000-1,500,000 t)
- Roads/landfill capping/soil amelioration (200,000– 500,000 t)
- Construction materials such as bricks, tiles, or ceramics (100,000-300,000 t)
- Other, for example, refractory, adsorbent, or acid mine drainage treatment catalysts

Currently, there is particular interest in recovering REEs, which are essential constituents of modern permanent magnets; nickel-metal hydride batteries and lamp phosphors, with dramatic growth expectations driven by increasing demand for electric and hybrid cars; wind turbines; and compact fluorescent lights. Another area of focus is the recovery of scandium, which has a growing demand in high-strength aluminum alloys. The tragic accident at the Ajka alumina plant in Hungary in 2010 in which caustic red mud slurry inundated a village following a breached dam, the growing cost of remediating closed residue disposal sites, and the availability of EU and other funding has encouraged a resurgence of work at various universities and institutions as well as collaborative development activities between industry and universities.

#### ALUMINA PLANT COSTS AND ECONOMY OF SCALE

Economic evaluations of an alumina refinery project require generating (discounted) annual cash flows over its lifetime and applying several criteria to ascertain if it meets threshold levels (net present value [NPV], internal rate of return [IRR], etc.).

#### **Key Inputs to Project Economics**

Key inputs to annual cash flows are (P.J.C. ter Weer 2006)

- On the revenue side, the amount of product generated and its sales price; and
- On the cost side, capital cost, operating cost, and tax payable.

The quality of the bauxite deposit and the design of the refinery also significantly affect an alumina refinery project's capital and operating costs.

#### **Bauxite Deposit Quality Criteria**

The main bauxite deposit quality criteria affecting alumina project economics are (P.J.C. ter Weer 2014)

- · Country infrastructure capital cost;
- Distance from the bauxite resource to the export port (bauxite, alumina);
- Disturbed acreage per metric ton of alumina produced;
- · Material handled per metric ton of alumina, consisting of
  - Material mined and
  - Residue to disposal;
- Alumina in boehmite;
- Total caustic consumption per metric ton of alumina;
- Ratio of the extractable organic carbon to available Al<sub>2</sub>O<sub>3</sub>; and
- · Resource-contained alumina.

# Alumina Refinery Design Criteria

The main plant design criteria affecting economics are as follows (P.J.C. ter Weer 2015):

- · Liquor productivity/yield
- · Digestion temperature
- · Digestion technology
- · Bauxite residue settling and washing technology
- · Heat interchange technology
- Precipitation technology
- · Power- and steam-generation technology
- · Calcination technology
- Bauxite residue disposal technology
- · Overall plant
  - Design and layout
  - Production capacity
  - Equipment and additives
  - Control equipment

#### **Economy of Scale**

Increasing plant production capacity is achieved by debottlenecking the plant area that limits plant capacity (this is often, but not always, the digestion area). This may be accomplished by adding another *train/unit* with commoning up in some areas, but also through higher flows of the liquor circuit, additional tank volume, pumps, piping, and so forth, and through increased liquor productivity/yield (approximately twofold over the past 40 years).

The design of alumina refinery production capacities of greenfield projects outside China have evolved from approximately 0.5–1.0 Mt/yr alumina 25–30 years ago to 1.4–3.3 Mt/yr alumina for more recently constructed and future planned projects. A refinery project represents a major investment with an expected operating life of 30–50 years.

Actual production capacities of existing projects have significantly increased as a result of brownfield expansions, debottlenecking, and improved process efficiencies and operations performance. Rationale for this trend is the economy of scale: An increased production capacity is required to improve the economics of greenfield projects to meet corporate economic criteria.

#### **Economy of Scale and Operating Cost**

Economy of scale affects operating costs (P.J.C. ter Weer 2006), which include variable and fixed costs.

# Variable Costs

Variable costs include bauxite, caustic soda, coal, and so forth. Overall plant online time of an alumina refinery with more than one production unit/train (e.g., a digestion unit) is generally slightly higher than a plant with only one unit (indicatively 0.2%–0.5% absolute) because of increased flexibility in equipment operation and maintenance. As a result of an increase in production units, the plant operates with fewer interruptions, and operating efficiencies improve (e.g., consumption of bauxite, caustic soda, and energy; indicatively by 0.5%–3%).

#### **Fixed Costs**

Fixed costs include labor, maintenance materials, contract services, administration, and so forth. Economy of scale may have a significant impact because of the dilution of fixed annual expenses by a larger production volume (drop in cost per metric ton of alumina produced). If the increase in production capacity includes an increase in the number of production units, the dilution effect is reduced. In addition, the requirements of complex and large alumina refineries may result in disproportionate increases of overhead costs.

Table 10 illustrates this concept for a greenfield project evaluated at different production capacities. The larger refinery capacity shown in Example 1 is mainly the result of more production units in several areas (e.g., digestion), causing a limited improvement of fixed costs per metric ton of alumina. The decrease of variable costs is mainly caused by improvements in efficiencies from operating two production units instead of one.

In another case (Table 10, Example 2), a greenfield project increased its design capacity from 2.8 to 3.3 Mt/yr maintaining the number of production units. This change represented an increase in equipment size at similar process conditions. This had two major consequences: virtually unchanged variable operating costs and significantly diluted fixed costs. Example 2 shows a drop in fixed costs (\$3/tA [metric ton of alumina] at a production increase of 0.5 Mt/yr), which in relative terms is much larger than the drop in fixed costs of Example 1 (\$5/tA at a production increase of 1.8 Mt/yr).

In summary, economy of scale has a significant effect on fixed operating costs, especially for plant-capacity increases resulting from an increase in equipment size rather than equipment number. The effect on variable operating costs is generally small, unless the increased production capacity results in an increase in production trains, particularly going from one to two trains, because of an improved online time.

Table 10 Economy of scale effect on operating expenditures (OPEX)

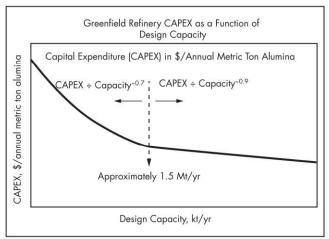
Example 1: Increased Number of Operating Units				
Plant Capacity, Mt/yr	1.4	3.2		
Variable Costs				
Bauxite	14	14		
Energy	90	88		
Consumables*	32	31		
Other variable costs†	19	_18		
Total Variable Costs, \$/tA <sup>‡</sup>	155	151		
Fixed Costs				
Maintenance (materials and contract services)	18	18		
Labor	12	8		
Other fixed costs	8	_7		
Total Fixed Costs, \$/tA	38	33		
Total OPEX, \$/tA	193	184		
Example 2: Increased Equipme	ent Size			
Plant Capacity, Mt/yr	2.8	3.3		
Total Variable Costs, \$/tA	152	151		
Fixed Costs				
Maintenance (materials and contract services)	20	18		
Labor	9	8		
Other fixed costs	_7	_7		
Total Fixed Costs, \$/tA	36	33		
Total OPEX, \$/tA	188	184		

Source: P.J.C. ter Weer 2013

<sup>\*</sup> Caustic soda, lime, etc.

<sup>†</sup> Including transport costs.

<sup>‡</sup> tA = metric tons of alumina.



Source: P.J.C. ter Weer 2013

Figure 13 Capital expenditure versus design capacity

# **Economy of Scale and Capital Cost**

The overall impact of the economy of scale is a drop in capital cost per metric ton of alumina produced at higher production capacities, although its impact on equipment and plant infrastructure differ (P.J.C. ter Weer 2007, 2013). In most cases, increases in plant/project capacity are a combination of increases in equipment size and equipment number (e.g., increased number of production trains).

In addition, an increased project scope adds (sometimes disproportionally) to project complexity. As a result, actual capital cost per metric ton of alumina produced as a function of plant capacity will not show a smooth curve. Canbäck et al. (2006) refer to a study of 20 industries showing that at the plant level, beyond a minimum optimum scale, few additional economies of scale can be exploited.

Available information for the alumina industry suggests that with respect to the relationship between the refinery capital expenditure (CAPEX) and design capacity, a differentiation may be made in two ranges as illustrated in Figure 13:

- 1. Up to  $\sim 1.5$  Mt/yr with a power factor of  $\sim 0.7 \pm 0.05$
- 2. Above  $\sim 1.5$  Mt/yr with a power factor of  $\sim 0.9 \pm 0.1$

The production capacity of  $\sim 1.5$  Mt/yr is consistent with the current maximum production capacity of a refinery with one digestion unit/train. This appears reasonable because this area is generally taken as a plant design bottleneck because of its high unit CAPEX and its requirement for constant flow to achieve optimum performance levels.

In summary, the impact of economy of scale on alumina refinery CAPEX appears most pronounced for design production capacities up to ~1.5 Mt/yr, with less potential to improve capital cost per metric ton of alumina at larger capacities. Note that 1.5 Mt/yr is not a fixed number, but indicative only (range ~1.4–1.7 Mt/yr) and may increase over time as equipment sizes increase.

# Infrastructure Costs and Overall Economics

Several new and future projects have been designed with production capacities well above 1.5 Mt/yr. The reason for this is that greenfield projects have infrastructure requirements that may include access roads, bridges, railway lines, port facilities, and so forth. When requirements are extensive, the

related CAPEX is significant and has a disproportional impact on the economics of greenfield projects with relatively small production capacities.

An example illustrates this point for two greenfield project options at the same location: 1.5 and 3 Mt/yr alumina design capacity. The following infrastructure requirements have been assumed: 100-km railway line, railway wagons and locomotives, port jetty and wharf, port ship loading/unloading, and storage and handling facilities. Table 11 provides indicative numbers for capital, operating, and sustaining capital costs for these two options, as well as their indicative economics.

Table 11 shows that despite the refinery CAPEX per annual metric ton of alumina for the two options essentially following the trend illustrated in Figure 13, overall project economics flip from a significant positive NPV (8%), with an IRR of 8.6%, payback period of 10 years, and a value over investment ratio (VIR) of 5.7% for the 3-Mt/yr case to a significant negative NPV (8%), with an IRR of 6.7%, payback period of 11.5 years, and a VIR of –10.5% for the 1.5-Mt/yr case. The major contributor to this is the disproportional increase in cost per metric ton of alumina of the infrastructure CAPEX for the smaller project.

The reasoning could also be turned around: A significant increase in project scale is required to achieve acceptable overall project economics.

Summarizing, economy of scale and infrastructure requirements are two key design criteria to consider when deciding on the production capacity of a greenfield (bauxite and) alumina project.

# **Alternative Project Approaches**

Economy of scale and infrastructure requirements have resulted in ever-increasing production capacities for recently built and future planned greenfield refinery projects. As a consequence, the complexity of greenfield projects has significantly increased, and capital cost in many cases has grown to several billion dollars, with vital consequences:

Table 11 Economy of scale effect on capital expenses and overall economics (indicative)

Plant Capacity, Mt/yr	1.5	3
Capital Cost		
Mine	115	200
Refinery	1.800	3,200
Infrastructure	430	500
Total Capital Cost, million \$	2,345	3,900
\$/Annual tA*	1,563	1,300
Operating Cost, \$/tA <sup>†</sup>	193	186
Sustaining Capital, \$/tA	8	8
Economics (indicative)‡		
Net present value (8%), million \$	-248	221
Internal rate of return, %	6.7	8.6
Payback period, yr§	11.5	10
Value over investment ratio, %**	-10.5	5.7

Source: P.J.C. ter Weer 2013

<sup>\*</sup> tA = metric tons of alumina.

<sup>†</sup> Including infrastructure operating expenditures.

<sup>‡</sup> Alumina price at \$360/tA; 30 years' operation.

<sup>§</sup> After start of operations.

 $<sup>^{**}</sup>$  Capital efficiency ratio net present value (8%) as a percentage of capital expenditure.

- Project owners aim at risk reduction through project financing and formation of joint ventures, further complicating project implementation (Kjar 2015).
- Globally, only a limited number of (large) companies have the human and financial resources to develop greenfield bauxite and alumina projects.
- Only a limited number of engineering firms have the skills and experience required to successfully implement these megaprojects.
- · Only (very) large bauxite deposits get developed.

The uncompetitive capital cost of recent Western-developed greenfield alumina projects is a result of (among other reasons) large project size and increased project complexity (Kjar 2010). To quickly and more cost-effectively build a large plant/project, increasing capacity in small increments and replicating modern plant design is recommended (Kjar 2010).

A new approach from a slightly different angle aims at designing an alumina refinery for a dedicated production capacity without provisions for future expansions (P.J.C. ter Weer 2011). This enables optimizing plant layout for the targeted production capacity, for example, with respect to positioning similar equipment close to each other, use of common spare equipment, and so forth. Possible future (brownfield) capacity expansions should justify themselves on their own economic merits.

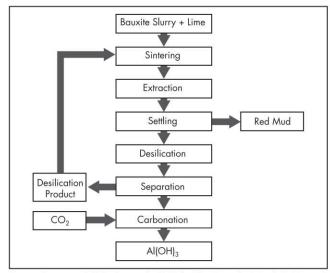
Both of these alternative approaches result in improved project economics.

# OTHER BAUXITE/ALUMINA PROCESSES

In China, there has been an enormous growth in alumina production capacity from about 2–4 Mt/yr in 2000 to approximately 80 Mt/yr in 2017, with an improved utilization rate from 66% in 2009 to 76% in 2013 (Clark 2014). China, however, is facing the problem that more than 95% of its domestic bauxite reserve is diasporic bauxite with a decreasing A/S ratio (Songqing 2008). Such bauxites require very aggressive digestion conditions of high caustic concentration, temperatures >260°C, and fine grinding of the abrasive bauxite. To achieve such digestion temperatures, direct steam injection using very high-pressure steam is required, which becomes economically inefficient. Consequently, many alternative processes using diasporic bauxite have been developed in China (Songqing 2008).

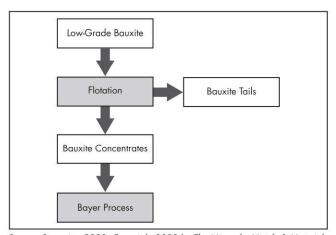
## **Processing Diasporic Bauxite**

The lime-soda sinter process (Figure 14) has been used for many years to produce alumina from diasporic bauxites. Bauxite with soda ash and lime is sintered at approximately 900°C, and the solid discharge is leached to recover the sodium aluminate. The alumina is then recovered from the sodium aluminate solution, not by seeding, but by carbonation of the liquor that results in very high supersaturations and in virtually all the alumina being precipitated. The precipitation process is rapid, as it is essentially a nucleation rather than a growth process. The spent liquor, now primarily a sodium carbonate solution, is then recycled to the kiln. The addition of high amounts of lime is needed to recover the alumina that can be lost to silica minerals—the CO<sub>2</sub> from lime production being the source of CO<sub>2</sub> for the precipitation. Consequently,



Source: Songqing 2008. Copyright 2008 by The Minerals, Metals & Materials Society. Used with permission.

Figure 14 Sintering process

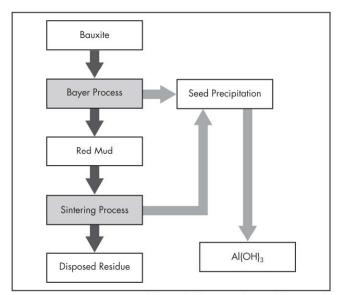


Source: Songqing 2008. Copyright 2008 by The Minerals, Metals & Materials Society. Used with permission.

Figure 15 Flotation Bayer process

there is a high energy usage of the order of 35 GJ/tA (Wanxing 2011), or more than three times the current usage of the modern Bayer process (<10 GJ/tA).

The 800,000-t/yr flotation Bayer process (Figure 15), was introduced after successful removal of silica by flotation as described earlier, reducing the energy consumption to about 15 GJ/tA (Wanxing 2011). However, there is more investigation to be done with respect to optimizing the flotation process to further increase the yield of alumina and lower the energy consumption. The trend has been to add Bayer digesters to sinter plants (using either internal coil heaters in the digesters or tube digesters) to increase capacity. Although the sinter process does a good job of recovering alumina and soda from the residue, especially with the decrease in the bauxite A/S ratio, the overall energy consumption will always be greater with a combined process than with a straight Bayer process.



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Figure 16 Series Bayer-sinter process

The series Bayer-sinter process (Figure 16) was developed for bauxite that is first treated using digesters to recover the easy-to-dissolve alumina. The residue (together with some additional bauxite and lime), which still contains significant amounts of alumina (as well as a lot of soda tied up as DSP), is used to feed the sinter kilns. The alumina is recovered as well as the soda via reaction of the DSP with the lime. This serial combination process reduces the overall energy requirement to about 25 GJ/tA.

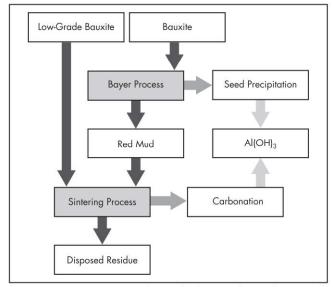
The combined Bayer-sinter process (Figure 17) has a higher alumina output than the serial Bayer process, and thus slightly higher energy consumption as well. One benefit of this combination process is that the kiln destroys both organic and inorganic carbon, and the resulting sodium aluminate liquor is very clean; that is, it is an effective impurity removal process (although costly). Consequently, white hydrate can be produced from such liquor that is required in many non-SGA markets, and those markets are less concerned about the sizing and toughness of the product.

# **Processing Other Alumina-Silicate Raw Materials**

Because of the strategic nature of aluminum and because many countries do not have viable bauxite resources, there has been a large amount of work investigating production of SGA from other aluminum-rich resources. The most notable is recovery of alumina from various aluminosilicates, such as nepheline (Smirnov 1969; Skaarup et al. 2013), clays, feldspars, and fly ash, of which only nepheline and fly ash (Shen 2012) have reached proven commercial-scale operation. Production of alumina from fly ash would certainly be good, as there are enormous deposits of fly ash available from coal-fired power plants (Shen 2012).

Many other processes (Nunn and Chuberka 1979; Primeau and Gilbert 2012) have been studied—some acid processes, some chlorination-type processes—but to date, none have come to commercial fruition in terms of SGA production.

Most such processes do not regenerate their reagent as does the Bayer process, and construction materials would be



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Figure 17 Combined Bayer-sinter process

significantly more costly. Such processes, although producing a chemically refined alumina, do not produce SGA with the physical requirements of the modern smelter, namely flow characteristics, particle size, and toughness. Such processes can produce low-soda alumina, something that is impossible to achieve directly from the Bayer process.

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