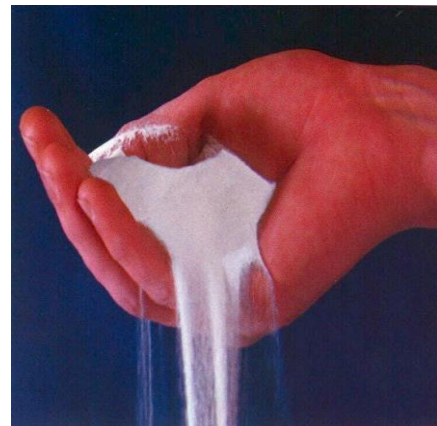


THE ALUMINIUM STORY

BAUXITE TO ALUMINA: THE BAYER PROCESS

An Introductory Text



A N Bagshaw

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ISBN 978-0-646-97867-3

Foreword

This book is designed as an introductory text to the extraction of alumina, the feedstock for aluminium production, from bauxite ore. The audience is high school students and teachers, university undergraduates and people starting work in the alumina/aluminium industry. Some questions are included in most of the Sections, to promote a broader understanding of the topics. The appendix contains reference to more detailed technical articles if a deeper understanding is sought.

Acknowledgments

After nearly 40 years of involvement with the aluminium industry I am grateful to the many people who over the years have helped me better understand the Bayer Process. In addition, I have always had an interest in science education, both at the secondary and tertiary levels. These factors have contributed to my writing this introductory text.

I am especially grateful to Dr Greg Power for his advice and contributions to this text.

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October 2017

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An Introductory Text

1. *Introduction*

Aluminium is the most abundant metal in the Earth's crust. Unlike metals such as copper and gold, it is never found by itself, but always in combination with the most abundant element, oxygen, and often with the second and fourth most abundant elements, silicon and iron. Yes, aluminium is *more* abundant than iron!

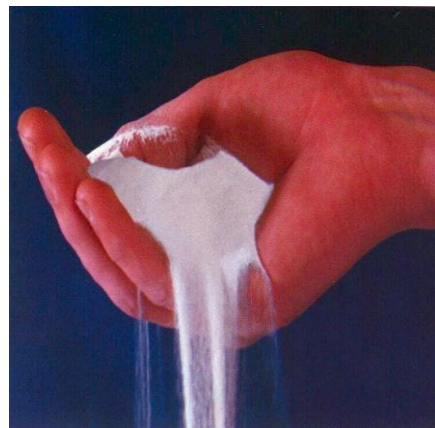
Because of its lightness, resistance to corrosion and ability to be readily recycled, aluminium is extensively utilised in many applications. This requires a worldwide industry for its production, via the aluminium oxide (alumina) intermediate, and aided by the extensive deposits of aluminium ores.

2. *Bauxite Ores*

Aluminium is a reactive metal and is not found in its elemental form in nature. There are a wide range of minerals containing aluminium almost exclusively as the oxide and often in combination with other oxides, especially silica and iron oxides.



Bauxite Ore

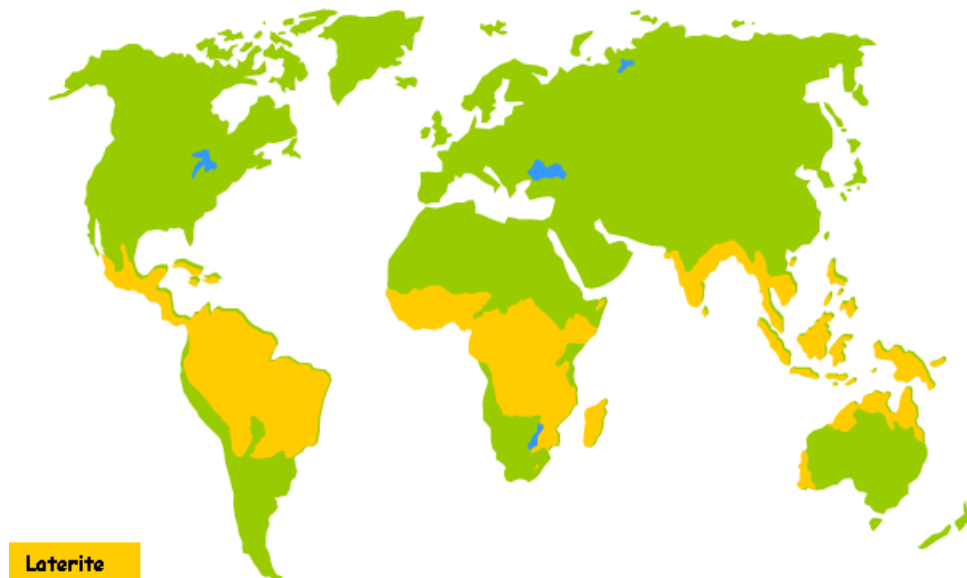


Alumina Product

Bauxite is the most widely distributed ore used for alumina production. It is named after the small town in southern France called Les Baux, where it was first mined. Bauxite is typically a mixture of hydroxides of aluminium with iron oxides, silica and aluminosilicates. It results from the weathering, over geological time, of the parent rock to remove components such as sodium, potassium, magnesium and calcium salts and some silica, leaving an ore richer in aluminium. The weathering has predominantly occurred in the tropical and semi-tropical regions of the world, where there is plenty of moisture, so that the major bauxite deposits are found closer to the equatorial regions rather than to the poles.

Most bauxites are produced from lateritic deposits, which are layered close to the surface; others are karstic, containing voids and associated with limestone. The latter deposits are geologically older.

After Bardossy / Aleva. 1990



The major producer up to about 1970 was Jamaica. From then until about 2000, Australia produced the most bauxite. Now China is the major producer. Other producers include Brazil, Guinea and India.

The aluminium minerals present are gibbsite ($\text{Al}(\text{OH})_3$, often referred to in the industry as alumina trihydrate or hydrate, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), boehmite ($\text{AlO}(\text{OH})$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, aluminium oxyhydroxide or monohydrate) and diasporite (the same chemical formula as boehmite).

Bauxites containing mainly gibbsite are more amenable to processing by the Bayer Process (described in the next Section) and are termed low-temperature bauxites. Bauxites containing boehmite and especially diasporite are more intractable to treatment and are termed high-temperature bauxites.

For a bauxite ore to be economically processed it typically contains 30-50% of extractable (termed *available*) alumina, up to 20% of iron oxides and 2-5% of silica in reactive clays (typically kaolinite). Silica can also be present as quartz which is essentially unreactive in the Bayer Process.

Questions

- Aluminium is slightly more abundant than iron in the earth's crust, yet production of aluminium metal is less than 4% of steel production. Both metals are vital materials for the modern world. What factors influence this large difference in production?
- Whilst in many cases alumina refineries are located close to bauxite deposits, nevertheless significant tonnages of bauxite are shipped around the world, from mines to refineries. Why is this?

3. *The Bayer Process*

The extraction of metals from their ores is commonly achieved via two processing routes: hydrometallurgy (where the metal is selectively dissolved in a liquid – usually water-based) or pyrometallurgy (where heat is applied and the metal may be in molten form). Sometimes a combination of the two routes is applied.

In the production of aluminium from bauxite, the intermediate alumina (Al_2O_3) is produced by a combination process; the alumina is subsequently smelted to aluminium via a pyrometallurgical process.

If bauxite is treated hydrometallurgically with an acidic solution (say hydrochloric acid), not only the aluminium dissolves but also a significant number of other elements in the ore (especially iron), producing a complex solution from which the aluminium has to be selectively extracted.

However, aluminium is an amphoteric metal, meaning it dissolves in both acidic and alkaline solutions. If bauxite is treated with an alkaline (caustic) solution, the aluminum dissolves but most of the other elements present (including iron) are insoluble. This amphoteric property of aluminium was exploited by the Austrian chemist Karl Josef Bayer who patented his process in 1888. After nearly 130 years this is still the process used worldwide to extract alumina; in 2016 over 115 million tonnes of alumina were produced from bauxite.

Questions

- (a) Can you find examples of other metals where the current process for producing them is based on one developed many years/centuries ago?
- (b) Identify other metals which exhibit amphoteric properties. Is this feature used in their production?

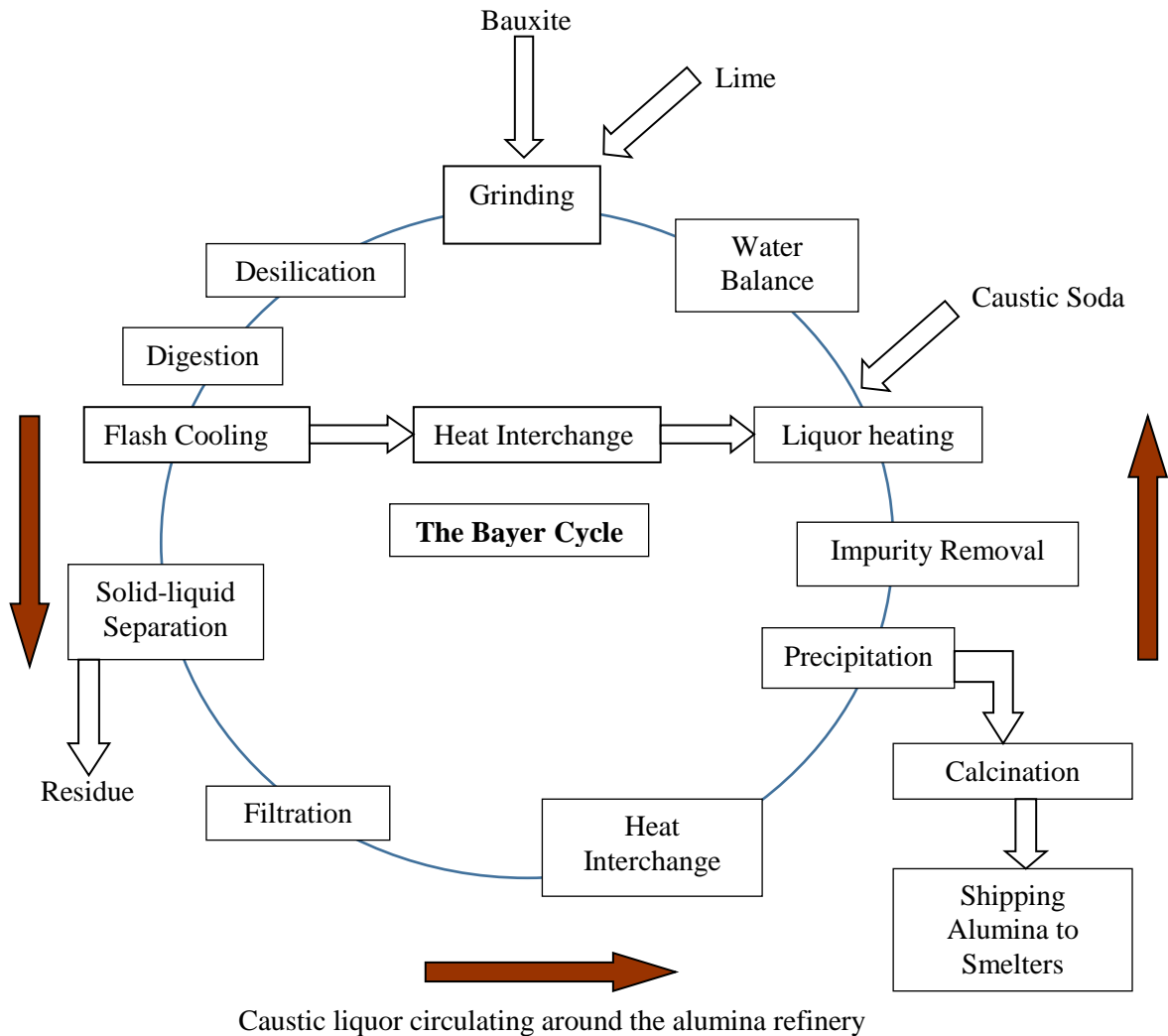
4. *Process Flowsheet and Raw Materials including Liquor Properties*

The basis of a hydrometallurgical process is addition of a solid ore to a solution, usually water-based (aqueous), containing the reagent which attacks that ore and dissolves the valuable component. This can be undertaken in a batch (or once-off) way but this is not very efficient; it involves more handling steps and wastes reagent. The far more efficient way is to make the hydrometallurgical process continuous: the aqueous reagent is the medium which continually circulates around a circuit, dissolving ore at the “front” end and removing the dissolved metal as the “back” end. This is the essence of the continuous Bayer Process used by the industry today.

Caustic liquor (a strong caustic soda solution) is the medium moving around the circuit. When bauxite is added, the aluminium dissolves and a “green” (or pregnant) liquor richer in aluminium is formed. The liquor is not actually green in colour; we discuss the colour in more detail later in this Section. As we go around the circuit, the aluminium concentration is decreased in the Precipitation (or crystallisation) step, and we end up with a “spent” liquor. This spent liquor (now poor in dissolved aluminium) completes the circuit to treat more bauxite.

So the crux of the Bayer Process is dissolution of aluminium from its ore in the early part of the circuit followed by deposition of (pure) aluminum hydroxide in the later part.

The circuit is comprised of a number of unit operations shown in the diagram; these are described in subsequent Sections.

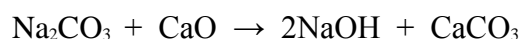


Some caustic soda is lost in the circuit, to residue and to calcination. So to maintain optimal concentration caustic soda in a 50wt% liquid form is added to the circuit. Typically 100kg of caustic is consumed for each tonne of alumina produced.

Because bauxite ores are usually found in near-surface deposits (see Section 5) they contain significant traces of humic (soil) matter, even tree roots. In the aggressive caustic environment these high molecular weight humic compounds break down into carbon dioxide and a range of low molecular weight compounds (see Section 17). The CO_2 reacts with the caustic soda to produce sodium carbonate:



As a result the effective caustic soda concentration is reduced and the process is less efficient. To avoid adding excess amounts of fresh caustic soda, lime (usually produced offsite by calcining limestone CaCO_3) is added in appropriate proportions (typically 50kg per tonne of alumina produced) with the bauxite. This lime reacts with the sodium carbonate to regenerate sodium hydroxide in a step termed *causticisation*:



The calcium carbonate exits the circuit as part of the residue.

The humic materials reacting with the caustic liquor are responsible for the colour of the liquor: a deep olive brown with a characteristic odour.

A modern alumina refining plant has a production capacity of around 4 to 6 million tonnes of alumina a year; this is typically comprised of four to five identical modules or units, each with a capacity of 1 million tonnes. Construction will cost in excess of \$1 billion.



In this overview of an alumina refinery notice the predominant colours: white in the foreground and red behind. This reflects what is happening in the unit operations: the “white” side involves mainly handling hydrate and alumina, whereas the “red” side involves mainly bauxite and residue which exhibit the ruddy colouration of iron oxides.

Questions

- Would a hydrometallurgical process be more or less energy-intensive than a pyrometallurgical one?
- What are the advantages of a continuous process compared to a batch process?
- What are the important factors to consider when selecting the location of a new alumina refinery?

5. *Ore Preparation and Grinding*

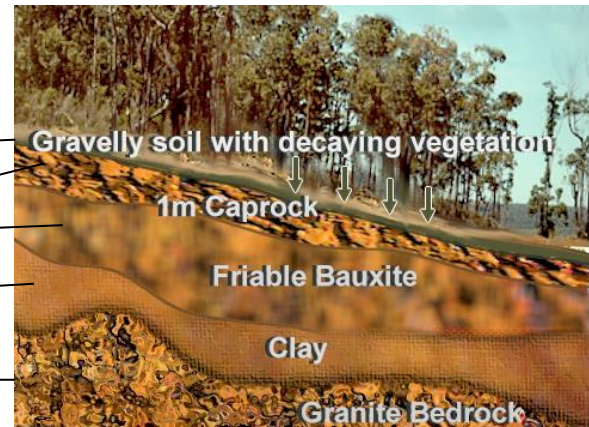
As mentioned in Section 2, bauxite ores are usually found in near-surface deposits. Typically they are covered with a hard caprock which is overlaid by soil and vegetation, including trees. The ore is formed by weathering of the base rock. The weathering process first produces aluminosilicate clays, which underlie the younger weathering product, the bauxite. Bauxite is formed as the silicate aspect of the clays is leached out. Mining of bauxite therefore typically occurs as an open-cut operation, with the cut-off at the clay horizon. Below is a schematic representation of a bauxite profile typical of many commercial deposits around the world.

Organic matter, salts

Gibbsite, boehmite, goethites

Aluminosilicates, goethites

Alkali aluminates, silicates, ferrites



Once the lateral definition of a deposit is determined, a typical mining operation is to first remove the trees and vegetation, scrap off the soil overburden on top of the caprock and store it for subsequent rehabilitation of the minesite once all ore is removed. The caprock is fractured or blasted, and the bauxite (usually quite friable) is removed by excavators. The depth to which economic ore is removed is determined by the clay (kaolinite) content underlying the bauxite. Typically the bauxite deposit may be 5-15 metres in thickness. A primary crusher at the minesite reduces the bauxite to less than 150 mm diameter lumps.



Primary crusher

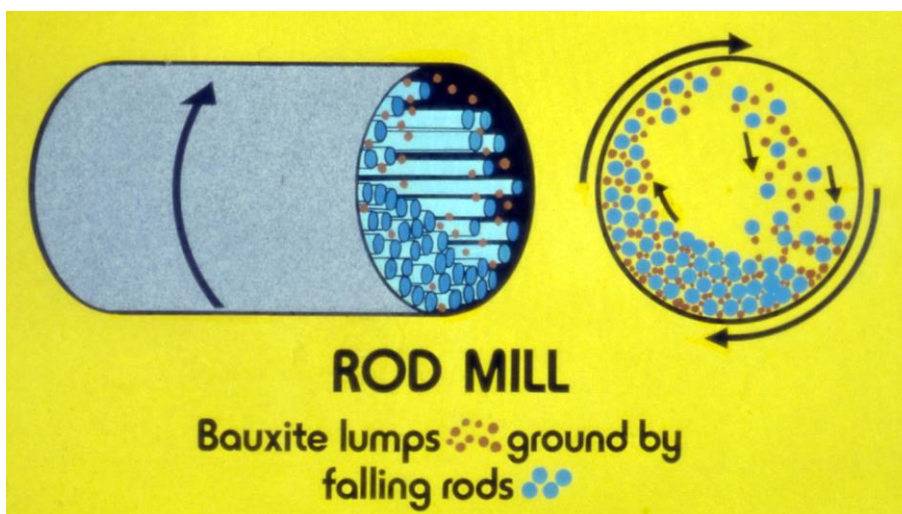
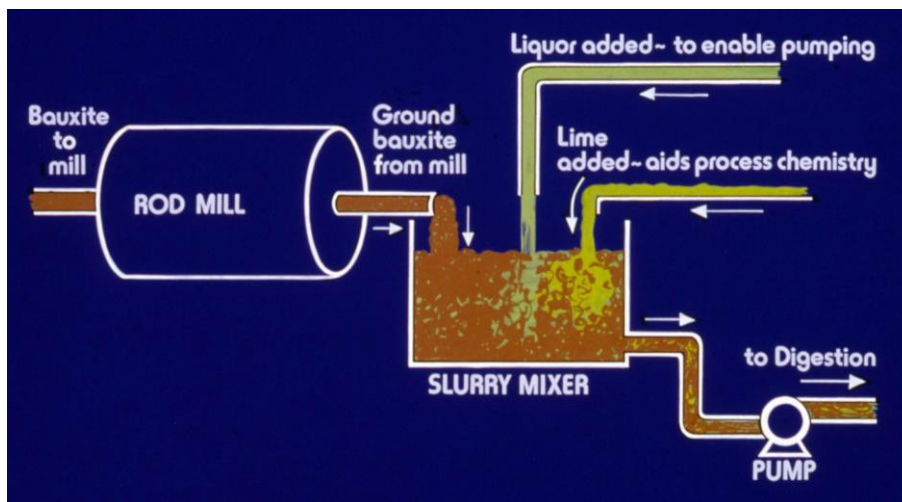
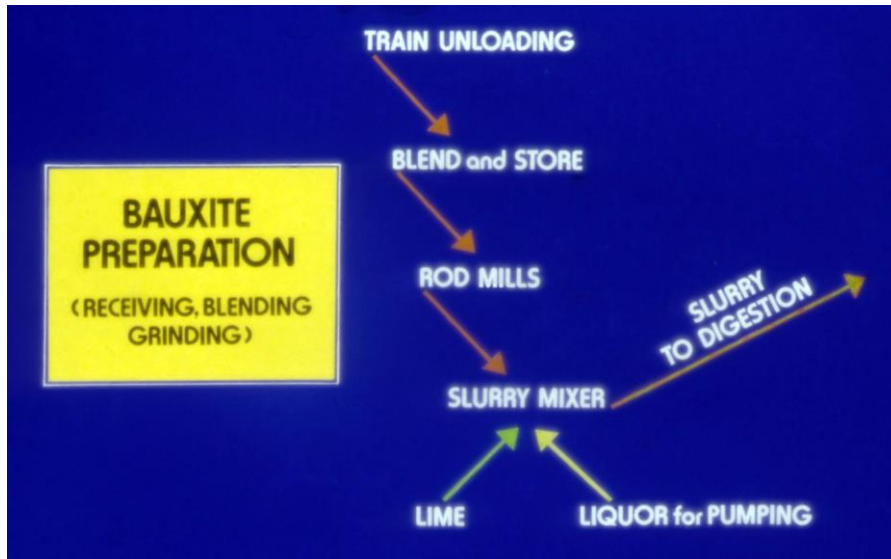
The ore is then transported by conveyor, pipeline or truck to the alumina refinery (if close by) or to a shipping point (if the refinery is located overseas).

Depending on the quality and variability of the overall deposit the ore may be blended and stockpiled at the minesite or at the refinery.

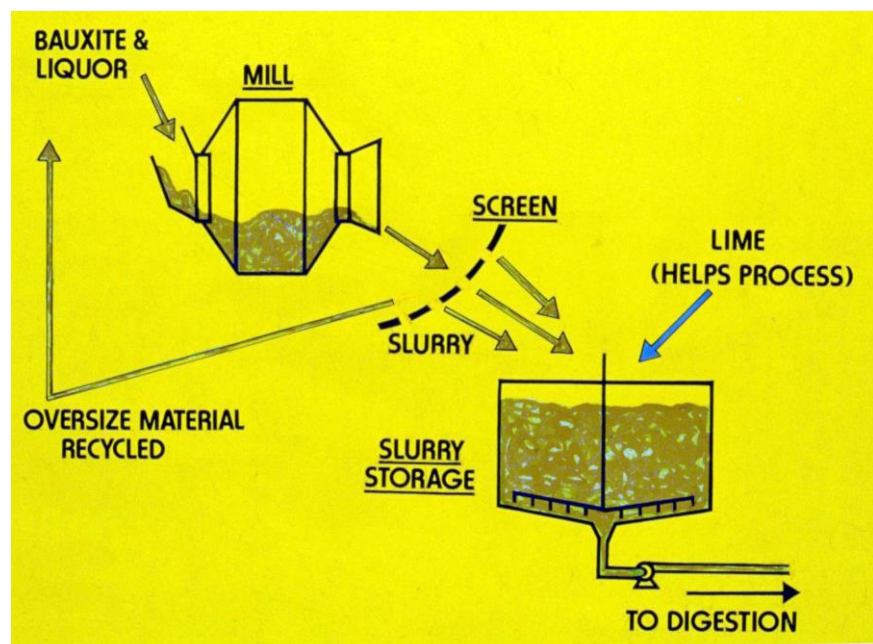
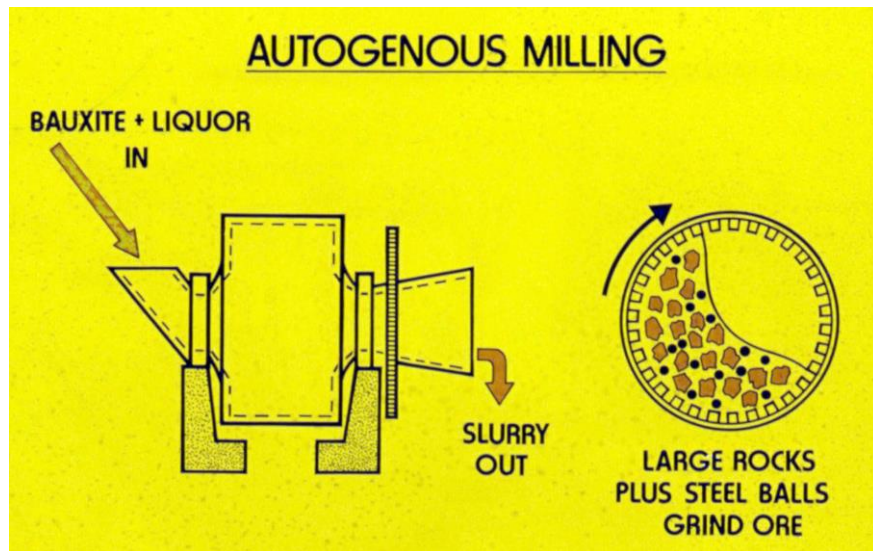
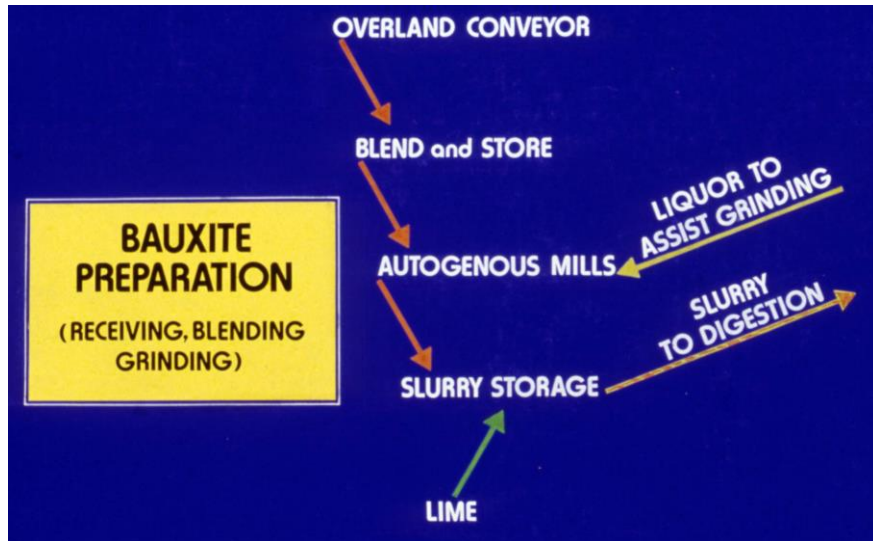
The first step in the Bayer circuit is grinding: the ore must be reduced in size to less than 150 μm (0.15 mm) particles for efficient extraction of the aluminium. The ore is added to the mill together with spent liquor and lime. Three types of mill are used:

- Rod mills, holding a charge of steel rods which crush the ore by impact (now being phased out);
- Ball mills, holding a charge of steel balls for crushing; and
- Autogenous mills, which utilise the larger lumps of ore to crush the smaller ones; in some cases steel balls are also added for semi-autogenous milling.

For rod milling:



For autogenous milling:





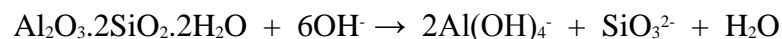
Semi-autogenous mills

Questions

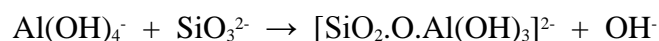
- How would you conduct an exploration program to define a new bauxite deposit for mining and processing?
- A clay layer, often rich in kaolinite, usually underlays a bauxite layer. Why is it important to know where this boundary is?
- When steel rods or balls are used in the grinding process do you think they contaminate the final alumina product?
- Crushing, grinding and milling are energy-intensive processes. Suggest less energy-intensive methods for producing the fine bauxite for processing.

6. Desilication

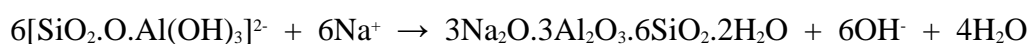
As mentioned in Section 2, bauxites do contain some clays which are termed *reactive* in the Bayer Process, namely they react with the caustic liquor and dissolve. The most common reactive clay is kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and under Bayer conditions it dissolves:



The aluminate and silicate ions then react to form a complex ion:



and in the presence of caustic soda this complex ion forms an insoluble *Desilication Product* (DSP):



This DSP exits the circuit with the residue. However, 0.8 tonne of caustic soda is lost for every tonne of kaolinite in the bauxite as well as almost one tonne of alumina which is unavailable. As caustic soda is an expensive reagent, its loss should be minimised which implies that the kaolinite content of the bauxite should be minimised. Whilst this is a worthy

target, it has its dangers: if too little kaolinite is present, the silica formed in solution from its dissolution is inadequate to form the insoluble DSP: the silica remains in solution and contaminates the final alumina produced from the circuit. An optimum kaolinite content in bauxite is 2-5%.

To ensure that formation of the DSP is as complete as possible, the liquor slurry containing the milled bauxite is kept in holding tanks at about 90°C for at least 8 hours before proceeding to Digestion.

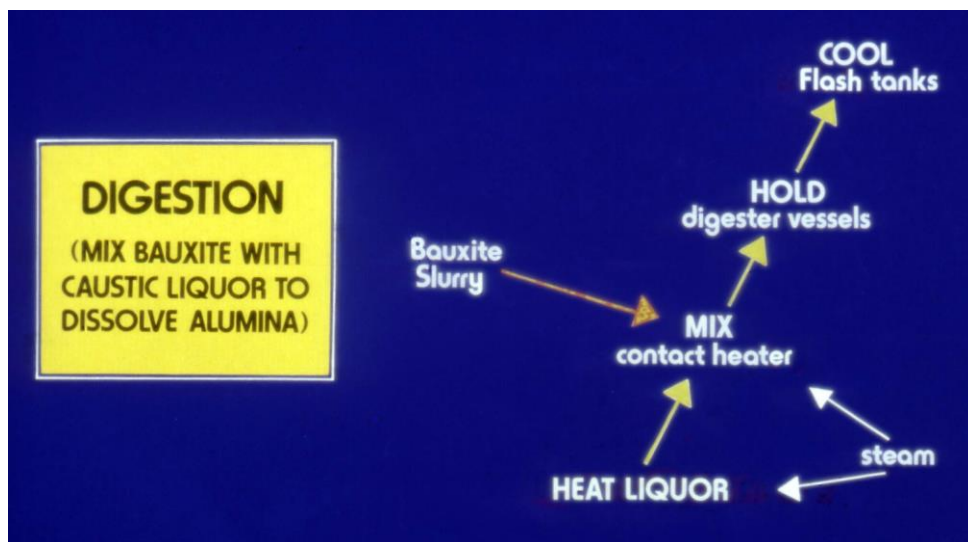
The DSP has an interesting crystal structure: the aluminosilicate units form a negatively charged cage structure balanced by the sodium cations. The cages can enclose (“capture”) a range of suitably sized anions, such as chloride and sulfate and serve as an impurity removal process as discussed in Section 17.

Question

(a) Compare the structure and properties of DSP with those of molecular sieves.

7. Digestion

The slurry from the desilication tank is pumped into the train of digester vessels where it is held for an appropriate time.



The extraction of aluminum from the bauxite into the caustic solution is dependent on the particular aluminum mineral present. Gibbsite is most readily attacked; the digestion temperature is usually in the range 140-150°C for 20 minutes. Whilst dissolution of the

gibbsite occurs in about 5 minutes, extra time in digestion allows completion of the desilication reaction, forming DSP. Boehmite is less readily attacked and temperatures in the vicinity of 250°C for 10 minutes are required. Diaspore is the least reactive mineral and temperatures up to 280°C may be required. All these digestion temperatures are above the boiling point of the caustic liquor so the digester is held under pressure; dependent on the mineral the pumps and digester vessel must be able to handle the pressure. The temperature for digestion is achieved by injecting high pressure steam into the slurry.

After digestion the slurry is flashed down to atmospheric pressure and the steam and heat evolved are collected; refer to more details in Sections 18 and 19.

In simple terms the aluminum dissolves to form the aluminate ion $\text{Al}(\text{OH})_4^-$ as the sodium salt. However, the actual picture in these strongly caustic liquors is much more complex, and many studies have been undertaken to determine exactly what is the form of the aluminium ion in solution. Most likely the aluminate forms polynuclear species and hydrogen bonding of extra water molecules may be involved.

The concentration of aluminum in solution is well above its equilibrium value (the liquor is supersaturated); this presents a number of challenges to prevent the aluminium precipitating (crystallising) out of solution before the Precipitation step.

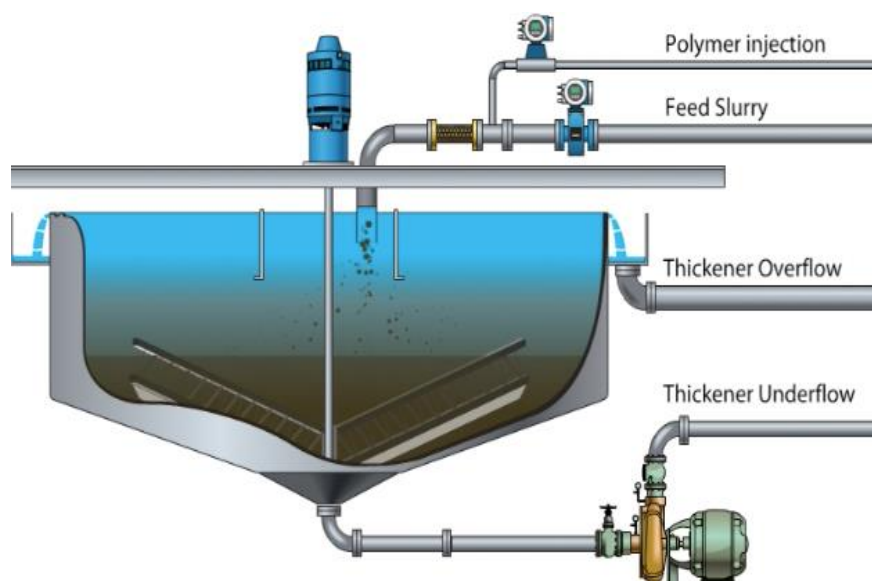
Question

- (a) The digestion of bauxite occurs at temperatures above the boiling point of the liquor, and so must be carried out under pressure. How would you design the digester train to contain this pressure?

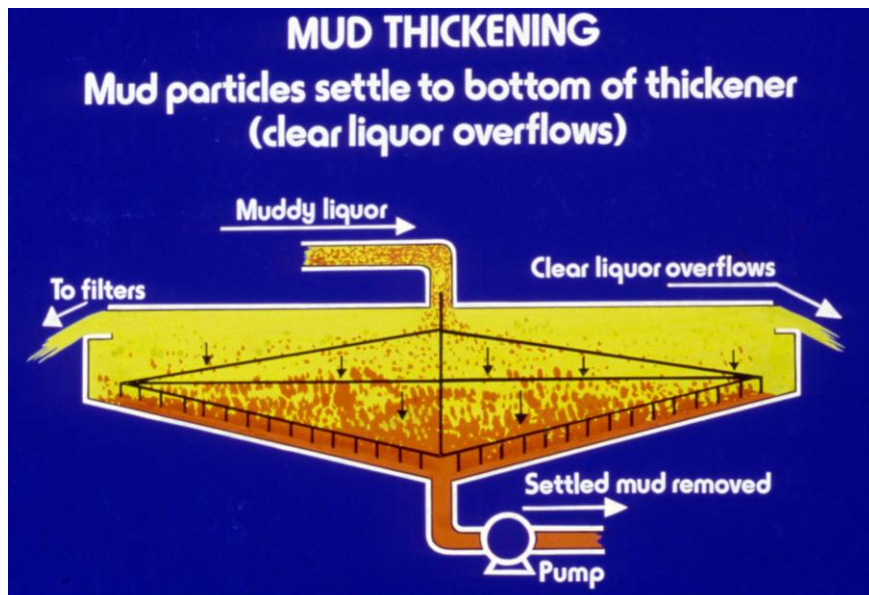
8. Solid-Liquid Separation

The solids remaining in the slurry leaving digestion must be removed to the greatest possible extent before the aluminium in the pregnant/green liquor is crystallised (termed *precipitation* in Bayer parlance) out as aluminium hydroxide (*hydrate or trihydrate*). It is essential that the hydrate is as pure as possible to ensure the final alumina product meets the quality requirements of the smelter customer.

To this end the first stage is solid/liquid separation in large vessels called thickeners.



Thickener



These are 40 m diameter tanks with a cone base; the slurry is injected at the top on the periphery and flocculant (coagulant – a specially designed polymer formulation) is added (to assist in smaller particles aggregating into larger ones). A large rake in the vessel rotates around, and the solids settle to the base and exit at the bottom of the cone (thickener underflow). The clarified pregnant/green liquor exits at an overflow weir at the top (thickener overflow). Typically a train of 5 thickeners in series is used in each unit. The solids, in a dense slurry, exiting the last thickener are pumped to the washers (Section 15).

Questions

(a) Do you think hydrate scale would be found in the thickeners? Why?

9. Filtration

The liquor from the thickeners still contains low levels of fine solids and must be subject to polish filtration before the Precipitation step. Pressure filters force the liquor through specially designed polymer cloths.

Questions

(a) Could the polymer cloths become blocked/blinded with fine particles? How could they be cleaned?

10. Heat Interchange

The liquor exiting filtration is at temperatures around 95°C; this must be cooled to about 80°C before entering the Precipitation vessels. The liquor is passed through heat exchangers and the evolved heat captured. Refer to Section 18.

Question

(a) How could the heat removed from the liquor be used elsewhere in the process?

11. Precipitation and Equilibrium Considerations

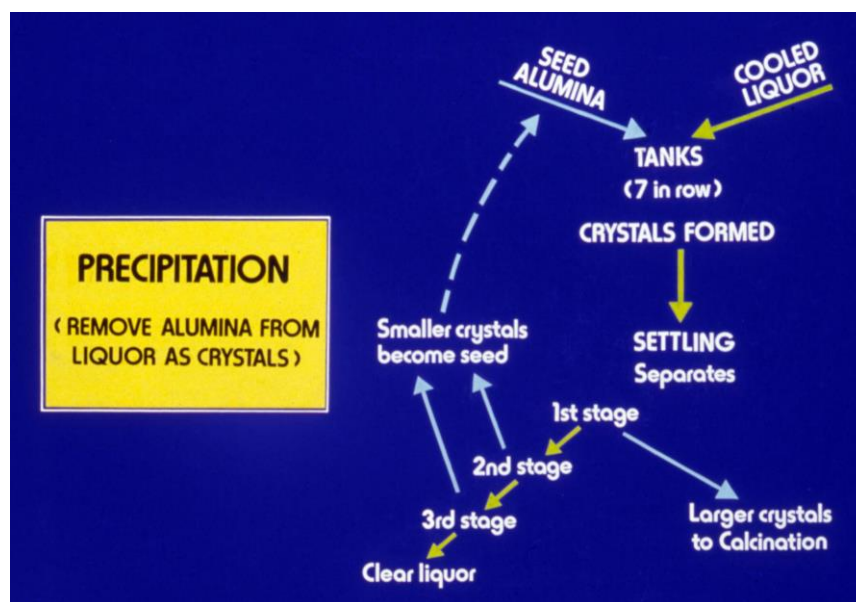
As mentioned in Section 7 the pregnant/green liquor is supersaturated with dissolved aluminium. The crystallisation of aluminium hydroxide $\text{Al}(\text{OH})_3$ (hydrate) from this liquor is

the slowest part of the Bayer cycle; the kinetics of the overall reaction are controlled by chemical steps, not by mass transfer. Therefore, long holding times are required, and it is necessary to provide a large recirculating mass of hydrate seed to accelerate the reaction. The seed provides a catalytic surface to encourage the formation of aluminium hydroxide, and a surface on which it can grow.

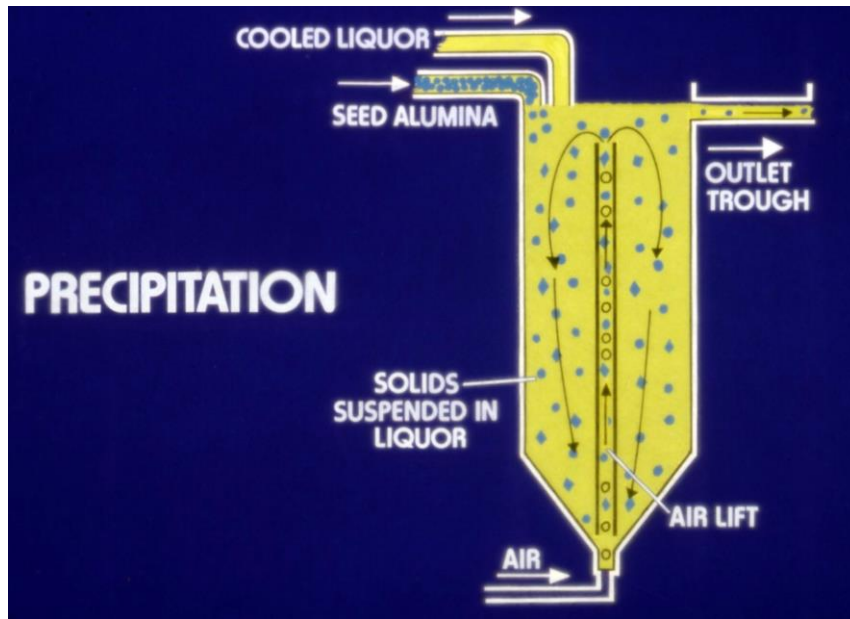
It is very important that the crystals produced are of the right form and structure to ensure that they pass through the calcination stage (to form alumina) and shipping to arrive at the aluminium smelter meeting all quality criteria.

So the crystallisation must be carefully controlled to ensure the best outcomes in relation to

- Hydrate yield, and therefore operating cost;
- Hydrate (and ultimately alumina) product strength;
- Hydrate (and ultimately alumina) particle size distribution; and
- Hydrate (and ultimately alumina) product purity, especially with regard to soda and silica contents.



Hydrate seed (fine crystals), previously screened from the Precipitation step, is added to the first precipitator; the aluminium hydroxide crystallises onto these seeds in a controlled way. The precipitator is a large vertical tank (typical dimensions 30 m high and 15 m diameter with volume about 4.5 ML) with some form of agitation to maintain suspension of the solids in the liquor. Earlier forms of tank had a cone bottom with air injection to provide the agitation; these tanks were called Pachucas (originally devised in New Zealand, but first practically introduced in Pachuca, Mexico).



Precipitation Building with Pachuca tanks

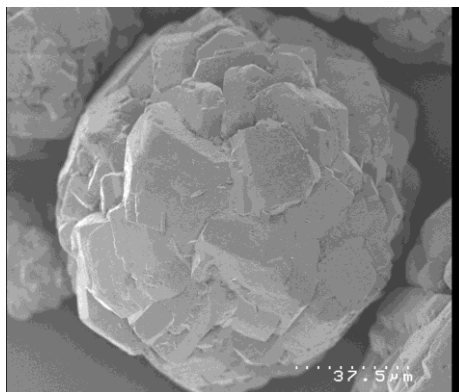
Modern refineries have flat-bottomed precipitation tanks with agitation via a stirred propeller to maintain suspension of the solids in the liquor.

Precipitation takes place over at least 24 hours as the hydrate slurry passes through up to 10 precipitators in a train. The number and size of the vessels are necessary to accommodate the slow Precipitation step in the Bayer cycle; all other unit operations are much faster. As the hydrate slurry (typically 500 g solids/L) passes down a precipitator bank the temperature is carefully reduced to provide a greater driving force for crystallization. The liquor (termed *spent*) leaving Precipitation is still somewhat saturated in dissolved aluminium.

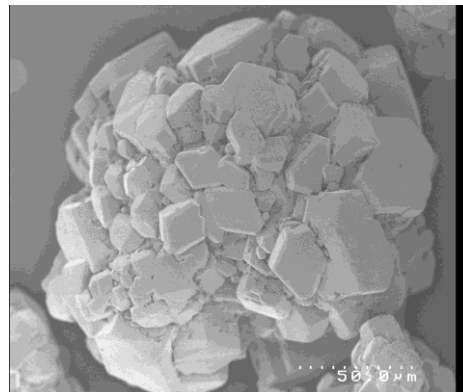
The yield of hydrate through the precipitator train is an important efficiency parameter. The greater the yield the more efficient the refinery. Typically the pregnant/green liquor entering Precipitation (at 75-80°C) will have an aluminium content of 140 g/L (expressed as Al₂O₃) and the spent liquor exiting Precipitation (at 55°C) a value of 50 g/L, giving a yield of 90 g/L.

The mechanism of precipitation involves a combination of agglomeration and growth. The first stage of precipitation involves the sticking together of small seed particles to form agglomerates. This is a relatively rapid process, which is favoured by high alumina supersaturations and high temperatures. It therefore is the predominant mechanism in the first stage of precipitation. The agglomerates so formed are of random shapes, and the overall strengths of the agglomerated particles are low. This is also the step in which most of the chemically included soda is incorporated into the hydrate crystals. It is therefore essential that the high yielding agglomeration stage is followed by a period of controlled growth. In this growth stage, as well as increasing in size the particles are strengthened, and their shapes are regularised. In addition, the overall soda content of the particles is diluted.

Depending on the precipitation conditions, temperatures and impurities in the liquor stream the final hydrate particles may display a predominantly radial or mosaic nature. The radial particles tend to be tougher and less prone to break up into smaller particles compared to the mosaic particles when transported and calcined, and so are preferred. These SEM images illustrate the two types of hydrate particle.



Radial (strong) gibbsite



Mosaic (weak) gibbsite

The optimum particle size distribution in the Precipitation product ranges typically from 45 to 150 µm in diameter with less than 5% in the <45 µm fraction and no more than 10% greater than 150 µm.

Exiting the last precipitator, the hydrate particles are screened from the spent liquor and washed with good quality water to ensure as much entrained liquor is removed. The moist filter cake is transported to Calcination.

The Precipitation step in the Bayer cycle is the most critical one. Two criteria:

- Aim to maximize product recovery in the minimum time to increase efficiency; and
- Aim to grow sufficiently large particles in a slow, controlled way to ensure the product hydrate meets size and toughness specifications

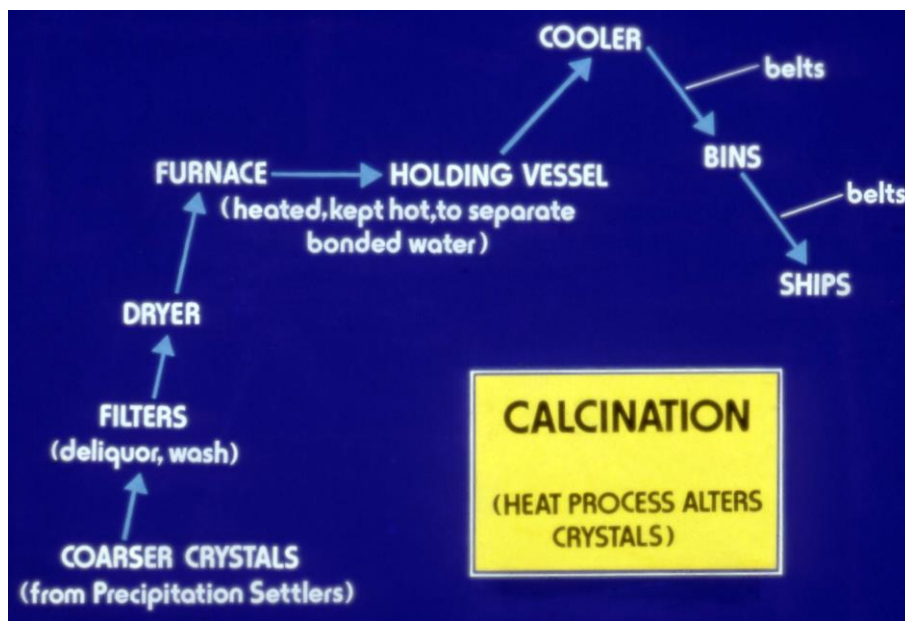
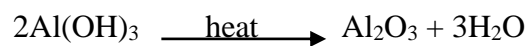
are essentially in conflict. So good control of Precipitation in a refinery is most important.

Questions

- (a) The Precipitation step is the slowest unit operation in the Bayer circuit. How would you speed up this process? Would this increase the productivity? What detrimental side effects might occur?

12. Calcination

The aluminium hydroxide (hydrate, often expressed as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ rather than more correctly as $\text{Al}(\text{OH})_3$) from Precipitation must be heated in some suitable fashion to remove the 3 molecules of “water” to produce anhydrous alumina (Al_2O_3) which is the desired smelter feedstock. The hydrate is in fact a genuine hydroxide and does not contain any water of crystallisation at all. Nevertheless, upon heating it does decompose with the release of three molecules of water per molecule of alumina produced, just as if it were a trihydrate.



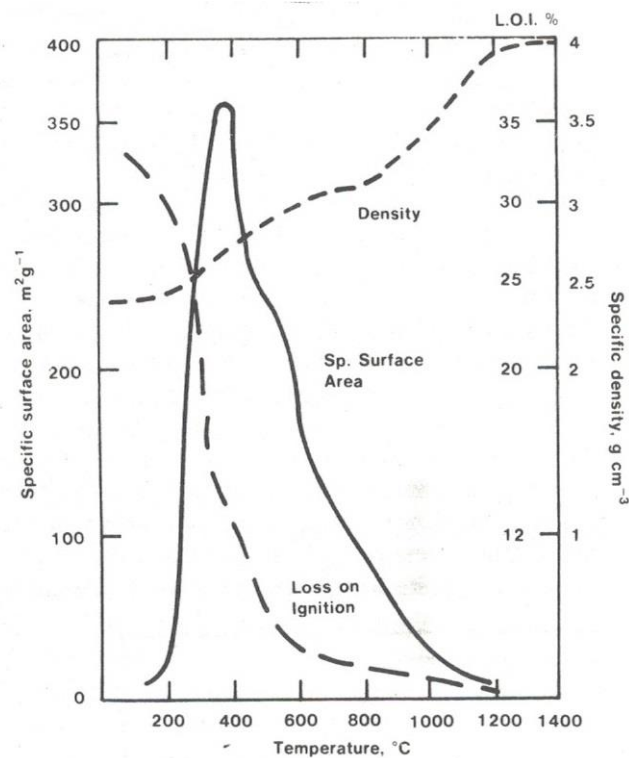
In earlier times long rotary kilns were used for this calcination; however, they are energy-intensive and have been superseded by calciners using natural gas fuel. These calciners utilise the fluid-bed principle whereby the injected gas suspends the hydrate particles as they are carried through the calcining profile over a period of seconds. The temperature applied is important, to ensure the right alumina product quality (refer to Section 13).



Gas suspension (fluid bed) calciners

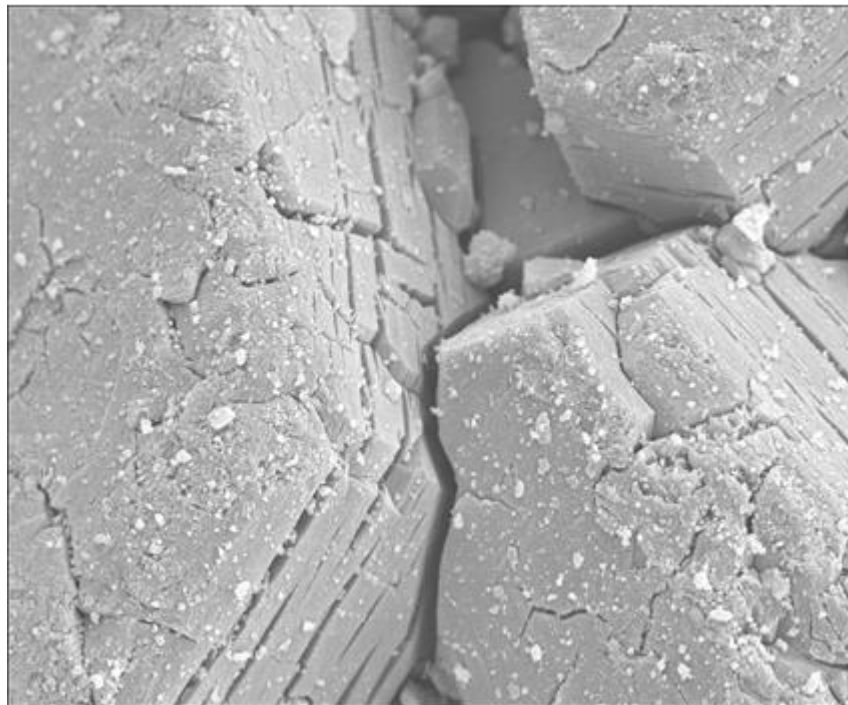
The decomposition of the hydrate to alumina is by no means as simple as might be implied by the above equation. The ultimate product of calcination is the most stable phase of alumina, corundum or α -alumina. This is, however, not desirable for smelting, because α -alumina is slow to dissolve in the bath (refer to Section 24). For the formation of Smelting Grade Alumina (SGA), calcination is carried out at around 950°C . At this temperature, the α -alumina content of SGA is generally kept at around 1%. The remainder is a complex mixture of anhydrous alumina phases.

The stages of dehydration are illustrated in the graph:



It can be seen that most of the weight loss occurs between 200 and 350°C, corresponding to the decomposition of the hydroxide to alumina and water. The range of temperatures from 350 to 500°C is where “activated alumina” is formed. Activated alumina has a very high surface area and is poorly crystalline. The higher temperatures are required to recrystallise the alumina to surface areas suitable for smelting. Prior to the introduction of the dry scrubbing system in aluminium smelters, surface areas (SSA) in the region of 40 to 50 m²/g were preferred. Current practice dictates SSAs in the region of 80 m²/g for effective fluoride removal. Higher SSA would be even better for fluoride removal, but would result in unacceptably high water contents, as measured by the Loss on Ignition (LOI). The correlation between SSA and LOI is apparent in the graph.

The recrystallisation from the hydroxide structure to the alumina structure involves a complete rearrangement of the structure of the material. The original gibbsite crystal is hexagonal layered hydroxide, typical of the clay minerals. During calcination, water is formed in the layers, and is expelled along the layer boundaries as steam. This causes shrinkage, and cracking of the crystals along the layer faces, as shown in this SEM image.



Close-up of calcined alumina showing inter-layer cracking

Some fine alumina (less than 20 µm in size) is produced as a result of the vigorous treatment of the hydrate particles in calcination; for example, edges of crystals are broken off as the particles become more rounded. This fine alumina dust (ESP dust) is collected in electrostatic precipitators adjacent to the calciners.

The calcination of aluminium hydroxide (hydrate) to alumina is an endothermic reaction (that is, heat is absorbed). This aspect is put to good use as hydrate is applied as a fire retardant in the manufacture of, for example, carpets, textiles and building materials.

Question

(a) Calciners usually emit a white smoke. What is the main component of this white smoke?

13. Alumina Product Quality

The alumina (SGA) produced by the bauxite refinery must meet tight specifications to be acceptable to the aluminium smelter customer. Refer to Section 24 for more details. Several criteria are important:

- *Impurities*
The more important ones are sodium, calcium, silicon and iron. Sodium and calcium can affect the smelting process; silicon and iron can contaminate the product aluminium. Other elements which should be minimised as they can also contaminate the aluminium are vanadium, beryllium and phosphorus.
- *Size of particles*
If the alumina particles are too large, they cause problems in efficiently dissolving in the smelting bath. If too small, they can cause dusting problems in transportation and in the smelter pot. The optimum size range is from 45 to 150 μm .
- *Strength of particles*
If the particles are friable (not having sufficient strength or bonding between the individual component particles and so breaking into smaller particles) they can cause dusting problems and segregation in transportation and in the smelting pot.
- *Surface area*
The alumina feedstock to a smelter, prior to addition to the smelting pot, is used to scrub fluoride-containing gases emitted from the pots, so an optimal surface area is required.
- *α -alumina content*
If this is too high (due to too high a calcination temperature or too long a residence time in the fluid-bed calciner) the alumina dissolution in the smelting bath is too slow and alumina sludge can form on the bottom of the smelting pot.
- *Segregation of particle sizes*
In transporting the alumina through pipes or storage in large tanks the particle size distribution can be affected: an excess of large particles can collect in the base of a tank and finer particles at the top. Steps must be taken to minimise this segregation.

Questions

- (a) What steps would you take if the alumina from a refinery is out of specification for a particular property?
- (b) Do you think that alumina supplied from one refinery is exactly the same in all its properties as one from another refinery? What factors might contribute to differences?

14. Scale

As mentioned in Section 7, the concentration of aluminium in the caustic liquor is well above its equilibrium value. Hence there is a driving force for hydrate to precipitate from solution in a less controlled way than that desired in the Precipitation step. The result is that hydrate scale can form in pipes and vessels, including the precipitators. This leads to loss of hydrate yield in the Bayer process as well as inefficiencies due to reduced flows in pipework and volume in tanks. Maintenance programs ensure that the hydrate scale is removed on a regular basis, adding to the overall cost of operation. But the hydrate scale can be returned to digestion, ensuring the valuable alumina is recovered.

Other scales can form in various locations, for example DSP scale in heat exchangers. This scale, which can form very hard deposits, cannot be removed by caustic attack; it is soluble in acids, so on a regular basis heat exchangers are taken off line and washed with sulfuric acid.

Questions

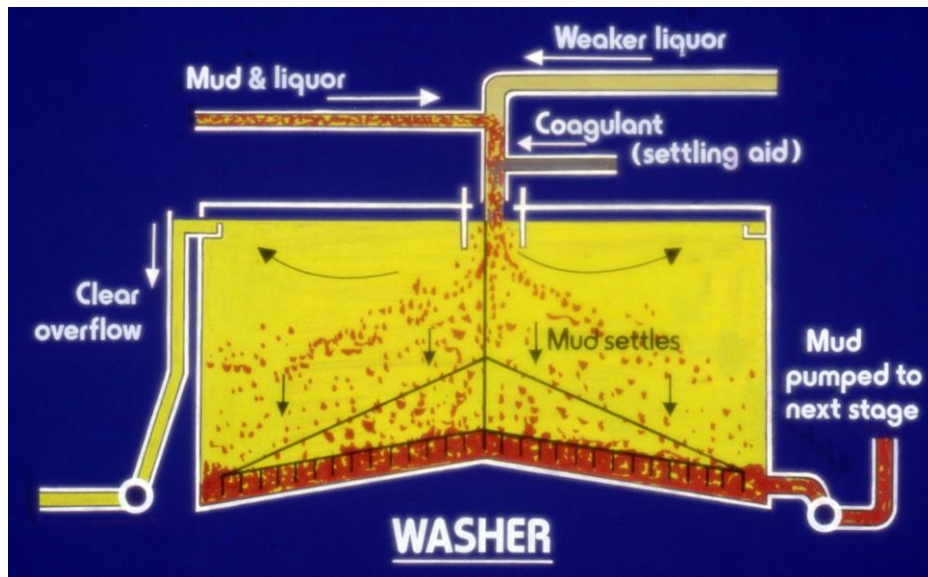
- Could the surfaces of pipes and tanks be treated in some way to prevent scale forming on them?
- Is there a “magic chemical” which, added to the liquor stream, reduces or prevents scale formation? Could this chemical affect other aspects of the Bayer process?

15. Mud Washing

The mud exiting the thickeners is comprised mainly of iron oxides and silica-based minerals, including quartz (SiO_2), as well as DSP and various calcium-based species resulting from the addition of lime for causticisation.

Depending on the quality of the bauxite, the amount of mud can be between one to two times the amount of alumina produced. For example, bauxite mined in the Darling Ranges of Western Australia is considered lower grade and almost three tonnes are required to produce one tonne of alumina. Bauxite produced in Weipa, North Queensland, is higher grade and just over two tonnes are required for one tonne of alumina.

To minimise loss of alumina and caustic soda in the liquor associated with the mud exiting the thickeners, it is directed to a series of washers (usually 5 to 6 in a train for each unit).



The wash water (lowest liquor concentration) entering the last washer exits at the top (overflow) and then is used as the wash water in the preceding washer; the underflow from the preceding washer enters the last washer. The underflow from the last washer is pumped to disposal areas. This process is termed countercurrent decantation; at each washing step the liquor concentrations are reduced, and the overflow liquor from the first washer is concentrated by evaporation and returned to the Bayer circuit.

Question

- What factors determine how many times you can wash the mud before it is stored?

16. Residue Disposal and Re-use

An alumina refinery of, say, 4 million tonnes per year production could produce around 8 million tonnes of mud (termed *residue*), dependent on the quality of the bauxite ore. Such an amount, and its special properties, requires stringent conditions on its proper disposal. The residue is caustic (alkaline) in nature, due to:

- Some residual entrained caustic liquor, which is a combination of sodium hydroxide and sodium carbonate (formed from sodium hydroxide by carbonation with CO₂); and
- The DSP which decomposes in less alkaline environments to release sodium hydroxide.

As well, the residue is fine grained in size (significant proportions are less than 45 µm and some less than 20 µm) so that when it dries it can result in caustic dusts forming.

In the past the residue slurry (about 500 g solids per litre of slurry) was pumped to specially built dams (residue storage areas, built with impermeable clay) where it was safely contained. The residue slowly settled, and the supernatant liquor was recovered and returned to the refinery. The dried residue was then covered with an impermeable layer of various materials.



Residue disposal area



Super thickener on disposal area

Current practice is to provide an underdrain system beneath the residue area, to capture any liquor escaping through the clay base (covered with synthetic plastic liner). Prior to disposal in the residue dam the mud is thickened in a “super thickener”, to remove as much entrained liquor as possible (about 75% solids); this leads to a dry stacking configuration. To prevent dusting the area is served by a water sprinkler system which is activated during adverse weather conditions (dry periods with strong winds).

The residue has potentially to be stored for very long periods of time (hundreds of years) before it becomes benign to the environment. This is a challenging situation, and much effort has been put into finding alternative uses for the residue so that it doesn't have to be stored. Some examples are:

- Ameliorating porous sandy soils to aid water and nutrient (fertiliser) retention;
- Replacing natural materials for road base in building highways;
- As a component of bricks and other construction materials.

Whilst residue contains a wide range of elements, some like iron and silicon in significant amounts, its processing to extract these commodities is very challenging, especially in finding economic processes.

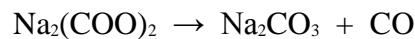
Since the amount of residue produced is substantial, any potential use should reflect this volume. In addition, transport of the residue to a market should be minimal and cheap, to ensure commercial economics. The alumina producers, potential end users and research providers continue to conduct a wide range of studies to find commercial markets for residue in order to avoid its long term, costly storage.

Questions

- (a) The caustic nature of residue is an important factor in safely storing it for long periods of time. Why not neutralise the residue with acid? What are the advantages and disadvantages in doing this?

17. Impurity Balances and Removal including Liquor Purification

It was mentioned in Section 4 that organic materials such as soil and tree roots within the bauxite do enter the Bayer circuit and are attacked by the high caustic concentration and temperature in digestion. The high molecular weight (up to a million) of the humic material breaks down to a complex mixture of lower molecular weight compounds. Some of these are quite simple, such as the sodium salts of formic (HCOOH) and acetic (CH₃COOH) acids. The most prevalent is sodium oxalate, Na₂(COO)₂. The sodium oxalate concentration in the liquor builds up to a saturation level where, if not reduced, it will contaminate the hydrate being crystallised in Precipitation. Therefore, steps are taken to reduce the oxalate by treating a sidestream of the spent liquor. In one process the sodium oxalate is crystallised from solution, filtered off, washed and put through a kiln or calciner where it decomposes to sodium carbonate:



The sodium carbonate is then converted back to sodium hydroxide by the lime addition in grinding.

A newer process utilises the ability of “bugs” (naturally occurring microorganism or bacterium) which selectively “consume” the oxalate and produce sodium carbonate.

The oxalate is seen as a detrimental impurity in the liquor as it can affect the quality of the hydrate product. However, there are other organic impurities in the liquor stream that are beneficial: they aid in maintaining the hydrate concentration in liquor well above the equilibrium value (the liquor is supersaturated with hydrate) and so enable controlled crystallisation in the Precipitation step rather than random crystallisation in other unit operations.

Depending on the origin and nature of the bauxite ore, the amount of organic material can range from 0.01% to 0.35% by weight, expressed as organic carbon. This organic mass can build up to substantial levels in the liquor (total organic carbon contents of up to 30 g/L). This can affect the viscosity of the liquor, requiring more energy in pumping and other side effects. So a process called *liquor burning* has been implemented in some plants: a small sidestream of the spent liquor is mixed with fine alumina dust (ESP dust produced in Calcination) and treated in a kiln. The organics are burned off to carbon dioxide. The product is solid sodium aluminate which is dissolved back into the spent liquor.

Inorganic anions such as chloride and sulfate enter the Bayer circuit from within the bauxite and in process water added. These species build up to equilibrium levels and exit the circuit entrained in the DSP cage structure.

Questions

- (a) Bauxites mined in different geographic locations have different levels of impurities, especially organic carbon. Would there be any advantages in treating a low organic carbon bauxite?
- (b) The organic carbon content within a bauxite deposit can vary slightly. When setting up a mine plan to extract the bauxite, would it be useful to take account of this organic carbon variability?

18. Energy Usage and Balance

The energy needed to produce one tonne of alumina from bauxite is about 12 GJ, but this will vary depending, amongst other factors, on whether the bauxite is predominantly gibbsitic (low-temperature digestion) or boehmitic (high-temperature digestion). Inputs and outputs include:

Energy In:

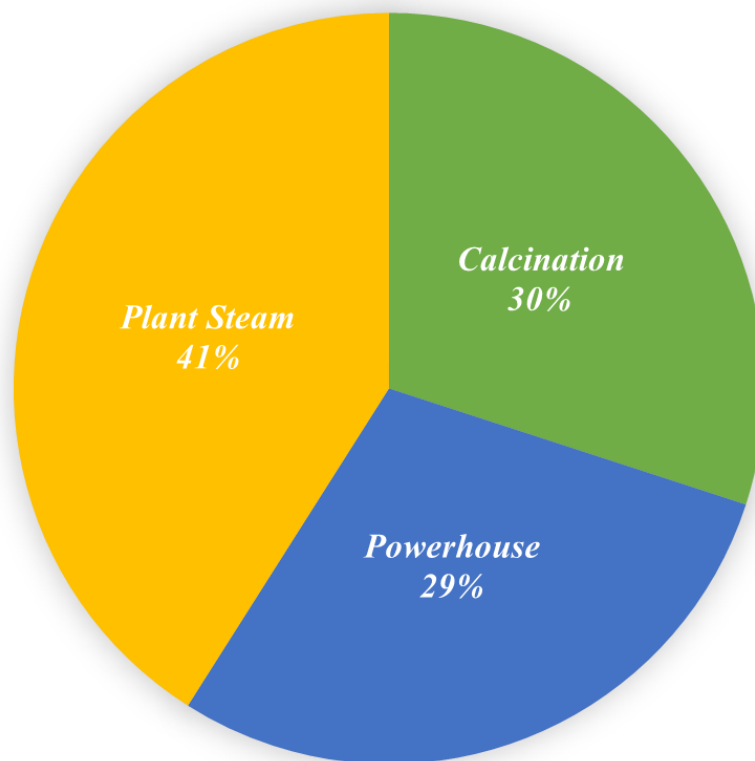
- Crushing ore at minesite
- Transport ore to refinery
- Stack ore in stockpiles
- Grind/mill ore
- Generate steam for heating digestion slurry
- Drive pumps
- Heat hydrate in calcination

Energy Out:

- Heat interchange

This chart indicates the breakdown of energy use:

Bayer Plant Energy Usage



Powerhouse energy use includes boiler loss 11%, powerhouse steam 10% and power generation 8%. Plant steam energy use includes digestion 25%, evaporation 12%, clarification (residue thickening and washing) 3% and precipitation 1%. The most energy-intensive unit operation is Calcination, followed by Digestion.

Needless to say there are strong drivers for reducing energy usage because of its cost. Substantial reductions have been progressively made (incremental improvements) as well as step changes (for example, from kilns to gas suspension calciners in Calcination).

Both electric power and steam are required to efficiently operate an alumina refinery. However, there is a delicate balance between the two. Often the refinery will have its own

power station, and it generates excess power compared to steam generation requirements, so it may sell power to a local electricity grid.

Question

- (a) The Precipitation building is large, with an extensive roof. Could solar power be used in a refinery?

19. Water Usage and Balance

Maintaining the optimal water balance in a refinery is challenging. Inputs and outputs include:

Water In:

Free moisture in bauxite
“Water” in gibbsite & boehmite
Injected steam
Caustic soda
Residue washing
Hydrate washing
Rain

Water Out:

Moisture in hydrate
Hydrate to calcination
Evaporation
Heat interchange flashing
Water in residue

At the residue storage area, which has a significant footprint, rainfall may add to the water balance and the supernatant liquor formed returned to the refinery. Alternatively, evaporation (in a hot climate) may exceed rainfall and make-up water may need to be added to the refinery circuit. Water is a valuable resource, so any addition (from scheme water or more usually from bores or groundwater) should be minimised.

Up to 4 kL of water are required for each tonne of alumina produced.

Questions

- (a) Why is so much effort put into recovering caustic from residue washing and hydrate washing?
- (b) In many refinery locations the weather is not constant, for example, it doesn't rain all the year and/or the sun doesn't shine all year. How would you cope with varying weather: just rain in winter (and so excess water) and hot sun in summer (and so excess evaporation)?

20. Process Control

An alumina refinery is a very complex operation, so controlling all its unit operations on the most efficient way is very challenging. This control is usually centralised to a plant control room, where the status of each process step can be illustrated and boundaries placed on particular machines (for example, a pump delivering pregnant/green liquor to Precipitation) to ensure it operates within these bounds.



Process control room

Sensors placed on line are increasingly being used for control purposes. A simple example would be a temperature indicator. A more complex one would measure aluminium in solution prior to and after Precipitation. Sensors must be resistant to the high caustic concentrations and temperatures, and not be subject to scale growing on them and biasing the measurements.

A comprehensive control structure is a significant investment in the cost of a refinery.

Questions

- (a) Could artificial intelligence be used to control an alumina refinery?
- (b) Are there types of sensors which don't have to be immersed in the process liquor stream?

21. A Sustainable Bayer Process

The modern alumina refinery should be efficient in utilising all its resources and meet all required environmental standards.

- *Mining*
In the mining operation any dust formation should be minimised.
Once the bauxite ore is extracted from a minesite it must be restored (rehabilitated) to its former environment. This requires replacing the topsoil and re-establishing the flora and fauna. Such rehabilitation requires years of effort to achieve acceptable goals. Climate can play a significant role in rehabilitation: warmer, wetter tropical climates deliver faster rehabilitation than cooler, drier temperate regimes.
- *Refining*
Spillage of any caustic liquor should be contained in bunds.
Any dusts formed (bauxite at the front end and alumina at the back end) should be suppressed.
- *Residue*
Liquor from the residue containment should not reach groundwater.
The residue should be contained within the structure.
Any dust should be suppressed.

Questions

- (a) In the Bayer process what are the unit operations which present the greatest environmental challenges? How would you reduce the environmental impacts?

22. Other Process Flowsheets

If the reactive silica component of an aluminium ore is too high for treatment by the Bayer Process then a lime-sinter approach has been utilised. Lime is added to the ore in a high-temperature treatment to produce a sinter (or slag) from which the alumina is extracted with a sodium carbonate solution. The silica is tied up with the lime and so is essentially removed from further involvement. This approach has been applied to fly ash, a by-product in coal-fired power stations, with up to half of the alumina being extracted.

Questions

- (a) The sinter process just described requires high temperatures. Do you think this process is more or less energy-intensive than the standard Bayer process? Why?

23. Other Aluminium Ores

Aluminium occurs widely in nature, and so is found in a wide range of minerals in various ores besides bauxite. As a result it is not surprising that efforts have been made to commercially extract aluminium from these non-bauxitic ores. Most rely on treating the ore by digestion in acid (hydrochloric, nitric and sulfuric acids have been used). For example, the Pechiney process precipitates aluminium sulfate from a sulfuric acid digest, converts the sulfate to anhydrous aluminium chloride which is then calcined to alumina.

Efforts have also been applied to the direct production of aluminium by carbothermic reduction of minerals containing aluminium oxide. The reactions are complex and intermediate compounds are formed.

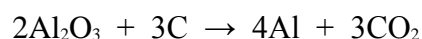
However, to date these processes are less efficient and more energy-intensive than the Bayer Process and have not achieved commercial production.

Questions

- (a) Do you think a new route to alumina will be developed to replace the Bayer process? What features would it have?

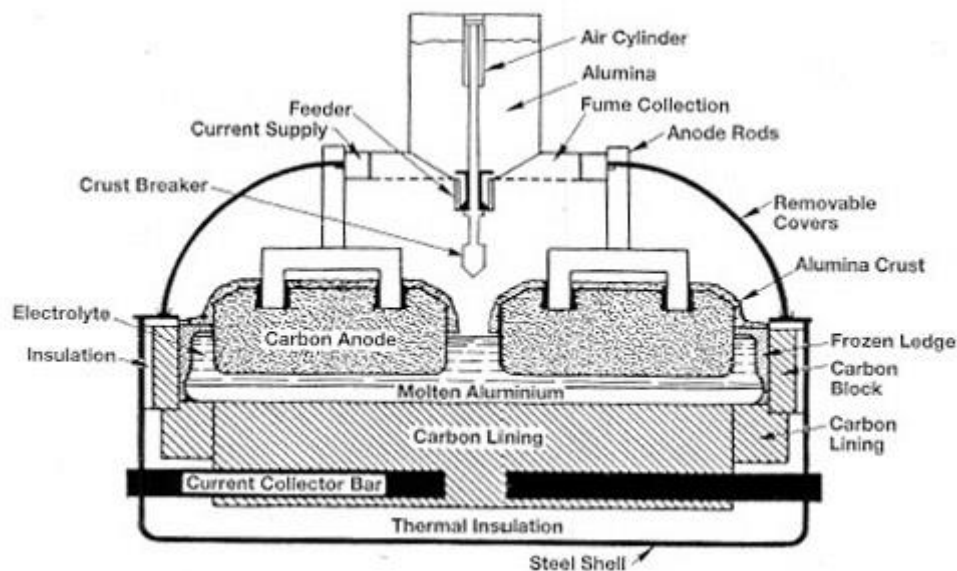
24. Smelting to Aluminium

The Hall-Heroult Process, currently used worldwide for the production of aluminium from alumina, is two years older than the Bayer Process! In 1886, Charles Martin Hall in the USA and Paul Heroult in France independently discovered that alumina, dissolved in a molten bath of sodium aluminium fluoride (cryolite, Na_3AlF_6), could be successfully electrolysed to aluminium metal. The overall reaction is:



Just under 2 tonnes of alumina are needed to produce one tonne of metal.

The components of a typical smelting cell (termed *pot*) are shown:



The alumina is fed into the top of the pot and dissolves in the molten cryolite at temperatures around 900°C. The cryolite is contained in a carbon cathode (the base of the pot); electrolysis occurs in conjunction with the carbon anodes. The molten aluminium (melting point 660°C) collects on top of the cathode and is occasionally siphoned off; carbon dioxide is emitted from the pot.

Since the smelting environment involves fluorine in various salts, reaction with moisture can form hydrogen fluoride gas. The alumina delivered to a smelter is first used as an adsorbent to scrub out this HF in the gas streams exiting the pots; this is why the alumina should have an adequate surface area, as described in Sections 12 and 13.

Smelting of alumina to produce aluminium is energy-intensive: about 51 GJ per tonne of metal (more than four times the energy needed to produce the alumina and sufficient to operate a 1 kW electric heater for a year!). This is why aluminium is sometimes referred to as canned electricity (as so much metal goes into making drink cans!). However, the positive side is that aluminium can be recycled, and producing new metal from recycled stock takes less than 5GJ per tonne (compared to the 51GJ for primary metal). And recycling rates are steadily increasing; in some counties it is greater than 70%.

In 2016 nearly 59 million tonnes of primary aluminium were produced around the world, separate to secondary aluminium produced by recycling scrap metal.

Questions

- Aluminium reacts readily with oxygen (in the air) and with moisture. But it is widely used in many applications. What happens to the surface of aluminium which makes it stable in these many applications?
- Why are aluminium smelters preferentially located near sources of hydroelectric power?

25. Appendices

Definition of technical terms

- Agglomerate
A particle made up of smaller particles (as happens in Precipitation to form hydrate) or the process of forming a larger particle from smaller ones.
- Autogenous grinding
Using the ore itself as the grinding medium to effect size reduction.

- Available alumina
The proportion of bauxite which can be extracted under the particular refining conditions.
- Calcination
Heat treatment to remove the “water” from hydrate (decompose aluminium hydroxide to alumina).
- Caprock
The hard, narrow layer lying between the overburden and the bauxite in an ore body.
- Causticisation
The recovery of sodium hydroxide from sodium carbonate by treatment with lime.
- Clarification
Collective term for thickening and washing of residue.
- Desilication
The dissolution of silica-containing minerals (especially kaolinite) followed by the precipitation of sodium aluminium silicates (DSP)
- DSP
Desilication product.
- Digester
A container operating under pressure in which the available alumina is extracted from the bauxite.
- Electrostatic precipitator (ESP) dust
The fine alumina produced in the calcination process.
- Flocculent
A chemical which causes smaller particles to agglomerate into larger clumps or flocs, used especially in the thickeners and washers. Also referred to as coagulant.
- Green liquor (or pregnant liquor)
Liquor produced in digestion; contains a high level of dissolved aluminium.
- Hydrate (or trihydrate)
Aluminium hydroxide in the gibbsite form.
- Liquor (or caustic liquor)
The solution containing mainly sodium aluminate, sodium hydroxide and sodium carbonate together with dissolved impurities which flows around the alumina refinery.
- Overburden
Material low in available alumina which sits over the bauxite ore.
- Precipitation
The crystallisation of aluminium hydroxide (also termed hydrate or trihydrate) from the pregnant/green liquor rich in dissolved aluminium.
- Precipitator
The tank in which precipitation (crystallisation) takes place.
- Pregnant liquor
See Green liquor.
- Reactive silica
The part of the bauxite which forms DSP.
- Scale
Material which deposits onto tanks, pipes, surfaces, usually DSP or hydrate.
- Semiautogenous grinding
Addition of metallic material (balls or rods) to assist the autogenous grinding.
- Sinter
Heating a material to temperatures close to its fusion point.
- Spent liquor

- Liquor exiting Precipitation; contains a low level of dissolved aluminium.
- Yield
The amount of hydrate produced in Precipitation.

Further reading

There is much useful information available on the Internet:

- Wikipedia
- Industry associations including:
 - International Aluminium Institute www.world-aluminium.org
 - Aluminum Association Inc. www.aluminum.org
 - European Aluminium Association www.european-aluminium.eu
 - Australian Aluminium Council www.aluminium.org.au

Books include:

- *Australasian Mining and Metallurgical Operating Practices* (Monograph 28, Third Edition) edited by W J Rankin (2013). Published in two volumes by the Australasian Institute of Mining & Metallurgy.
- *Essential Readings in Light Metals* Volume 1 Alumina & Bauxite, edited by D Donaldson & B Raahauge (2013). Published by Wiley.