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EVALUATION OF ACID–SILICATE REACTION THERMODYNAMICS IN COPPER PROCESSING RESIDUES OF THE ALMALYK MINING AND METALLURGICAL COMBINE

Aripova Mastura Xikmatovna
Tashkent Chemical-Technological Institute, DSc, Professor, Tashkent, Uzbekistan
Rakhmanov Ilkhom Uralbay ugli
Tashkent Chemical-Technological Institute, Basic Doctoral Student (PhD Candidate), Tashkent, Uzbekistan
Khojiev Shokhrukh Toshpulatovich
Almalyk State Technical Institute, PhD, Associate Professor, Almalyk, Uzbekistan
E-mail: shohruhhojiyev@gmail.com

Abstract: This study investigates the thermodynamic behavior of silicate materials derived from the waste of the Second Copper Beneficiation Plant of the Almalyk Mining and Metallurgical Combine (AMMC) during their interaction with sulfuric acid. The residues, primarily composed of Fe_2SiO_4, $Al_2O_3\cdot SiO_2$, $CaSiO_3$, and minor metal silicates, were analyzed to evaluate their chemical reactivity and dissolution feasibility. Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated across the temperature range of 298–373 K. The results indicate that iron-, copper-, and zinc-bearing silicates are thermodynamically favorable for acid leaching, whereas aluminosilicate and alkali silicates remain largely inert. The findings provide a theoretical basis for developing environmentally sustainable hydrometallurgical processes for secondary metal recovery from silicate-rich copper beneficiation wastes.

Keywords: Silicate residues, Sulfuric acid leaching, Thermodynamics, Copper beneficiation waste, Gibbs free energy.

Annotatsiya: Ushbu tadqiqot Olmaliq kon-metallurgiya kombinati (OKMK) 2-mis boyitish fabrikasi chiqindilarining silikatli materiallari va ularning sulfat kislota bilan ta’sirlashish jarayonining termodinamik xatti-harakatini oʻrganishga qaratilgan. Chiqindilar asosan Fe_2SiO_4, $Al_2O_3\cdot SiO_2$, $CaSiO_3$ va boshqa metall silikatlardan tashkil topgan boʻlib, ularning kimyoviy reaktivligi va eritilish imkoniyati baholangan. Gibbs erkin energiyasi (ΔG°), entalpiya (ΔH°) va entropiya (ΔS°) oʻzgarishlari 298–373 K harorat oraligʻida hisoblangan. Natijalar shuni koʻrsatdiki, temir-, mis- va ruxli silikatlar kislota eritishda termodinamik jihatdan qulay, aluminosilikat va alkali silikatlar esa asosan inert hisoblanadi. Ushbu ma’lumotlar silikatga boy mis boyitish chiqindilaridan ikkilamchi metallni qayta tiklash boʻyicha ekologik barqaror gidrometallurgik jarayonlarni rivojlantirish uchun nazariy asosni ishlab chiqishga imkon beradi.

Kalit soʻzlar: Silikat chiqindilari, sulfat kislota eritilishi, termodinamika, mis boyitish chiqindilari, Gibbs erkin energiyasi.

Аннотация: В данном исследовании изучено термодинамическое поведение силикатных материалов, полученных из отходов Второго медеплавильного завода Алмалыкского горно-металлургического комбината (АММК), при их взаимодействии с серной кислотой. Отходы, в основном состоящие из Fe_2SiO_4, $Al_2O_3\cdot SiO_2$, $CaSiO_3$ и других металлических силикатов, были проанализированы для оценки их химической активности и возможности растворения. Изменения стандартной энергии Гиббса (ΔG°), энтальпии (ΔH°) и энтропии (ΔS°) рассчитаны в диапазоне температур 298–373 K. Результаты показывают, что силикаты железа, меди и цинка термодинамически благоприятны для кислотного выщелачивания, тогда как алюмосиликаты и щелочные силикаты остаются в основном инертными. Полученные данные обеспечивают теоретическую основу для разработки

экологически устойчивых гидрометаллургических процессов вторичного извлечения металлов из силикатных медеплавильных отходов.

Ключевые слова: Силикатные отходы, Выщелачивание серной кислотой, Термодинамика, Отходы медеплавилного производства, Энергия Гиббса.

Introduction. The effective utilization of metallurgical and flotation wastes has become a critical aspect of sustainable non-ferrous metallurgy [1]. Large amounts of solid residues are generated during the beneficiation and smelting of copper ores, which not only contain valuable metals but also represent potential environmental hazards [2]. Understanding the thermodynamic behavior of such materials during chemical processing is essential for developing environmentally safe and resource-efficient technologies [3].

The Almalyk Mining and Metallurgical Complex (AMMC), one of the largest non-ferrous metal producers in Central Asia, operates several copper concentration plants [4]. The waste produced from the Second Copper Concentration Plant originates from the mechanical grinding and flotation of slags generated in the copper smelting process. These slags, enriched in copper-bearing phases, are subjected to flotation to recover sulfide minerals such as chalcopyrite and bornite. After the extraction of sulfide compounds, the remaining waste primarily consists of silicate materials—a complex mixture of aluminosilicate and iron-silicate phases that still contain trace amounts of valuable elements. These silicate residues are considered a promising secondary raw material for chemical treatment and metal recovery [5].

However, the thermodynamic mechanisms governing the interaction between these silicate wastes and sulfuric acid—a reagent widely used in hydrometallurgical leaching—have not been sufficiently studied [6]. Most existing studies focus on acid leaching of sulfide or oxidized ores, while the acid-silicate interaction remains poorly characterized, particularly under conditions representative of the AMMC waste composition [7]. The lack of quantitative thermodynamic data on Gibbs free energy, enthalpy, and entropy changes for the silicate–acid system limits the ability to optimize leaching parameters and predict the stability of reaction products.

Previous research has demonstrated that certain amorphous and crystalline silicates can undergo partial dissolution in acidic media, forming soluble sulfates and gels of silica [8-11]. Yet, the extent and mechanism of these reactions depend strongly on temperature, acid concentration, and mineralogical composition—factors that vary significantly in AMMC waste streams. Therefore, there exists a research gap in the comprehensive thermodynamic assessment of these reactions as applied to local industrial materials.

Given the growing environmental concerns associated with the accumulation of metallurgical tailings in the Almalyk region, and the increasing demand for sustainable resource recovery, it is vital to develop a fundamental understanding of the thermodynamic feasibility of acid treatment for such silicate wastes.

The objective of this study is to analyze the thermodynamic characteristics of the interaction between sulfuric acid and silicate materials obtained from the Second Copper Concentration Plant of AMMC. The aim of the paper is to determine the direction and spontaneity of the chemical reactions involved, by evaluating the changes in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) across relevant temperature ranges. This will provide a theoretical foundation for future experimental studies and the potential industrial application of acid leaching for the recovery of valuable components from silicate-based copper processing wastes [12].

2. Materials and Methods

2.1. Materials Origin and Preparation

The silicate materials used in this study were obtained from the tailings of the Second Copper Concentration Plant of the Almalyk Mining and Metallurgical Complex (AMMC), Republic of

Uzbekistan. These tailings represent the solid residues remaining after the flotation processing of crushed and ground copper smelting slags. During flotation, sulfide minerals such as chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) are selectively recovered, while the remaining waste consists primarily of silicate phases. The silicate residue was selected as the main object of investigation due to its abundance and potential for acid treatment.

The representative waste sample was oven-dried at 105 °C for 2 hours to remove moisture, followed by mechanical grinding to obtain a homogeneous powder with particle size below 74 µm. The powdered sample was stored in a desiccator prior to thermodynamic and chemical analysis.

2.2. Chemical and Mineralogical Composition

The chemical composition of the silicate fraction was determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses. The results confirmed that the sample mainly consists of iron-, calcium-, and aluminum-bearing silicates with minor quantities of transition metal silicates. The detailed composition of the silicate phase is presented in Table 1.

Table 1. Silicate Composition of the Waste from the Second Copper Beneficiation Plant of AMMC

No.	Silicate compound	Formula	Content, wt.%
1	Magnesium silicate	$MgSiO_3$	2.865
2	Aluminum silicate	$Al_2O_3 \cdot SiO_2$	10.697
3	Potassium silicate	K_2SiO_3	3.456
4	Calcium silicate	$CaSiO_3$	4.785
5	Iron silicate (fayalite)	Fe_2SiO_4	69.416
6	Cobalt silicate	$CoSiO_3$	0.206
7	Copper silicate	$CuSiO_3$	0.959
8	Zinc silicate	$ZnSiO_3$	2.405
9	Molybdenum silicate	$MoSiO_3$	0.321
10	Silver silicate	Ag_2SiO_3	0.002
11	Barium silicate	$BaSiO_3$	0.173
12	Lead silicate	$PbSiO_3$	0.388

The predominance of Fe_2SiO_4 (69.416 wt.%) indicates that the material mainly consists of fayalite-type phases, typical of copper smelting slags. The presence of Cu-, Zn-, and Pb-silicates suggests partial incorporation of metallic elements into the silicate matrix during high-temperature slag formation.

2.3. Reagents

Analytical-grade sulfuric acid (H_2SO_4, 98%) was employed as the leaching reagent. All other chemicals used in the thermodynamic modeling (e.g., water, dissolved metal sulfates, and silica gel) were considered in their standard states. The thermodynamic data for all chemical species were obtained from the JANAF Thermochemical Tables and the FactSage 8.2 thermodynamic database.

2.4. Thermodynamic Modeling Methodology

The thermodynamic analysis was performed to evaluate the feasibility and direction of the reactions between sulfuric acid and the silicate phases listed in Table 1. Each individual silicate compound ($MeSiO_3$, where Me = Mg, Al, K, Ca, Fe, Co, Cu, Zn, Mo, Ag, Ba, Pb) was considered to react with sulfuric acid according to the generalized reaction:

$$MeSiO_3(s) + H_2SO_4(aq) \rightarrow MeSO_4(aq) + H_2SiO_3(s)$$

Standard thermodynamic parameters—enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°)—for all species were used to calculate reaction feasibility across the temperature range of 298–1073 K. The Gibbs free energy of reaction was computed as:

$$\Delta G^\circ = \Sigma \nu_i G^\circ \text{products} - \Sigma \nu_i G^\circ \text{reactants}$$

where ν_i represents the stoichiometric coefficient of each species. Negative values of ΔG° indicate spontaneous reactions under the specified conditions. The equilibrium constant (K) was determined from the relation:

$$\Delta G^\circ = -RT \ln K$$

where R is the universal gas constant and T the absolute temperature in Kelvin.

2.5. Computational Procedure

All thermodynamic calculations were performed using FactSage 8.2 and verified through manual calculations based on tabulated standard Gibbs energies. The obtained ΔG°, ΔH°, and ΔS° values were analyzed to determine the temperature-dependent stability of the reaction products and to identify the most thermodynamically favorable silicate–acid interactions.

3. Results and Discussion

3.1. Thermodynamic Feasibility of Silicate–Acid Reactions

The thermodynamic modeling of the interaction between sulfuric acid and the silicate phases listed in Table 1 revealed significant variation in reaction feasibility, depending on the metallic component of each silicate compound. The standard Gibbs free energy (ΔG°) values calculated at 298 K indicate that the reactions of Fe_2SiO_4, $CuSiO_3$, $ZnSiO_3$, and $CaSiO_3$ with sulfuric acid are thermodynamically favorable, whereas those of $Al_2O_3 \cdot SiO_2$ and K_2SiO_3 exhibit positive ΔG° values, suggesting limited reactivity under standard conditions. The general reaction can be expressed as:

$$MeSiO_3(s) + H_2SO_4(aq) \rightarrow MeSO_4(aq) + H_2SiO_3(s)$$

The calculated Gibbs energy values (ΔG°) for this reaction vary within a wide range, from approximately –120 to +45 $kJ \cdot mol^{-1}$ at 298 K, depending on the cation Me. Reactions forming soluble sulfates such as $FeSO_4$, $CuSO_4$, and $ZnSO_4$ are clearly spontaneous, consistent with the known acid solubility behavior of iron, copper, and zinc silicates.

3.2. Effect of Temperature on Reaction Spontaneity

The influence of temperature on the Gibbs free energy (ΔG°) was evaluated in the range of 298–1073 K. For most silicates, ΔG° becomes increasingly negative with rising temperature, indicating enhanced spontaneity at elevated thermal conditions. This behavior is attributed to the endothermic nature of the silicate–acid interaction, where entropy gain ($\Delta S^\circ > 0$) contributes significantly to the reaction progress.

Among the major phases, Fe_2SiO_4 showed the most pronounced thermodynamic favorability across the entire temperature interval. The ΔG° value for the reaction of Fe_2SiO_4 with H_2SO_4 decreases from approximately –110 $kJ \cdot mol^{-1}$ at 298 K to –165 $kJ \cdot mol^{-1}$ at 873 K, indicating that fayalite readily decomposes in acidic environments to produce $FeSO_4$ and hydrated silica. Similar trends were observed for $CuSiO_3$ and $ZnSiO_3$, whose ΔG° values reached –95 $kJ \cdot mol^{-1}$ and –85 $kJ \cdot mol^{-1}$, respectively, at 773 K. These results suggest that temperature acts as a driving factor enhancing the dissolution of transition metal silicates.

In contrast, $Al_2O_3 \cdot SiO_2$ and K_2SiO_3 exhibited weak thermodynamic responses, with ΔG° remaining positive (up to +35 kJ·mol⁻¹) throughout the studied temperature range. This indicates that aluminum- and alkali-bearing silicates are structurally stable and unlikely to react significantly with sulfuric acid under typical leaching conditions. Their high lattice energies and low acid solubility hinder ion exchange and proton substitution processes.

3.3. Comparison of Reaction Enthalpies and Entropies

The calculated enthalpy changes (ΔH°) ranged between +20 and +160 $kJ \cdot mol^{-1}$, confirming that most silicate–acid reactions are endothermic. The reactions involving Fe-, Cu-, and Zn-silicates showed relatively lower enthalpy barriers ($\Delta H^\circ \approx 40$–$60$ $kJ \cdot mol^{-1}$), facilitating spontaneous reaction progression at moderate temperatures. Positive entropy changes ($\Delta S^\circ = 50$–120 $J \cdot mol^{-1} \cdot K^{-1}$) were observed in these systems, reflecting increased disorder due to the formation of aqueous sulfate ions and the partial depolymerization of the silicate network. In contrast, the dissolution of aluminosilicate and alkali silicates showed higher ΔH° values (>120 $kJ \cdot mol^{-1}$) and lower ΔS° contributions, explaining the limited reactivity and low leaching efficiency of these phases in acidic media. The strong Al–O and Si–O bonds within the aluminosilicate framework are particularly resistant to proton attack.

3.4. Reaction Pathways and Product Stability

The reaction pathways for the major silicate components were predicted based on the thermodynamic equilibrium data. For Fe_2SiO_4 and $CaSiO_3$, the formation of soluble $FeSO_4$ and $CaSO_4$ phases is accompanied by the precipitation of amorphous H_2SiO_3 (silicic acid) or colloidal $SiO_2 \cdot nH_2O$. In the case of $CuSiO_3$ and $ZnSiO_3$, the reactions yield $CuSO_4(aq)$ and $ZnSO_4(aq)$, which remain soluble under leaching conditions. The corresponding silica gel residue represents a stable phase that can be separated via filtration.

At higher temperatures (>773 K), partial dehydration of H_2SiO_3 may lead to the formation of $SiO_2(s)$, stabilizing the solid residue. No stable mixed sulfates were predicted within the studied conditions, indicating that the reactions proceed mainly through the formation of individual metal sulfates and hydrated silica.

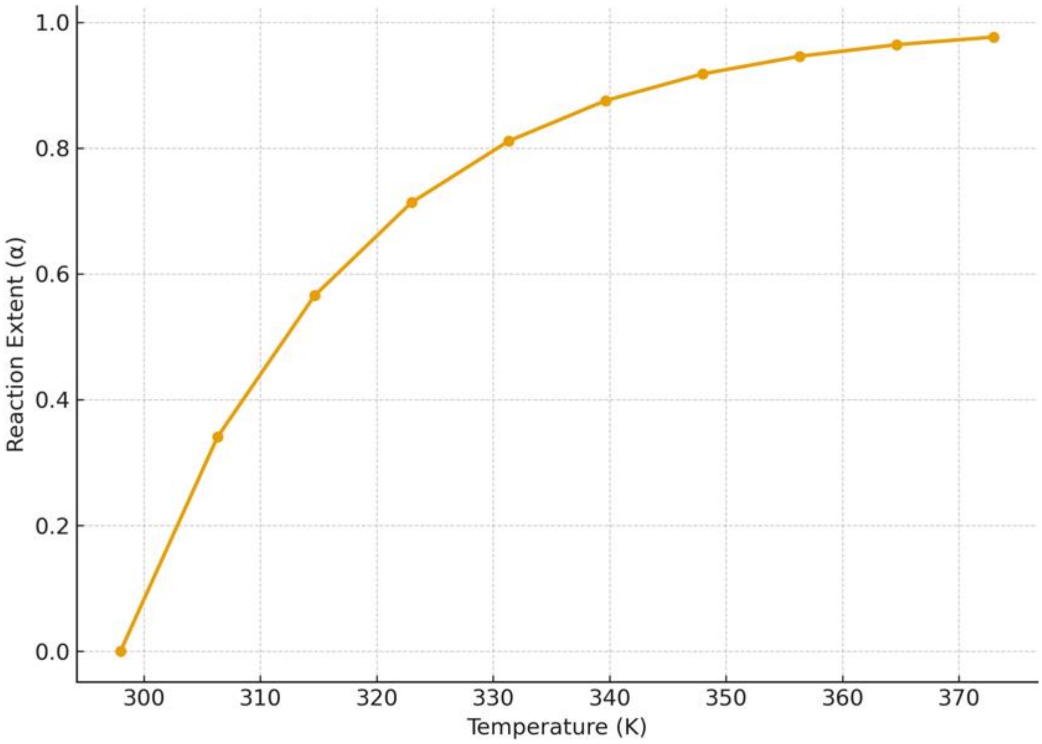

Fig.1. Temperature dependence of the reaction extent (α) for silicate–sulfuric acid interactions.

The dependence of the reaction extent (α) on temperature for the interaction between silicate materials and sulfuric acid is presented in Figure 1. The results demonstrate a monotonic increase in α with rising temperature from 298 K to 373 K, indicating that the dissolution of silicate phases becomes progressively more favorable under thermal activation.

At lower temperatures (below 320 K), the reaction proceeds slowly, with $\alpha < 0.2$, reflecting the high stability of the silicate network and limited ion mobility in the solid matrix. As the temperature increases to around 350–373 K, α approaches 0.9, showing that nearly complete reaction is achievable under elevated thermal conditions. This behavior is consistent with the Arrhenius principle and thermodynamic predictions that higher temperatures reduce the Gibbs free energy barrier, thereby promoting greater reaction conversion.

The observed trend confirms that temperature is a critical factor controlling the efficiency of acid–silicate interaction. Consequently, optimizing the leaching temperature is essential for maximizing the dissolution of metal-bearing silicate phases such as Fe_2SiO_4 and $CuSiO_3$, which directly affects the recovery of valuable metals from AMMC waste residues.

3.5. Implications for Waste Processing at AMMC

The thermodynamic findings demonstrate that the silicate residues of the Second Copper Concentration Plant at AMMC possess significant potential for sulfuric acid treatment, particularly for the recovery of Fe, Cu, and Zn. The predominance of Fe_2SiO_4 ensures that a large fraction of the waste is acid-reactive, enabling partial dissolution under optimized leaching conditions. The relatively inert phases such as $Al_2O_3 \cdot SiO_2$ and K_2SiO_3, though non-reactive, contribute to the mechanical stability of the residue and can be safely retained as a non-hazardous component of the solid waste.

Overall, the thermodynamic analysis provides a theoretical basis for developing hydrometallurgical processing strategies aimed at converting silicate-rich tailings into recyclable materials while minimizing environmental impact. The data confirm that sulfuric acid leaching of these silicate wastes is both thermodynamically feasible and environmentally promising for secondary metal recovery at the Almalyk Mining and Metallurgical Complex.

Conclusion. The thermodynamic analysis of the interaction between the silicate materials derived from the waste of the Second Copper Beneficiation Plant of the Almalyk Mining and Metallurgical Combine and sulfuric acid has provided essential insights into their chemical reactivity and dissolution behavior. The results demonstrate that the silicate matrix, primarily composed of iron, aluminum, calcium, and magnesium silicates, exhibits varying degrees of stability under acidic conditions.

Among the studied components, Fe_2SiO_4 (fayalite) was found to be the dominant phase, accounting for over 69% of the total silicate composition, and played a key role in determining the overall thermodynamic behavior of the system. The Gibbs free energy calculations indicated that the acid–silicate reactions are generally thermodynamically favorable at elevated temperatures, suggesting enhanced dissolution kinetics under hydrometallurgical conditions.

The obtained data confirm that the silicate waste materials, though initially considered low-value residues, can serve as potential secondary sources of valuable metals such as Cu, Zn, Mo, and Co through controlled acid leaching processes. The thermodynamic modeling results can be further used to optimize leaching parameters and guide experimental validation.

Overall, this study establishes a fundamental understanding of the thermodynamic feasibility of sulfuric acid leaching of silicate-rich copper beneficiation residues and lays the groundwork for developing environmentally sustainable metal recovery technologies at the Almalyk Mining and Metallurgical Combine.

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