

## Supporting Information

# Towards Greener and More Sustainable Manufactures of Bauxite-Derived Adsorbents for Water Defluoridation

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## 1. The Bayer Process (Producing Activated Alumina)

The Bayer process is the principal industrial means of refining bauxite to produce activated alumina ( $\text{Al}_2\text{O}_3$ ). Table S1 presents an overview of principle unit operations in the Bayer Process of refining alumina from bauxite. In the digestion step, a hot solution of the recycled sodium hydroxide (caustic soda,  $\text{NaOH}$ ) is added to the ground bauxite forming a slurry. Except alumina and silica, all other components in bauxite (e.g., calcium, iron and titanium oxides) do not dissolve in the caustic soda liquor. The digestion temperature and pressure are dependent on the mineralogical composition of the bauxite. Typically, the temperature ranges between 135 and 245 °C, while the concentrations of sodium hydroxide ( $\text{NaCl}$ ) are in the region of 3.5–5.0 M.<sup>1, 2</sup> For bauxite ores containing oxyhydroxides, an elevated temperature at 170–265 °C should be used with an  $\text{NaCl}$  concentration up to 7 M.<sup>2</sup> In the clarification step, the undissolved solid impurities (so-called red mud) settle down at the bottom of the mud thickeners, and then separate from the clear liquor solution of sodium tetrahydroxoaluminate ( $\text{NaAlO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaAl}(\text{OH})_4$ ). For every tonne of alumina produced, between 0.7 and 2.0 tonnes (dry wt.) of red mud residues are produced (in the extreme, vary from 0.3 to as high as 2.5 tonnes).<sup>3</sup>

In the precipitation step, the clear liquor is pumped from the settlers to the precipitators (thickening tanks) through heat exchangers, which transfer the heat from the solution to the cold spent (processed) liquor. Precipitation of aluminum hydroxide is promoted by seeding the liquor with pure alumina crystals acting as nuclei for the precipitation process. In calcination step, the aluminum hydrate crystals are washed, dried and then heated to a temperature 1850–2300 °F (1010–1260 °C) in a rotary kiln or fluidized bed calciners to drive off the molecules of hydrated water and produce powdered, high-grade metallurgical alumina.<sup>4</sup> At 750–1110 °F (400–600 °C) chemically active low temperature  $\gamma$ - $\text{Al}_2\text{O}_3$  forms. At the temperatures above 2100 °F (1150 °C)  $\gamma$ -alumina transforms into  $\alpha$ -alumina (corundum), which is chemically inert.<sup>4</sup> The final product is a dry white anhydrous  $\alpha$ -alumina powder with the particles 0.5–10  $\mu\text{m}$ .<sup>4</sup> The main impurity of calcined alumina obtained from the Bayer process is sodium oxide ( $\text{Na}_2\text{O}$ ) concentration of which may vary between 300 to 7000 ppm.<sup>4</sup>

**Table S1.** Principle unit operations in the Bayer Process of refining alumina from bauxite

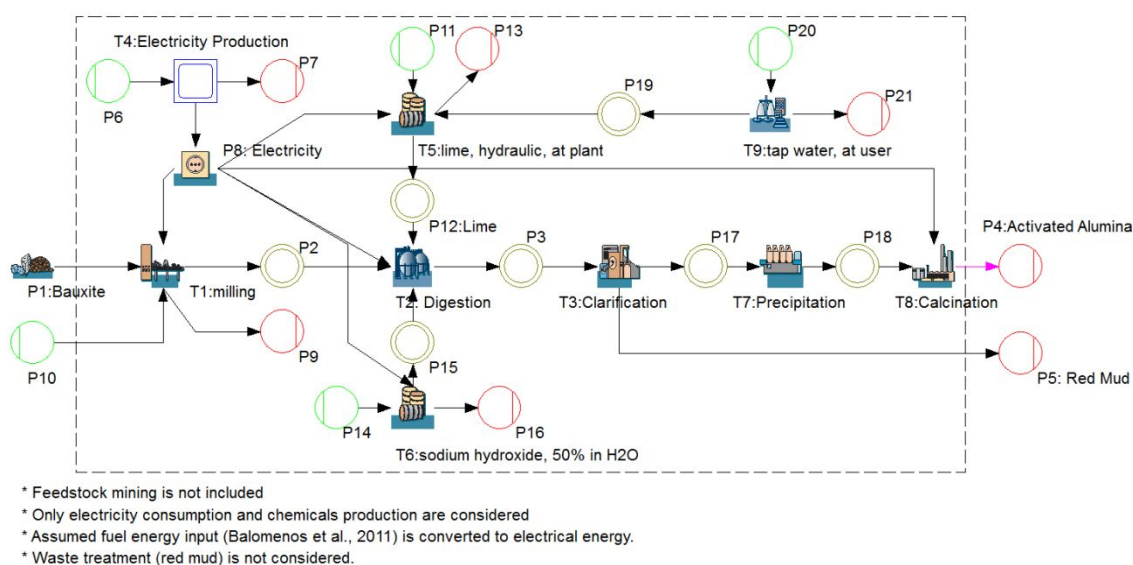
Unit	Description
Mill	Crushed and ground in mills to fine particles (max. size 1.5 mm) <sup>4</sup>
Digestion	<p><b>Duration:</b> 30–40 min <sup>5</sup></p> <p><b>Type of bauxite:</b></p> <ul style="list-style-type: none"> <li>• Gibbsite bauxites (140–150 °C under atmospheric pressure)<sup>3</sup></li> <li>• Boehmitic bauxites (220–270 °C)<sup>3</sup>, (235–250 °C)<sup>5</sup>, and (205–245 °C under atmospheric pressure)<sup>4</sup></li> <li>• Diasporic bauxites (250–280 °C at ~35 atm)<sup>3, 4</sup></li> </ul> <p><b>Formula of caustic solution:</b></p> <ul style="list-style-type: none"> <li>• Typically, 100 g bauxite per liter of Na<sub>2</sub>O pure caustic solution <sup>6</sup></li> <li>• Gibbsite bauxite (105–150 °C, 120–160 g/L) <sup>7</sup></li> <li>• Boehmitic and diasporic bauxite (220–280 °C, 180–250 g/L) <sup>7</sup></li> </ul> <p><b>Suggested operation in the literature:</b></p> <ul style="list-style-type: none"> <li>• Operated at 260 °C for 90 min with ferrous sulfate heptahydrate dosage of 50 g/L and caustic alkali concentration of 220 g/L.<sup>7</sup></li> </ul>
Clarification (Filtration)	<ul style="list-style-type: none"> <li>• Silica dissolved in the liquor is then precipitated from it by slow heating.<sup>4</sup></li> <li>• Separate undissolved solid impurities form (red mud)</li> </ul>
Precipitation	<ul style="list-style-type: none"> <li>• Clear liquor is pumped from the settlers to the precipitators (thickening tanks) through heat exchangers.</li> <li>• Seeding the liquor with pure alumina crystals at 60 °C</li> <li>• The coarser particles are separated from the fine particles and transferred to calcination, while the finer particles are filtered from the slurry and then used as seeding (nuclei) crystals.</li> <li>• 90% of aluminum hydrate is recovered from the liquor. <sup>4</sup></li> </ul>
Calcination	<ul style="list-style-type: none"> <li>• Aluminum hydrate crystals are washed and dried</li> <li>• Heated to a temperature 1850–2300 °F (1010–1260 °C) in a rotary kiln or fluidized bed calciners.<sup>4</sup></li> <li>• Energy consumption: 4 GJ/tonne <sup>a</sup> at a cost of \$0.03/GJ. <sup>5</sup></li> </ul>

<sup>a</sup> Assumed 1 million tonne/year alumina refinery

## 2. Scenario Set-up

### 2.1 Activated Alumina Adsorbent Produced from The Bayer Process (Bayer-AA)

Figure S1 shows the system boundary for the Bayer process used in the LCA in this study. In a typical Bayer process, the principle units include digestion, clarification (filtration), precipitation and calcination. The operations of digestion are largely dependent upon the form of the aluminium minerals present in the bauxite and varies considerably throughout the world. However, both precipitation and calcination steps are relatively similar the world over. Depending upon the quality of the ore, about 1.9–3.6 tonnes of bauxite is required to produce one tonne of alumina ( $\text{Al}_2\text{O}_3$ ) through the Bayer process.<sup>2</sup>



**Figure S1.** System boundary of manufacturing activated alumina from the Bayer process (Bayer-AA), including bauxite ore milling, digestion, clarification, precipitation and calcination.

In this study, the data of the Bayer process used in the LCA was gathered from Balomenos et al.<sup>8</sup> as summarized in Table S2. The digestion step in the Bayer process was assumed to be operated at 140–300 °C and 3.5 MPa, while the calcination was at 1,100 °C. According to their report, the Bayer process requires a total of 24.6 MJ energy for heating to produce one kilogram of alumina, which is supplied through fuel burning.<sup>8</sup> The negative effect of the organic matter on the Bayer process during the gibbsite precipitation stage was not considered in the LCA.



Table S3 presents the inventory data of the MPB process used in the LCA. An industrial low-temperature oven (Model E1, Electric Hot Box, Sahara) was used for raw bauxite drying. The oven possesses a bench treatment capacity of 455 kg with a power consumption of 3.6 kW.

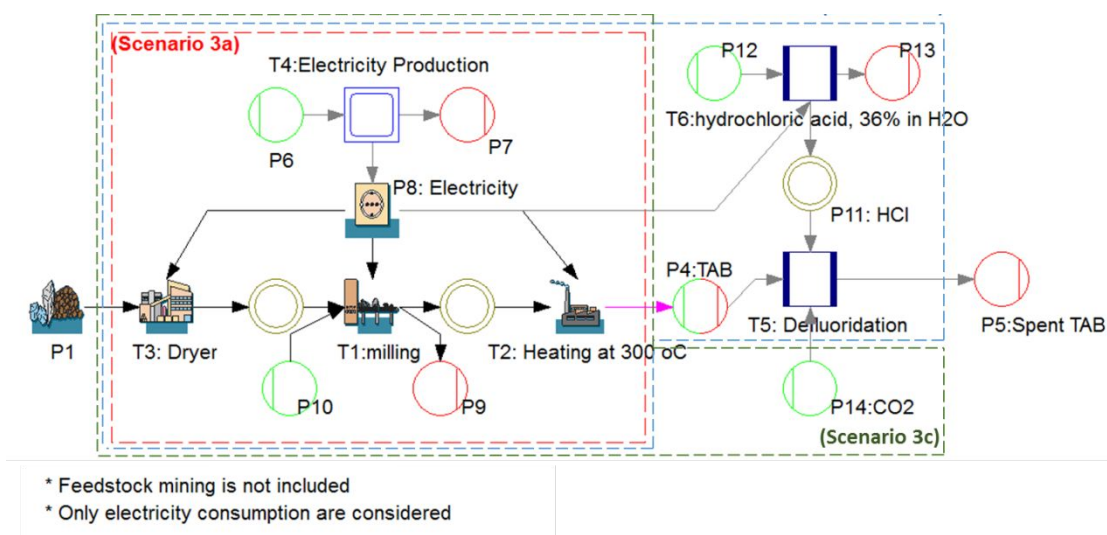
**Table S3.** Data inventory of the MPB Process in the LCA.

Unit	Description
Dried	<ul style="list-style-type: none"> <li>Assumed a bench treatment capacity of 455 kg ground bauxite in a low-temp oven (Model E1, Electric Hot Box, Sahara)</li> <li>Energy consumption at 100 °C for 1 hr: 0.0079 kWh per kg of ground bauxite</li> </ul>
Milling	<ul style="list-style-type: none"> <li>Energy consumption: 0.356 kWh per kg of bauxite</li> </ul>

<sup>a</sup> The density of bauxite was assumed to be 3.0 g/cm<sup>3</sup>.

### 2.3 Adsorbent Produced from The TAB Process with Combinatorial Treatment for Defluoridation

Figure S3 shows the system boundary of the TAB process, including bauxite ore drying, milling and thermal treatment, for manufacturing adsorbents.



**Figure S3.** System boundary of the TAB process, including bauxite ore milling, thermal and acid treatment.

Table S4 presents the inventory data of the TAB process used in the LCA. The ground bauxite was dried, milled and then went through the thermal treatment at 300 °C using a mechanical convection standard oven. The specification of the low-temperature oven for 1-hr dried at 100 °C was consistent to that used in the MPB scenario. For thermal treatment at 300 °C, an oven (Model

146, Blue M, Thermal Product Solutions) possesses a bench treatment capacity of 0.453 m<sup>3</sup> (~1360 kg) with a power consumption of 3.0 kW. We assumed an 80% of interior volume usage in the oven (e.g., ~1,085 kg per bench treatment).

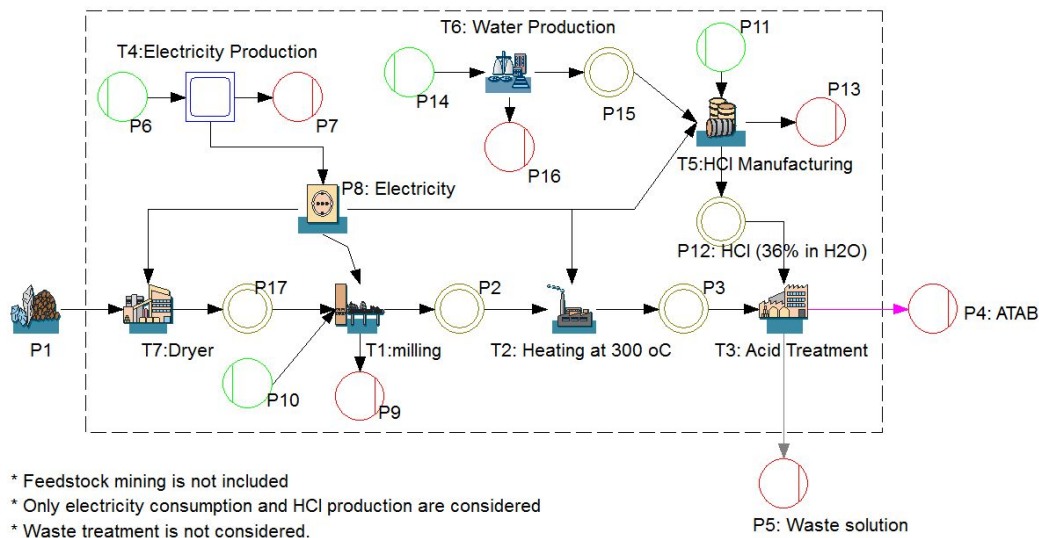
**Table S4.** Data inventory of the TAB Process in the LCA.

Types	Unit	Description
Manufacturing	Dried	<ul style="list-style-type: none"> <li>Assumed a bench treatment capacity of 455 kg ground bauxite in a low-temp oven (Model E1, Electric Hot Box, Sahara)</li> <li>Energy consumption at 100 °C for 1 hr: 0.0079 kWh per kg of ground bauxite</li> </ul>
	Milling	<ul style="list-style-type: none"> <li>Energy consumption: 0.356 kWh per kg of bauxite</li> </ul>
	Thermal treatment	<ul style="list-style-type: none"> <li>Energy consumption at 300 °C for 4 hr: 0.0691 kWh per kg of ground bauxite <sup>a</sup></li> <li>A bench treatment capacity of 1,085 kg ground bauxite</li> </ul>
Combinatorial defluoridation	None	<ul style="list-style-type: none"> <li>Direct defluoridation without acidification of groundwater</li> </ul>
	HCl	<ul style="list-style-type: none"> <li>Acidification by 1.1 M HCl to maintain pH at 6.0</li> <li>Dose: 211 mg HCl per liter of water</li> </ul>
	CO <sub>2</sub>	<ul style="list-style-type: none"> <li>Acidification by pressurized CO<sub>2</sub> to maintain pH at 6.0</li> <li>Empirical dose: 22.5 g-CO<sub>2</sub> per liter of water</li> <li>Theoretical dose at an open system: 0.46 g-CO<sub>2</sub> per liter of water</li> </ul>

<sup>a</sup> The density of bauxite was assumed to be 3.0 g/cm<sup>3</sup>.

## 2.4 Adsorbent Produced from The ATAB Process

Figure S4 shows the system boundary for the ATAB process, including bauxite ore drying, milling, thermal activation, and acid treatment.



**Figure S4.** System boundary of the ATAB process, including bauxite ore milling, thermal and acid treatment.

Table S5 presents the inventory data of the ATAB process used in the LCA. The ground bauxite was first dried, milled, and then went through the thermal treatment at 300 °C. The specification of the ovens for drying (100 °C) and thermal activation (300 °C) was consistent to that used in the scenarios of MPB and TAB. The thermally activated bauxite was further treated with 5 M HCl at room temperature. After the entire processes of synthesis, an 83% mass recovery of raw bauxite was achieved, where the remaining became waste solution

**Table S5.** Data inventory of the ATAB Process in the LCA

Unit	Description
Dried	<ul style="list-style-type: none"> <li>Assumed a bench treatment capacity of 455 kg ground bauxite in a low-temp oven (Model E1, Electric Hot Box, Sahara)</li> <li>Energy consumption at 100 °C for 1 hr: 0.0079 kWh per kg of ground bauxite</li> </ul>
Milling	<ul style="list-style-type: none"> <li>Energy consumption: 0.356 kWh per kg of bauxite</li> </ul>
Thermal treatment	<ul style="list-style-type: none"> <li>Assumed a bench treatment capacity of 1,085 kg ground bauxite in an oven (Model 146, Blue M, Thermal Product Solutions)</li> <li>Energy consumption at 300 °C for 4 hr: 0.0691 kWh per kg of ground bauxite<sup>a</sup></li> </ul>



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Acid treatment	<ul style="list-style-type: none"> <li>• Hydrochloric acid (36% in H<sub>2</sub>O) from reacting propylene and chlorine at plant</li> <li>• 5 M HCl was added to thermally-treated bauxite at a ratio of 23.3</li> </ul>
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<sup>a</sup> The density of bauxite was assumed to be 3.0 g/cm<sup>3</sup>.

### 3. Cost and Benefit Analyses

#### 3.1 Prices of Materials and Chemicals

The material costs of crude-dry bauxite and commercial activated alumina (AA) filter media are assumed to be 0.03 USD/kg<sup>9</sup> and 1.5 USD/kg,<sup>10</sup> respectively, according to current market prices. For the free alongside ship (f.a.s.) for U.S. imports, the average price for consumption of metallurgical-grade alumina in 2017 was about 456 USD/tonne, and ranged between 395 and 576 USD/tonne.<sup>9</sup> This was 34% higher than that of the same period in 2016. Table S6 presents the average prices of other chemicals including limestone, sodium hydroxide and hydrochloric acid.

**Table S6.** Average prices of limestone, sodium hydroxide and hydrochloric acid.<sup>11</sup>

Item	Location	Description	Prices (USD/kg)
Limestone	Malaysia	Crushed limestone, 1-2 mm, density: 1.76-2.16	0.01–0.02
Sodium Hydroxide	Jinhong Weibang Corp., China	Caustic soda solid, 99% purity, industrial grade	0.30–0.33
Hydrochloric Acid	Hebei, China	31-37% HCl liquid, industrial grade. Assumed 31%=9.86 M.	0.25–0.27

### 3.2 Summary of Cost Benefit Analyses

For achieving the same service (remediating one tonne of water), Table S7 presents the inventory data of each scenario in terms of manufacturing costs and potential profits from carbon offsets.

**Table S7.** Inventory of each scenario for achieving the same service (remediating one tonne of water).

Item	Unit	Bayer-AA	MPB	TAB	ATAB
<i>Manufacturing costs</i>					
<b>Dose of adsorb.</b>	<b>kg/service</b>	<b>4.0</b>	<b>22.8</b>	<b>13.6</b>	<b>1.5</b>
Electricity (per kg)	kWh/kg	4.95	0.36	0.43	0.56
<b>Net electricity (A)</b>	<b>USD/service</b>	<b>1.34</b>	<b>0.56</b>	<b>0.40</b>	<b>0.05</b>
Bauxite input	kg/kg	2.65	1.01	1.18	1.20
<b>Net bauxite (B)</b>	<b>USD/service</b>	<b>0.08</b>	<b>0.03</b>	<b>0.04</b>	<b>0.04</b>
Chemicals (per kg)					
Limestone	kg/kg	0.03	-	-	-
NaOH	kg/kg	2.65	-	-	-
Water	kg/kg	6.00 <sup>a</sup>	-	-	-
HCl (31%)	kg/kg	-	-	-	11.4 <sup>c</sup>
<b>Net chemical (C)</b>	<b>USD/service</b>	<b>3.50</b>	<b>-</b>	<b>-</b>	<b>4.26 <sup>c</sup></b>
<b>Net direct costs (D)=(A)+(B)+(C)</b>	<b>USD/service</b>	<b>4.92</b>	<b>0.59</b>	<b>0.44</b>	<b>4.35</b>
<i>Benefits</i>					
Carbon footprint	kg/service	10.0	4.2	3.0	0.4
Carbon emissions fee	USD/service	0.145	0.061	0.044	0.006
<b>Carbon offsets (E)</b>	<b>USD/service</b>	<b>- (baseline)</b>	<b>0.085</b>	<b>0.105</b>	<b>0.145</b>

<sup>a</sup> The cost of water was not considered in the analysis. <sup>b</sup> Assumed the activated alumina price is 1.5 USD per kg. <sup>c</sup> Assumed a scale factor of 0.8 (in accordance with standard chemical engineering practice for scaling up)<sup>12</sup> for HCl use from 3 g capacity to 1 kg capacity.

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