

Enhancing the Sustainability of Alumina Refineries: Exergy Insights from Process Simulation

Eleni Mikeli¹, Efthymios Balomenos² and Dimitrios Panias³

1. PhD Candidate

2. Asst. Professor

3. Professor

National Technical University of Athens - Laboratory of Metallurgy, School of Mining
Engineering and Metallurgy, Zografu, Greece
Corresponding author: elenamikeli@mail.ntua.gr
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Abstract

The Bayer process is the dominant industrial method for alumina production, but it is highly energy-intensive, with significant thermodynamic inefficiencies and exergy losses occurring throughout the process. This study presents a simulation-based exergy analysis of a full-scale Bayer refinery, the key focus is on identifying the most exergy-intensive subprocesses, particularly in thermal and chemical exergy utilization. Beyond a base case analysis, scenario simulations are conducted by varying key process parameters to assess their impact on overall exergy efficiency and sustainability. This simulation-based approach enables a systematic evaluation of how process modifications can enhance energy efficiency, reduce waste heat losses, and improve the overall sustainability of alumina refining. The model's flexibility allows for its application across different refinery configurations, making it a valuable tool for optimizing alumina production in line with circular economy principles and also rigorously permits an allocation of impacts of all flows, products, residues etc.

Keywords: Bayer process, Exergy analysis, Sustainability, Process simulation, Energy efficiency.

1. Introduction

Developed in the 19th century, the Bayer process remains the predominant industrial method for alumina production worldwide, with more than 95 % of global alumina produced through this method [1]. Despite its robustness and industrial maturity, the Bayer process is notably energy intensive. Bayer process requires high-pressure steam for heating and combustion burners for the calcination of the hydrated alumina, both of which rely mainly on fossil fuel energy. Overall alumina refineries have a significant share of energy demand and contribute to the 1–2 % of the global greenhouse gas (GHG) emissions [2].

Sustainability efforts in the alumina sector have traditionally focused on energy reduction, residue management, and emissions control. Núñez and Jones [3], identified digestion and calcination as the most environmentally burdensome stages of the Bayer process, together accounting for more than 70 % of the process's total cumulative energy demand and global warming potential. Similarly, Guinoa et al. [2] disaggregated environmental impacts and demonstrated that calcination and digestion are responsible for up to 77 % of CO₂-equivalent emissions. In the specific refinery configuration modelled, which was based on natural gas combustion, fuel related emissions alone accounted for over 65 % of the total site emissions. Furthermore, bauxite mineralogy and transportation logistics emerge as critical sensitivity factors, with up to 51 % variance in emissions based solely on ore type and energy mix. While Life Cycle Assessments (LCAs) can provide valuable insights into the environmental impacts of alumina production, it does not explain the underlying thermodynamic causes of inefficiency and cannot pinpoint where

improvements can be most effectively applied. On the other hand, exergy analysis, grounded in the second law of thermodynamics, offers a complementary perspective by quantifying the quality and usability of energy and material flows throughout a system. Unlike traditional energy accounting, exergy assessment distinguishes between useful work potential and irrecoverable losses, thus providing deeper insights into process inefficiencies [4]. This methodology has the potential to bridge gaps in environmental assessments by translating energy consumption into thermodynamic impact, thereby enabling more targeted strategies for improving sustainability. Exergy analysis evaluates the quality of energy and its degradation within a system, offering a complementary perspective to LCA.

In this study the exergy analysis is used to identify the inefficiencies in the Bayer process and assess how the process variations affect sustainability performance. A full-cycle Bayer simulation model is developed in the HSC Chemistry software. Initially a baseline model is calculated, to identify the major exergy demands of the Bayer process. A sensitivity analysis is also conducted for the digestion stage, where the effect of the digestion temperature and caustic addition is evaluated in terms of alumina extraction rate compared to exergy efficiency. The goal of this work, is to support more energy-efficient, lower-emission, and circular approaches within the alumina industry, aligning with broader goals of industrial decarbonization and resource optimization.

2. Methodology

2.1 Concept of Exergy Analysis

The concept of exergy analysis is based on the second law of thermodynamics, which states that in every real (irreversible) process a part of “the quality of the energy” is destroyed, meaning that the ability of the specific system to produce useful work is reduced. The useful part of the energy of the system, hence the part of energy that can be transformed into useful work (of any type), is defined as exergy [4].

An exergy analysis includes a detailed analysis of the energy and materials flows of the system/process under consideration, to identify the sources of exergy destruction and loss. In practice, an exergy analysis involves the identification and quantification of all input and output streams, as well as the determination of their exergy values using appropriate thermodynamic data. For any chemical process an exergy balance can be calculated using the Equation (1).

$$E_{input} = E_{useful\ products} + E_{output\ wastes} + E_{distruction} \quad (1)$$

In an exergy balance the input exergy (E_{input}) is always greater than the output exergy, which is the sum of the exergy values of the useful ($E_{useful\ products}$) and waste output (E_{wastes}) of the process, as a result of the second law of thermodynamics (2LT).

The calculation of exergy requires the use of reference environment conditions for the determination of the exergy potential of a substance or stream. Essentially, the exergy potential of a substance or a stream is the maximum amount of useful work that could be potentially released if the substance or stream reach thermodynamic equilibrium with the reference environment (dead state). Or vice versa, exergy potential is the minimum input work required for the production of the substance or stream from the reference environment. In processes where the external energy (kinetic and potential) is insignificant, the exergy of a substance or stream can be calculated by the sum of thermal and chemical exergy (Equation (2)) [4].

$$E_{stream,total} = E_{ph} + E_{ch} \quad (2)$$

where physical exergy (ph) is associated with the temperature and pressure of a substance or stream and chemical exergy (ch) is associated with the chemical potential of the substance or stream. The physical exergy is the amount of useful work when the substance comes to environmental state (Equation (3))

$$E_{ph} = [H_i - H_0] - T_0[S_i - S_0] \quad (3)$$

where H_i , and S_i are the total enthalpy and entropy of the species at a temperature T_i and H_0 , S_0 are the enthalpy and entropy of the species in standard state accordingly.

The chemical exergy is the maximum amount of useful work that can be obtained when a system is placed at a temperature of T_0 and pressure p_0 to achieve a chemical equilibrium with the environment (Equation (4).), where $T_0 = 25 \text{ }^\circ\text{C}$ and $p_0 = 1 \text{ bar}$.

$$E_{ch} = \sum n_k b_{k,ref} + \Delta G_f^0 \quad (4)$$

Where n_k is the stoichiometric amount of element k in the species, $b_{k,ref}$ the elemental exergy of element k in the reference environment and ΔG_f^0 is the free Gibbs energy of formation of the species.

Based on the above-mentioned equations, the exergy amount of every process stream (material, thermal energy, electricity) can be calculated. For the scope of this study, electric exergy was considered equivalent to the electric energy. The reference state environment was considered in standard state ($p_0 = 1 \text{ atm}$ and $T_0 = 25 \text{ }^\circ\text{C}$). All thermodynamic data and thermodynamic calculations were performed using HSC 10 software [5]. Where chemical compositions of streams were not available due to lack of data, compositions were estimated with thermodynamic tools (like HSC 10, Metso Outotec) based on basic assumptions. The exergy destruction and loss in each process step is then calculated, along with the exergy efficiency of the system (Equation (5)).

$$n_{ex} \% = 100\% \frac{\text{Exergy of input products}}{\text{Input Exergy}} \quad (5)$$

Where the feeding exergy is the sum of all the exergy constituents entering the system under consideration and the exergy of useful products is the sum of all the exergy constituents of the products of the system.

The results of the analysis provide valuable insights into the thermodynamic limitations of the system, and can be used to optimize energy use, reduce emissions, and improve the overall performance of the process.

2.2 Modelling the Bayer Process

The Bayer process comprises digestion, clarification, precipitation, and calcination. High-pressure steam and fossil fuel combustion are integral to digestion and calcination, making these units focal points of energy inefficiency. A full-cycle simulation of the Bayer process was developed using HSC Chemistry software and the snapshot of this model is presented in Figure 1. This model integrates a cogeneration power plant for provision of steam and includes all major process units. Exergy balances were constructed using thermodynamic properties calculated through HSC's database. Sensitivity analysis was performed on key digestion parameters: temperature, caustic ratio (A/C).

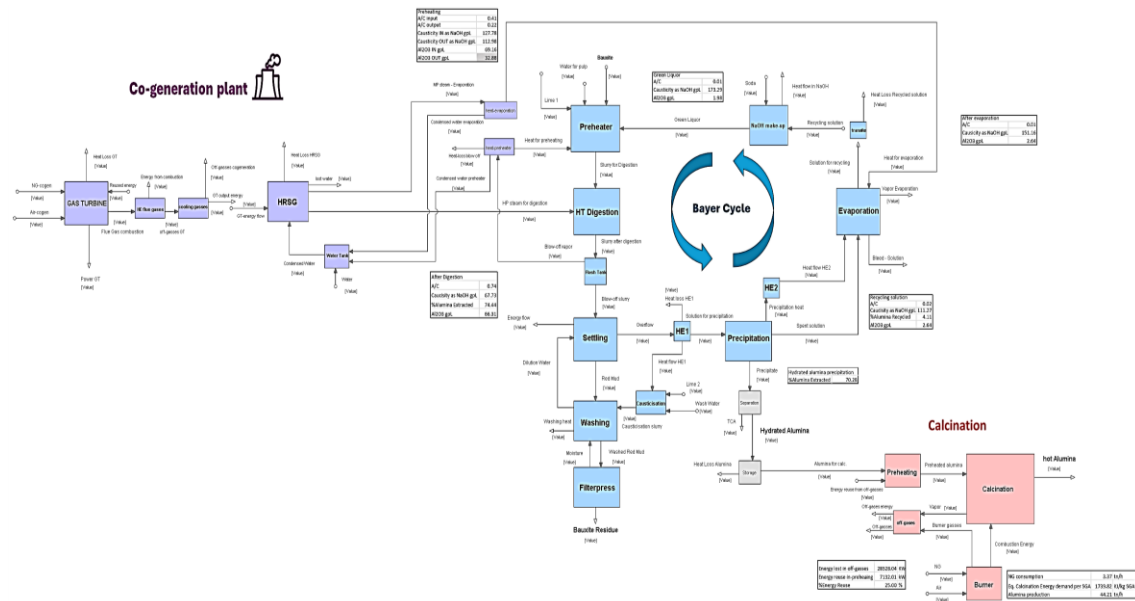


Figure 1. HSC software model: cogeneration plant (purple); Bayer (blue); alumina calcination (red).

The process parameters used to build the baseline model are listed in Table 1, the values for these parameters were taken from literature [6].

Table 1. Basic parameters for the baseline model of the complete Bayer process.

Unit operation	Parameter	Value
Preheating	Temperature	95 °C
	pulp density	5 wt % Bauxite
	NaOH solution	A/C = 0.4
	CaO addition	5 %wt. of bauxite ore
Digestion	direct steam injection	250 °C, 40 bar
Precipitation	Temperature	60 °C
Evaporation	indirect steam use	150 °C, 5 bar
Calcination	NG burner	
	Temperature	1000 °C

3. Results

3.1 Exergy Balance of Baseline Process

The mass and exergy balances focused on the Bayer cycle were calculated using the baseline conditions and are presented in Figure 2 as a function of 100 tonnes of Bauxite ore treatment.

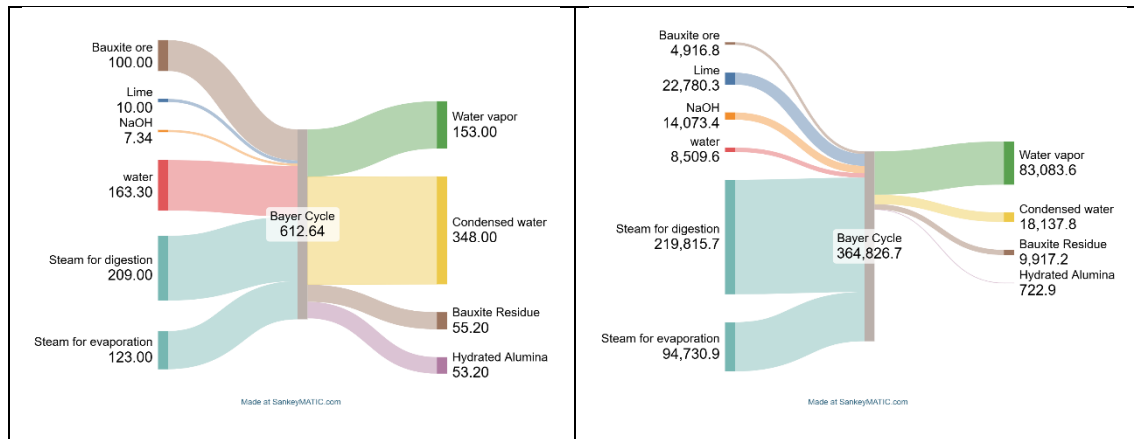


Figure 2. (a) Mass balance and (b) Exergy balance of the Bayer process using the baseline parameters expressed in tonnes and MJ accordingly.

The mass and exergy flow data of the baseline Bayer model reveal important insights into the system's thermodynamic performance and inefficiencies. The exergy input is overwhelmingly carried by steam, particularly the digestion steam, which alone accounts for 220 GJ per 100 t of Bauxite ore treatment, or 63 % of total exergy input.

Based on this data, an approximate exergy efficiency can be calculated less than 1 %. This illustrates the extremely low exergy yield, consistent with literature that reported exergy efficiencies below 3 % [7]. Balomenos et al. provided a comprehensive exergy-based review of the aluminium value chain and reveal that the Bayer process has an exergy efficiency of just 2.94 % [7]. Water vapor and condensate water, totalling ~101 221 MJ, represent large exergy carriers leaving the system without being recovered, indicating major waste heat losses. Bauxite residue carries away ~9 917 MJ, a non-negligible amount (~2.7 %) of the input exergy. Most of the input exergy is destroyed irreversibly, likely through heat dissipation and chemical irreversibilities, which occur mainly during the high-pressure steam condensation during digestion procedure. The model does not take into account the work spent for growing the particle size of the hydrated alumina crystals during the precipitation, which would increase the exergy efficiency of the process.

3.2 Sensitivity Analysis in the Digestion Procedure

To understand the impact of operational conditions during the digestion stage of the Bayer cycle, a sensitivity analysis was carried out, assuming the system described in Figure 3. Two key parameters were varied: digestion temperature and the caustic concentration (A/C ratio). The input streams for this analysis were the raw materials (Bauxite ore, lime and caustic soda) and the caustic solution that is typically recirculated within the Bayer process. The heating for the digestion was supported by high-temperature steam and for the preheating stage, heat from the autoclave's blow-off steam was utilized. The final product of the system was assumed the digested slurry.

The results of exergy calculations for each individual stage of the digestion procedure of the Bayer process using the baseline parameters, are illustrated in the Sankey format in Figure 4.

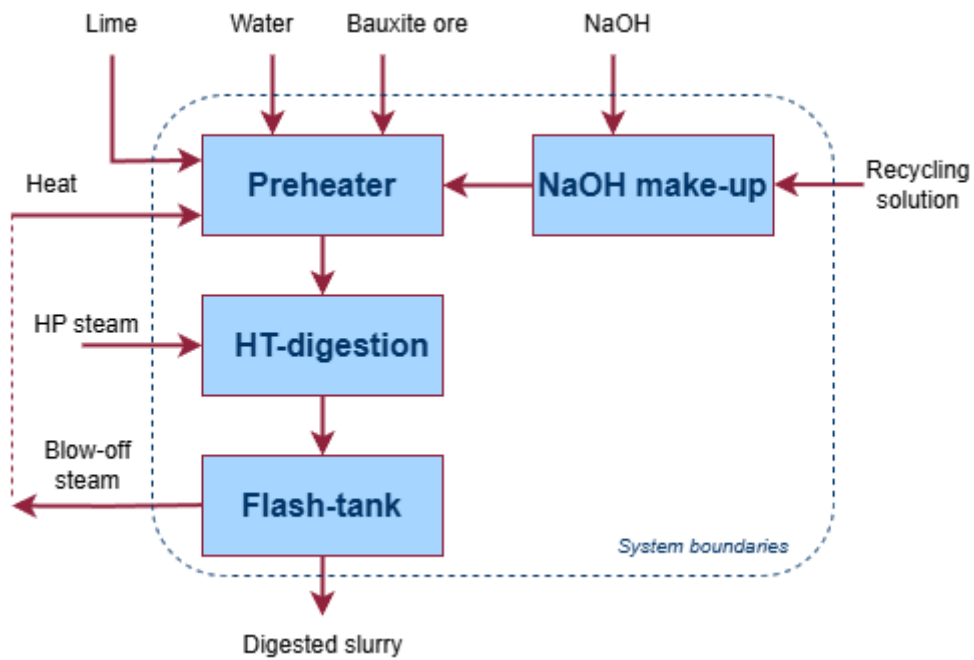


Figure 3. System boundaries for the analysis of Bayer digestion stage.

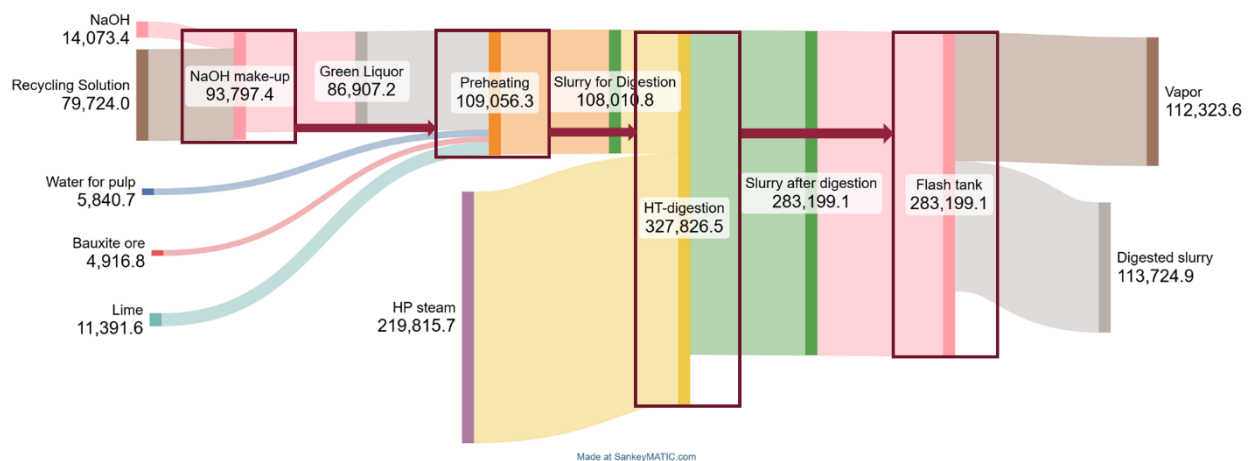


Figure 4. Sankey diagram representing the exergy balance during the individual process of the digestion stage of the Bayer process.

From the exergy balance, it is interpreted, that the steam is the largest single exergy input ($ex_{\text{steam}} = 65.5\%$), significantly outweighing the chemical exergy of raw materials ($ex_{\text{raw materials}} = 34.5\%$). This underscores that thermal input, not raw materials, is the primary energy quality carrier in digestion. The exergy efficiency is calculated 33.5 % where most of the exergy in the digested slurry is allocated to the production of the sodium aluminate phases. Moreover 16 % of the exergy destruction occurs after the digestion stage and 17 % in the flash tank, due to irreversible reaction like dilution and pressure drop. Finally, 33.5 % of exergy is lost in the sensible heat of the vapor.

3.2.1 Impact of Digestion Temperature

The sensitivity analysis illustrates the impact of digestion temperature (190–280 °C) on three key performance indicators: alumina extraction efficiency (%Al₂O₃ recovered), live steam demand,

and exergy efficiency ($n_{ex\%}$). As shown in the Figure 5, alumina extraction increases steadily with temperature, rising from 50 % at 190 °C to 87 % at 280 °C. This aligns with thermodynamic expectations: higher temperatures accelerate the dissolution of alumina-bearing minerals, particularly boehmite and diasporic ores. However, this benefit comes at a cost. Live steam demand (measured in Nm^3) rises sharply with temperature, more than tripling over the same range. This is because raising the digestion temperature requires injecting significantly more high-pressure steam, which carries high thermal exergy. This increased demand results in pronounced thermodynamic penalties. Consequently, exergy efficiency ($n_{ex\%}$) declines with temperature, falling from ~48 % at 190 °C to below 30 % at 280 °C. This inverse trend reflects growing exergy destruction, primarily due to higher thermal gradients, unutilized sensible heat, and larger vapor losses. The trade-off is clear: while higher temperatures improve process yield, they significantly degrade thermodynamic performance.

From a sustainability standpoint, this analysis underscores the need to balance yield improvements with energy quality losses. Strategies such as heat integration, steam cascading, or even partial electrification may be required to decouple extraction efficiency from thermal exergy destruction. In this context, technologies such as mechanical vapor recompression (MVR) and industrial heat pumps offer promising opportunities. MVR, already proven in evaporation systems, can be applied in digestion to recover and reuse low-pressure blow-off steam, significantly reducing the need for fossil-based high-pressure steam. As noted by Scarsella and Gasafi [8], a modern alumina refinery may lose up to 40–100 t/h of blow-off steam, and MVR can recover a meaningful portion of this using electrically driven centrifugal blowers, especially if powered by renewable energy. Similarly, industrial heat pumps offer potential for recovering low-grade waste heat and upgrading it to usable process temperatures, enabling steam savings in preheating or liquor conditioning stages. Both technologies can reduce exergy destruction while supporting electrification and decarbonisation goals without compromising process performance.

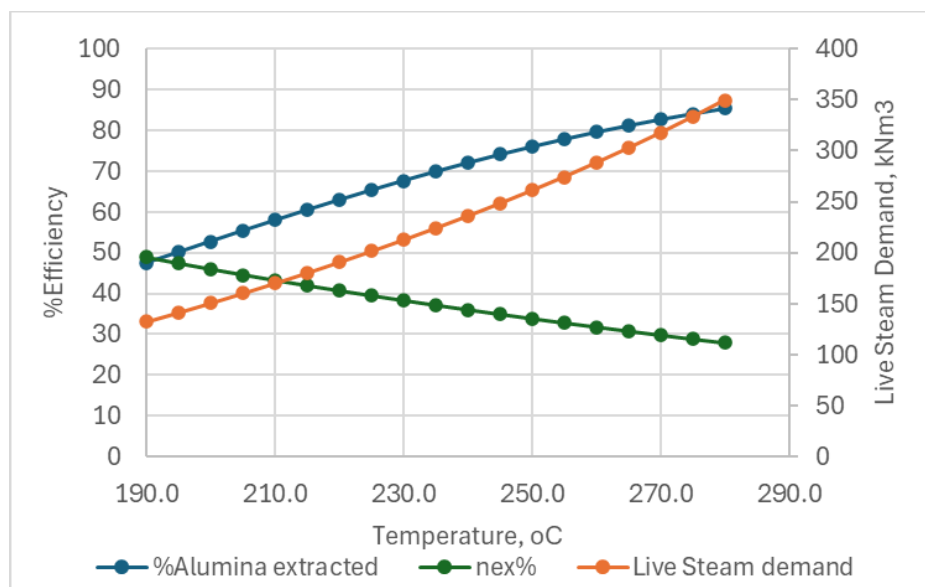


Figure 5. Live steam demand, exergy efficiency and alumina extraction rate as a function of digestion temperature.

3.2.2 Impact of A/C Ratio

Figure 6 illustrates the effect of varying the Alumina-to-Caustic (A/C) mass ratio on process performance indicators, including the alumina extraction efficiency (% Al_2O_3 recovered), live steam demand, exergy efficiency ($n_{ex\%}$) as well as the absolute demand in raw material exergy

($ex_{\text{raw materials}}$) and exergy of steam (ex_{steam}). As the A/C ratio decreases from 0.44 to 0.32, alumina extraction increases from 72 to 86 %. This reflects the increased solubility of alumina in the digestion liquor as caustic concentration increases. A low A/C means more NaOH per unit of alumina, favouring the digestion and increasing the yield.

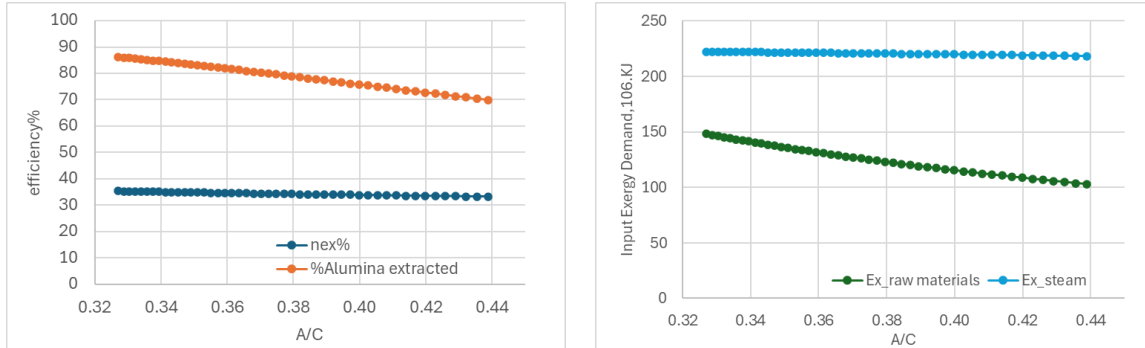


Figure 6. (a) Exergy efficiency and alumina extraction rates and (b) exergy demand in raw materials and live steam as a function of A/C ratio (caustic addition).

Even though the decrease of A/C in higher alumina extraction yields, the overall exergy efficiency is slightly affected. The decrease of A/C ratio is highly affected by rising the chemical exergy demand, reflecting mainly to the change of NaOH demand. This indicates that while material input may increase, the process becomes less effective at converting exergy into useful product.

4. Conclusions

This study presents a comprehensive simulation-based exergy analysis of the Bayer process, with particular focus on the digestion stage which is the most energy and exergy intensive unit operation in alumina production. By quantifying both material and energy flows and conducting targeted sensitivity analyses, this work identifies the fundamental thermodynamic inefficiencies that constrain the sustainability of the process. The key findings include:

- Extremely low overall exergy efficiency (> 1 %) in the baseline process, confirming literature reports that the Bayer cycle remains one of the least exergy-efficient metallurgical processes despite its industrial maturity.
- Steam for digestion dominates exergy input, accounting for over 60 % of the system's total exergy. Most of this is lost as low-grade vapor, underscoring the need for thermal integration or alternative heating strategies.
- Digestion sensitivity to temperature reveals a strong trade-off: higher temperatures improve alumina yield but sharply degrade exergy efficiency and significantly increase live steam demand. Steam demand is one of the primary drivers of global warming potential (GWP) in alumina production, as the live steam used in digestion is typically generated by fossil fuel combustion. As digestion temperature increases, so does steam consumption, and with it, the associated CO₂ emissions increase as well. This emphasizes the importance of process optimization that balances thermodynamic efficiency with extraction performance.
- A/C ratio analysis shows that reducing caustic concentration leads to lower chemical input but also lower recovery efficiency and unchanged steam demand, resulting in declining exergy performance. Without adjusting thermal input accordingly, the process becomes less sustainable despite reduced reagent use.

These results validate exergy analysis as a critical complement to environmental assessments such as LCA. While LCA highlights impact hotspots, exergy reveals why those hotspots exist and where process-level improvements can be most effective. Overall, the work demonstrates that advancing the sustainability of alumina refining requires more than just reducing emissions or reagent use. It requires addressing the underlying thermodynamic drivers of inefficiency, and exergy analysis provides the framework to do that. The developed simulation model can be used as a diagnostic and optimization tool for existing refineries and can support the design of more circular, energy-efficient, and decarbonized alumina production systems.

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