# Thermodynamics and Kinetics of Leaching High Alkali Red Mud with Dilute Sulfuric Acid

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## Abstract



This study conducted an in-depth analysis of the thermodynamic and kinetic characteristics during the sulfuric acid leaching process of high-alkali red mud, aiming to optimize leaching parameters for efficient recovery of valuable components. Thermodynamic analysis revealed that the Gibbs free energy change ( $\Delta G_T^\circ$ ) for $Fe_2O_3$ and $Al_2O_3$ leaching reactions increases with rising temperature, inhibiting their dissolution, whereas the $\Delta G_T^\circ$ values for $Na_2O$ and CaO decrease with temperature elevation, indicating enhanced leaching efficiency for these two components. Specifically, the $Fe_2O_3$ leaching reaction becomes non-spontaneous above 309 K, while $Na_2O$ demonstrates the strongest leaching tendency and would be preferentially extracted. By controlling temperature and pH in the leaching system, selective extraction of components can be optimized. For instance, $Na_2O$ can be individually leached at temperatures exceeding 323 K with pH maintained between 4.0 to 7.0. Kinetic analysis showed that sulfuric acid reacts completely with most sodium-containing compounds in red mud within 10 minutes at 298 K or 5 minutes at 323–348 K, achieving sodium leaching rates approaching 99 %. Model fitting indicated that the leaching process is predominantly controlled by mixed mechanisms involving both internal diffusion and chemical reactions, with the optimal kinetic function described as 1/3ln(1-x)-1+(1-x)-1/3. The calculated apparent activation energy of 12.07 kJ/mol further corroborated this conclusion. This research provides theoretical foundations for efficient high-alkali red mud leaching and contributes to promoting its sustainable utilization in industrial applications.

**Keywords:** High alkali red mud, Dilute sulfuric acid leaching, Leaching thermodynamics, Leaching kinetics.

## 1. Introduction

Red mud, an alkaline byproduct generated during the bauxite refining process, exhibits a high pH ranging from approximately 10 to 12.5 [1]. It contains substantial concentrations of heavy metals (e.g., Cd and Cr), radioactive elements (including Th, Hf, U, and rare earth elements), as well as fluorides[1–11]. Owing to its elevated alkalinity and heavy metal content, the stockpiling of red mud not only requires extensive land occupation but also poses environmental risks due to the leaching of contaminants, which can adversely affect surrounding soil and groundwater [12, 13]. Acid neutralization, as one of the most common methods for red mud alkali removal, is characterized by high solid-liquid separation efficiency and thorough alkali removal. Under appropriate conditions, the dealkalization rate can exceed 95 %. However, this method consumes a significant amount of acid, making the identification of suitable waste acids to reduce costs or the recovery of valuable elements critical for its efficient industrial application [14].

This study addresses the challenge of strong alkalinity in red mud from current alumina industrial production systems. By utilizing titanium white waste acid as a neutralizing agent for red mud and calcium-based salts as auxiliary additives in the acid leaching dealkalization process, it achieves directional regulation of silicate and metal ion dissolution and migration behaviours. The research provides theoretical and technical support for the comprehensive utilization of red mud, thereby helping to resolve the environmental pollution and safety issues caused by red mud in aluminium smelting. Meanwhile, this study is dedicated to an in-depth thermodynamic analysis of the leaching process, aiming to establish a solid theoretical foundation for leaching experiments and elucidate the response mechanisms of leaching reactions to variations in solution composition and environmental conditions. Through systematic investigation of these thermodynamic properties, we can precisely guide experimental design and optimize operational parameters. The ultimate objectives are to enhance leaching efficiency while minimizing energy consumption and environmental impact, thereby contributing to more sustainable and environmentally friendly industrial production practices.

## 2. Computational Analysis and Research Methods

### 2.1 Thermodynamic Calculation

The branch of thermodynamic analysis in chemical thermodynamics focuses on investigating the spontaneity, directionality, and limits of chemical reactions. This discipline establishes theoretical models and conducts quantitative analyses to predict the feasibility and extent of chemical reactions under specific conditions, thereby providing theoretical support for experimental design. The application of thermodynamic principles to experimental practice helps reduce uncertainties in experimental exploration and optimize experimental protocols, consequently enhancing both the efficiency and scientific rigor of experiments.

HSC Chemistry (by Metso) is a powerful thermochemical analysis software that integrates comprehensive functionalities in general chemistry, thermodynamics, and mineral processing. The software features an extensive thermochemical database encompassing thermodynamic properties (enthalpy (H), entropy (S), and heat capacity (C)) of more than 29 000 compounds. It also incorporates multiple computational modules, including process simulation, reaction equations, heat and material balances, and E-pH diagrams (also known as Pourbaix diagrams).

The E-pH diagram module provides a clear visualization of element speciation in specific aqueous media, delineating the conditions under which reactions proceed spontaneously and identifying stability domains for various species in aqueous solutions. Such diagrams are indispensable for understanding and predicting the chemical behaviour of metals under diverse environmental conditions.

### 2.2 Kinetic Calculation

Leaching kinetics, as an important branch of chemical kinetics, focuses on studying the rates and influencing factors of chemical reactions during leaching processes. By constructing kinetic models for leaching systems and employing various experimental techniques and mathematical methods for quantitative analysis, it reveals the intrinsic mechanisms of leaching reactions. This enables a deeper understanding of rate-limiting steps at different stages of the reaction process, such as diffusion control and chemical reaction control, as well as the degree of influence of factors like temperature, concentration, particle size, and agitation intensity on leaching rates. Applying leaching kinetics theory to actual production allows for precise regulation of leaching process parameters, improving leaching efficiency and selectivity, reducing costs, and achieving efficient resource utilization and environmentally friendly industrial production.

12.07 kJ/mol, indicating that the sodium leaching process is predominantly controlled by mixed mechanisms: both diffusion and chemical reactions.

## 4. Conclusions

Thermodynamic and kinetic analyses systematically elucidate the leaching behaviour of high-alkalinity red mud. Thermodynamic calculations reveal distinct temperature dependencies: the $\Delta G_T^{\circ}$ values for $Fe_2O_3$ and $Al_2O_3$ leaching increase with temperature, becoming positive above 309 K, while $Na_2O$ and CaO exhibit decreasing $\Delta G_T^{\circ}$ trends. Notably, $Na_2O$ demonstrates the most negative $\Delta G_T^{\theta}$ values, indicating its preferential leaching tendency. These thermodynamic insights suggest that controlling temperature (> 323 K) and pH (4.0-7.0) can selectively extract $Na_2O$ while suppressing Fe/Al dissolution.

Kinetic investigations demonstrate that approximately 90 % sodium extraction can be achieved within 5-10 minutes across 298 K-348 K. The leaching kinetics are best described by the mixed control model [$1/3 \ln(1\text{-}x) – 1 + (1\text{-}x)^{-1/3}$], showing excellent correlation superior to pure chemical reaction or diffusion models. This mixed control mechanism is further confirmed by the calculated apparent activation energy of 12.07 $kJ \cdot mol^{-1}$, which falls within the characteristic range for combined diffusion-chemical reaction control. The comprehensive understanding of both thermodynamic and kinetic aspects provides a scientific basis for optimizing the leaching process to achieve efficient and selective sodium extraction from high-alkalinity red mud.

## 5. References


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