SUSTAINABILITY IN ALUMINA PRODUCTION FROM BAUXITE

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ABSTRACT

Alumina (Al₂O₃) is the main material used for the aluminum production, which is originated from bauxite ore through hydrothermal processes. Although bauxite conversion to alumina can be done through a few competitive processes, the main commercial process is still the well-known Bayer process. This process has specific environmental challenges and in more than a century the mining and aluminum industry could not overcome them. For instance, red mud disposal that is produced in the digestion step of the bauxite is high in iron oxide and also contains significant amount of aluminum oxide. However, there have not been successful approaches in Bayer process for preventing red mud production, and even there is not still a promising method for its consumption in other industry. In the present research work, different processes for alumina production from bauxite are studied and compared with regard to sustainability; the integrated processes, their alumina yield, energy consumption, waste materials, and so on are evaluated and discussed.

INTRODUCTION

Alumina is a valuable material with many industrial applications; its most important usage is for the production of aluminum metal. The production of aluminum and alumina has been almost continually increased in the past as illustrated in Figure 1 for the recent years. More than 57 million tons primary aluminum was produced in 2015, while the global alumina production was more than 115 million tons. The main principle raw material sources for alumina production are bauxite and nepheline ores, while alumina extraction from kaolin and high alumina containing clays have been interested so far with many research activities. Over 95% of the alumina being produced around the world is through the application of the commercial Bayer process. Bauxite ore is available in many countries and the estimated bauxite reserves is more than 30 billion tons. The main bauxite reserves are in Guinea, Australia, and Brazil. When bauxite is used in the Bayer process a residue is produced, which is called "red mud". In the other alumina production processes, however, other types of residue and byproducts are produced. Red mud production in the Bayer process accompanies with loss of Fe and Al units in this byproduct. Moreover, the production of red mud has significant environmental challenges due to both its properties and also its storing. Therefore, preventing red mud production, developing economic processes to consume it, or application of alternative sustainable processes with no red mud production is interested. In the present study, the Bayer process is compared with Pedersen process for alumina production and the authors show that Pedersen process, which was run for many years in commercial scale is in principle more sustainable with no red mud problem.



Figure 1: Annual alumina and aluminum production during 2000-2015.

BAYER PROCESS

Alumina is mainly produced from bauxite ore through the well-known Bayer process, a hydrometallurgical process invented by Carl Josef Bayer in 1888-1892. ¹ A simplified process flowsheet for the process is illustrated in Figure 2. In this process bauxite ore is digested with lime addition by a solution of caustic soda (NaOH). The main reactions can be written as:

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow Na^{+} + Al(OH)^{-}_{4(aq)}$$
(1)

$$Al(OH)_{(s)} + NaOH_{(aq)} + H_2O \rightarrow Na^+ + Al(OH)^-_{4(aq)}$$
⁽²⁾

This causes a saturated solution of sodium aluminate with insoluble impurities. The suspended solid particles are separated in a clarification step through the addition of flocculants in thickeners and the residue, the red mud, is discarded. Aluminum hydroxide (Al(OH)₃) crystals are precipitated from the sodium aluminate solution through the addition of fine Al(OH)₃ seeds and a caustic solution is reproduced:

$$Na^{+} + Al(OH)^{-}_{4(aq)} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$$
(3)

The produced caustic solution is reused in the digestion step. Solid Al(OH)₃ particles/agglomerates are classified and fine particles are reused as seed for the precipitation step to obtain a high precipitation rate. The calcination of produced aluminum hydroxide agglomerates at temperatures above 960°C yields alumina product:²

$$Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$$

$$\tag{4}$$



Figure 2: A simple flowsheet of material flow in the commercial Bayer process for alumina production.

As seen the main process byproduct is the red mud that contains significant amount of iron oxide, usually in the range 30-50% Fe₂O₃, and also significant amount of aluminum oxide, usually in the range 15-25%Al₂O₃.³ Typical chemical compositions of red muds produced from different types of bauxites (from specific regions) in the Bayer process are presented in Table I. Obviously, red mud production in the Bayer process causes a direct loss of the iron and aluminum units contained in the ore.

The Red Mud production indeed represents an environmental problem because of its alkalinity and being stockpiled/stored in holding ponds.⁴ The process residue (slurry) must be transported to the holding ponds and it has some cost for the alumina producers. The stockpiling requires special procedures to minimize the risk of red mud flooding. Red mud has shown significant negative environmental effects i.e. the red mud flooding several towns in Hungary in 2010.⁵ Moreover, red mud has alkalinity and it requires neutralization to reduce its environmental impact; decreasing PH to lower acceptable levels is necessary. This can be done through different methods such as acid neutralization, CO₂ treatment, seawater neutralization, bioleaching and sintering.⁶ However, all these processes are costly for the alumina producers.

Although there have been many research activities about red mud processing and minimizing its production, there is not still a global economic solution for red mud usage. It is worth mentioning that red mud contains rare earth elements such as Ga, Sc, Li, Rb, ... and with regard to the production of huge amount of red mud around the world, the extraction of these metals is interested.

Table I: Chemical compositions of red mud produced from different bauxite sources in dry basis (wt%)							
Bauxite source	Fe ₂ O ₃	Al ₂ O ₃	CaO	TiO ₂	Na ₂ O	SiO ₂	
Greec ^{7,8,9}	47.74	16.22	10.73	5.93	2.51	6.08	
	44.6	23.6	11.2	5.7	2.5	10.2	
	40.2	16.68	9.86	3.83	2.87	8.9	
India ⁶	35-37	18-21	2-3	17-19	5-6	6-7	
	35-36	17-19	3-5	14-16	5-6	7-9	
	44-46	19-21	1-2	17-19	3-4	5-7	
	44-47	17-20	1-3	8-11	3-5	7-9	
	40-46	18-22	1-3	3-4	4-5	12-16	
	48-54	17-20	1-2	3-4	3-5	4-6	
Australia ¹⁰	28.5	24	5.26	3.11	3.4	18.8	
	31.7	18.8	4.44	3.17	4.2	20.2	
	29.6	17.3	3.64	2.65	3.2	30.0	
	56.9	15.6	2.39	4.46	2.2	3.0	
	34.8	23.2	2.25	8.03	7.1	9.2	
	30.7	18.6	2.51	7.01	8.6	16.0	
Brazil ¹⁰	45.6	15.1	1.16	4.29	7.5	15.6	
Germay ¹⁰	44.8	16.2	5.22	12.33	4.0	5.4	
Spain ¹⁰	37.5	21.2	5.51	11.45	3.6	4.4	
USA ¹⁰	35.5	18.4	7.73	6.31	6.1	8.5	
Jamaica ¹¹	42.3	16.4	9.1	6.0	4.6	8.0	
	49.5	16.5	5.5	7.0	2.3	3.0	

PEDERSEN PROCESS

An alternative sustainable process for alumina production was patented in 1920s by Harald Pedersen¹², which was commercialized and had production of 17000 ton per year until 1969 in Høyanger, Norway. The process flowsheet is shown in Figure 3. In this process, bauxite ore is smelted with lime as the flux and is partially reduced by coke. As seen this yields pig iron due to the carbothermic reduction of the iron oxides to metallic iron, and formation of a calcium-aluminate slag, which is further hydrometallurgically treated for alumina extraction. The slag is disintegrated during cooling due to volume expanding phase change, it is then pulverized and further digested by using a sodium carbonate solution. The following main reactions occur between the calcium aluminate slag components and the solution for sodium aluminate solution formation are:

$$(CaO.Al_2O_3)_{(s)} + Na_2CO_3_{(aq)} \rightarrow Na_2O.Al_2O_3_{(aq)} + CaCO_3_{(s)}$$
(5)

$$(3CaO.Al_2O_3)_{(s)} + 3Na_2CO_3_{(aq)} \rightarrow 3Na_2O.Al_2O_3_{(aq)} + 3CaCO_3_{(s)}$$
(6)

$$(12CaO.7Al_2O_3)_{(s)} + 12Na_2CO_3_{(aq)} \rightarrow 7Na_2O.Al_2O_3_{(aq)} + 12CaCO_3_{(s)} + 10NaOH_{(aq)}$$
(7)

The non-soluble residue is separated from the produced sodium aluminate solution in the classification step, which is called grey mud. This residue can be used in production of cement, fertilizer, etc. The precipitation of aluminum hydroxide from the solution is through carbon dioxide injection, which yields also a sodium carbonate solution that is recycled to the digestion step. The precipitated Al(OH)₃ is calcined to produce alumina.



Figure 3: Flowsheet of material flow in Pedersen process for alumina production.

SINTERING PROCESS

In addition to the above processes, sintering process is also used for alumina production from bauxite. In this process, Na₂CO₃ is added to react with Al₂O₃ in bauxite at high temperatures i.e. 1000°C and water-soluble NaAlO₂ is formed. The NaAlO₂ compound in the sinter is leached by water and Al(OH)₃ is further precipitated from the solution by CO₂. The process residue contains iron and aluminum and there will be loss of these elements. Moreover, the bauxite ore contains usually some SiO₂, and in the sintering step Na₂SiO₃ is formed, which is unwanted. In practice, lime is added to the sinter to form insoluble calcium silicate compounds.

SUSTAINABILITY IN ALUMINA PRODUCTION

The Bayer process and Pedersen process were invented long time ago. The Bayer process is the dominant commercial process at present and more than 95% of alumina is produced by this method. Pedersen process was in operation in a commercial scale for 40 years and it was closed down due to economic reasons. The Pedersen process is based on the processing of laterite ores with low Al₂O₃:Fe₂O₃ ratio, while the Bayer process has serious problem for this type of ore with huge amount of red mud production and high amount of aluminum oxide loss in the residue. Pedersen process is in principle a more sustainable process compared to Bayer process with

regard to no red mud production, and production of consumable by-products; pig iron and grey mud.^{12,13, 14, 15,16} In this process the Al(OH)₃ precipitation is fast compared to Bayer process and the introduction of seed is not required.

Although the Pedersen process contains a smelting step and lime is used, which are raising the processing costs, the integrated process can be more profitable due to the production of valuable and consumable pig iron and grey mud. In addition, there is no problem with red mud production, its storing, neutralization, etc. In the smelting part of the process, coke is used and CO_2 is produced. Since, this CO_2 is collected and reused in the precipitation step, the process has low CO_2 emission. These environmental issues were not important when Pedersen process was in operation, while they are very important challenges for the society at present. These may motivate us to re-commercialize the process.

Table II: Comparison of Bayer and Pedersen process					
	Bayer process	Pedersen process			
Overall process characteristics	Hydrometallurgical	Pyrometallurgical &			
		hydrometallurgical			
Ore type	High Al ₂ O ₃ :Fe ₂ O ₃ ratio	Low Al ₂ O ₃ :Fe ₂ O ₃ ratio			
Main by-products	Red mud	Pig iron (consumable)			
	(not consumable)	Grey mud (consumable)			
Leaching conditions	Digestion by NaOH	Digestion by Na ₂ CO ₃			
	150-250°C	40-80°C			
	High pressures	Atmospheric pressure			
Al(OH) ₃ precipitation	45-80°C	70-80°C			
	48-70 hour	6-10 hour			
Electric energy consumption	Reference process	10% higher ¹⁷			
Using TiO ₂ and SiO ₂ containing ores	Reference process	More flexible			
Raw materials costs	Reference process	Higher (~ 40% in average) ¹⁷			
Process costs for unit mass of alumina	Reference process	30-50% lower ¹⁷ (more than $50%$			
		lower capital and investment costs)			

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