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Eco-Efficient Oxidative Leaching of Zinc Sulfide Concentrates Using Manganese Dioxide: A Thermodynamic and Process Analysis

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Abstract— This study investigates the thermodynamic and kinetic feasibility of oxidative selective leaching of zinc sulfide (ZnS) using manganese dioxide (MnO_2) as an oxidizing agent in a sulfuric acid medium. Based on the calculated Gibbs free energy (ΔG) and equilibrium constant (K) values for three possible reaction pathways, the process was found to be most thermodynamically favorable within the temperature range of 45–55 °C. The combined oxidation–acid leaching reaction ($ZnS + MnO_2 + 4H^+ \rightarrow Zn^{2+} + Mn^{2+} + S + 2H_2O$), maintains negative Gibbs free energy values (ΔG ≈ –197 kJ/mol) across this range, confirming its spontaneous nature and high thermodynamic stability. The process ensures efficient dissolution of zinc while producing elemental sulfur as a valuable by-product. Subsequent purification of manganese through ozone oxidation allows for selective MnO_2 regeneration, supporting a cyclic and resource-efficient operation. The proposed approach not only minimizes zinc losses in solid residues but also enriches the acid-insoluble fraction with precious metals such as gold and silver, enhancing the economic and environmental performance of the overall hydrometallurgical process. The results provide a reliable scientific basis for developing an energy-efficient, eco-friendly, and cost-effective technology for the complete hydrometallurgical processing of zinc sulfide concentrates.

Keywords: Zinc sulfide; Sphalerite; Manganese dioxide; Oxidative leaching; Thermodynamic analysis; Equilibrium constant; Gibbs free energy; Selective dissolution; Hydrometallurgy; Eco-efficient technology.

1. INTRODUCTION

Zinc (Zn) is one of the key strategic metals in non-ferrous metallurgy, distinguished by its high corrosion resistance, favorable mechanical properties, and excellent alloy-forming ability. It is widely used in galvanic coatings, brass, bronze, and other alloys, as well as in the chemical, electrical, and mechanical engineering industries [1].

At present, the global production of zinc amounts to 13–14 million tons per year, with a significant portion obtained through hydrometallurgical processes [2].

The primary raw material for zinc production is sphalerite (ZnS) and polymetallic ores containing it. These ores typically include additional accompanying elements such as lead, copper, iron, cadmium, indium, germanium, and others. Therefore, zinc production processes are not only aimed at extracting zinc but also at efficiently recovering associated valuable elements [3].

Modern zinc production technologies are based on pyrometallurgical (Waelz process, electric furnace smelting) and hydrometallurgical (roasting of zinc sulfide concentrates, selective leaching, and electrolytic deposition) methods [4].

Hydrometallurgical techniques are considered advantageous due to their environmental safety, ability to produce high-purity metal, and relatively low energy consumption [5].

However, the residues generated in these technological processes — such as calcines, slags, hydrometallurgical cakes, and dusts — still contain significant amounts of zinc and other valuable metals. The non-utilization of these materials leads to resource losses.

In recent years, special attention has been given to the development of zero-waste and comprehensive processing technologies in zinc production. This direction aligns with the state policy of the Republic of Uzbekistan aimed at environmental protection and sustainable industrial development. In particular, the declaration of 2025 as the "Year of Environmental Protection and the Green Economy" by President Shavkat Mirziyoyev further emphasizes the importance of introducing energy- and resource-efficient, low- or zero-waste technologies in industrial sectors, including zinc production [6].

Currently, zinc production in Uzbekistan is carried out at the Almalyk Mining and Metallurgical Complex JSC (AMMC). In this enterprise, zinc sulfide concentrates are first roasted in fluidized bed furnaces. The resulting calcine is then selectively leached in sulfuric acid solution, and after purification, metallic cathode zinc is obtained by electrolysis [7].

In recent decades, the technologies for processing zinc concentrates have undergone significant development, evolving from conventional pyrometallurgical methods to advanced hydrometallurgical, bioleaching, and combined approaches. The main objective of these processes is to achieve the maximum extraction of zinc and associated metals (Pb, Fe, Cd, In, Ga, etc.) while ensuring environmental safety and energy efficiency [8].

Liu et al. [9] proposed an integrated hydrometallurgical process for the treatment of low-grade oxidized zinc ores, which includes stepwise leaching and purification in sulfate solutions. This method enables the utilization of lean raw materials and improves zinc recovery. Chen et al. [10] studied an enhanced leaching process of zinc calcine using reduced wet grinding, which resulted in higher zinc dissolution efficiency and reduced hazardous waste generation.

Raghavan et al. [11] developed an innovative pyrometallurgical process for complex sulfide ores that integrates flotation and smelting stages, achieving higher recovery of zinc and lead. Fuls et al. [12] compared the efficiency of pyrometallurgical and hydrometallurgical processing routes for zinc concentrates, emphasizing their economic and environmental performance.

Ruonala et al. [13] presented an overview of the latest developments in zinc production technologies, particularly the recycling of zinc-bearing dusts and oxides in Waelz kilns, as well as the advantages of electric smelting and oxidative leaching processes. Soltani, Hosseini, and Zandvakili [14] investigated the purification of zinc from bioleaching solutions using solvent extraction, followed by electrowinning, demonstrating the potential of integrated hydrometallurgical systems for sustainable zinc recovery.

Ahmadi et al. [15] also studied the purification of zinc from bioleaching solutions through precipitation and solvent extraction, which reduced impurities and improved metal recovery efficiency. Huston et al. [16] analyzed the distribution of critical elements such as indium, gallium, germanium, and cadmium in zinc ores and concentrates, emphasizing their significance in refining and by-product recovery processes.

Feng and Aldrich [17] provided an extensive review of the bioleaching of zinc from complex sulfide concentrates, highlighting the kinetics and environmental benefits of bacterial leaching. Abbruzzese et al. [18] proposed a combined leaching–solvent extraction–electrowinning route for zinc recovery from industrial wastes, demonstrating the feasibility of integrated metallurgical recycling.

The reviewed literature indicates that hydrometallurgical and bioleaching technologies are becoming dominant in modern zinc concentrate processing due to their low energy consumption, reduced emissions, and capability to recover valuable by-products. However, future progress in zinc metallurgy will likely rely on the integration of thermo-hydrometallurgical systems, combining the advantages of both thermal and aqueous processes to achieve high recovery efficiency and environmental sustainability.

However, the main reason for the low economic efficiency of this technology lies in the high iron content of the concentrate. During roasting, iron binds part of the zinc in the form of ferrite compounds, which are insoluble in sulfuric acid during selective leaching and therefore pass into the residue cake — leading to metal losses.

To recover zinc from this waste (zinc cake), the Waelz process is additionally applied. However, this process requires large amounts of natural gas, coke, and electrical energy, while also complicating the recovery of precious metals such as gold and silver from the cake. As a result, the overall economic efficiency of zinc production decreases, and energy consumption increases.

Therefore, the need to improve the existing production technology by introducing energy- and resource-efficient as well as low-waste processes has become increasingly urgent.

Based on this, the main goal of the present research is to develop a highly efficient technology for the hydrometallurgical processing of zinc sulfide concentrates to simplify the recovery of zinc and valuable metals.

To achieve this objective, a step-by-step thermodynamic study of the selective leaching of zinc sulfide concentrates in sulfuric acid solution was conducted.

2. MATERIALS AND METHODS

As the material for research, a zinc sulfide concentrate produced at the Almalyk Mining and Metallurgical Complex JSC was used. This concentrate, derived from sphalerite-based polymetallic ores, was found to contain on average 52–56% Zn, 8–12% Fe, 0.5–1.0% Pb, and 0.3–0.5% Cu according to preliminary chemical analyses. The main sulfide minerals identified in the concentrate are sphalerite (ZnS), marmatite ((Zn,Fe)S), galena (PbS), and chalcopyrite ($CuFeS_2$) [19].

At the initial stage, a thermodynamic assessment was performed to determine whether the process could occur spontaneously under standard conditions. Since the main mineral in the zinc sulfide concentrate is sphalerite (ZnS), it was selected as the main object of study. A sulfuric acid solution (H_2SO_4) was used as the leaching reagent.

However, the direct reaction between ZnS and H_2SO_4,

$$ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g) \quad (1)$$

produces hydrogen sulfide (H_2S) — a highly toxic gas, making the process hazardous for practical application. As a result, the technical and safety requirements for such leaching equipment significantly increase. Moreover, this reaction is endothermic, requiring a large external heat source.

Considering this, an energy-balancing chemical approach was adopted, where endothermic systems are coupled with exothermic reactions to improve energy efficiency and productivity. This principle, developed at the Department of Metallurgy of the Almalyk State Technical Institute, was taken as the methodological basis of the study.

To apply this approach to the selective leaching of sphalerite in sulfuric acid, the above ZnS–H_2SO_4 reaction was considered as the endothermic system. To enhance its thermal balance, the oxidation of zinc sulfide was introduced as an exothermic reaction:

$$ZnS(s) + MnO_2(s) \rightarrow ZnO(s) + MnO(s) + S(s) \quad (2)$$

In this case, pyrolusite mineral (main component — manganese dioxide, MnO_2) was chosen as the oxidizing reagent. Its advantage lies in the possibility of regenerating manganese dioxide by ozonating the leach solution and re-precipitating MnO_2. Thus, the process ensures not only energy efficiency but also reagent recyclability.

To evaluate the feasibility of this approach, a theoretical justification for enhancing the reactivity of the sphalerite–sulfuric acid system through the introduction of MnO_2 was carried out.

A thermodynamic analysis was performed to determine the reaction direction, heat effects, and energy benefits.

During the research, the thermodynamic parameters — enthalpy ($\Delta H°$), entropy ($\Delta S°$), and Gibbs free energy ($\Delta G°$) — of the reactions were calculated for standard conditions. The calculations were based on the Nernst equation, Ellingham diagrams, and the equilibrium constant relations.

3. RESULTS AND DISCUSSION

To ensure clarity and consistency in the analysis, a comparative thermodynamic evaluation was performed following a defined sequence (algorithm).

At this stage of the study, three key chemical reactions involved in the selective leaching of zinc were selected. Their stoichiometric equations and corresponding Gibbs free energy expressions are presented in Table 1.

According to the analysis results, the three chemical reactions presented in Table 1 allow for evaluating the thermodynamic behavior of zinc sulfide (ZnS) under various conditions.

The first reaction represents the direct decomposition of zinc sulfide in an acidic medium. As seen from the expression for ΔG_1, the value of Gibbs free energy decreases with increasing temperature; however, the initially positive value (31.5 kJ/mol) limits the spontaneity of the reaction at lower temperatures. Therefore, this process becomes thermodynamically favorable only at elevated temperatures.

The second reaction describes a solid-state redox interaction. In this case, the negative value of ΔG_2 indicates that the reaction proceeds spontaneously over a wide temperature range. Consequently, MnO_2 acts as an effective partial oxidizing agent for zinc sulfide, leading to the formation of zinc oxide (ZnO).

Table 1: Gibbs Free Energy Equations for Reactions Involved in Selective Zinc Leaching

№	Chemical reactions	Gibbs free energy equation
1.	$ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g)$	$\Delta G_1=31.5-0.09511\cdot T$
2.	$ZnS(s) + MnO_2(s) \rightarrow ZnO(s) + MnO(s) + S(s)$	$\Delta G_2=-7.5-0.02611\cdot T$
3.	$ZnS(s) + MnO_2(s) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + Mn^{2+}(aq) + S(s) + 2H_2O(l)$	$\Delta G_3=-218.78+0.06565\cdot T$

The third reaction is a combined form of the first two, involving both solid-phase oxidation and participation of protons in the solution phase. The ΔG_3 expression shows that this reaction is thermodynamically favorable across a broad temperature interval. The initially negative value suggests that the reaction proceeds spontaneously even at low temperatures, while a slight decrease in stability is observed as the temperature increases.

Overall, comparative analysis revealed that the reactions of ZnS in the presence of MnO_2 (reactions 2 and 3) create the most favorable conditions for zinc oxidation and its transition into a soluble form, both in acidic and solid-phase environments. Therefore, MnO_2 is recommended as an effective oxidizing component in the selective leaching process of zinc sulfide concentrates.

To comprehensively evaluate the behavior of zinc sulfide (ZnS) under oxidative leaching conditions, the Gibbs free energy (ΔG) and equilibrium constants (K) were calculated for three possible reactions involving sulfur oxidation and zinc dissolution. These reactions represent (1) the direct acid dissolution of ZnS, (2) the solid-state redox interaction between ZnS and MnO_2, and (3) the combined acid–oxidant leaching process.

The calculated Gibbs energy values describe the thermodynamic feasibility of each reaction, while the corresponding equilibrium constants (K) reflect their kinetic tendencies and reaction directionality. As temperature increases, the data allow comparing how the spontaneity and rate-limiting characteristics evolve across different reaction pathways. The summarized results are presented in Table 2.

Table 2: Comparative Thermodynamic and Kinetic Data for Possible Reactions during the Oxidative Leaching of Zinc Sulfide with Manganese Dioxide

№	Temperature		Gibbs free energy, kJ/mol			Equilibrium constants		
	T (K)	T (°C)	ΔG_1	ΔG_2	ΔG_3	K_1	K_2	K_3
1	298	25	3,16	-15,28	-199,22	0,9987	1,0062	1,0838
2	299	26	3,06	-15,31	-199,15	0,9988	1,0062	1,0835

3	300	27	2,97	-15,33	-199,09	0,9988	1,0062	1,0831
4	301	28	2,87	-15,36	-199,02	0,9989	1,0062	1,0828
5	302	29	2,78	-15,39	-198,95	0,9989	1,0061	1,0825
6	303	30	2,68	-15,41	-198,89	0,9989	1,0061	1,0822
7	304	31	2,59	-15,44	-198,82	0,9990	1,0061	1,0819
8	305	32	2,49	-15,46	-198,76	0,9990	1,0061	1,0816
9	306	33	2,40	-15,49	-198,69	0,9991	1,0061	1,0813
10	307	34	2,30	-15,52	-198,63	0,9991	1,0061	1,0810
11	308	35	2,21	-15,54	-198,56	0,9991	1,0061	1,0807
12	309	36	2,11	-15,57	-198,49	0,9992	1,0061	1,0804
13	310	37	2,02	-15,59	-198,43	0,9992	1,0061	1,0801
14	311	38	1,92	-15,62	-198,36	0,9993	1,0061	1,0798
15	312	39	1,83	-15,65	-198,30	0,9993	1,0061	1,0795
16	313	40	1,73	-15,67	-198,23	0,9993	1,0060	1,0792
17	314	41	1,64	-15,70	-198,17	0,9994	1,0060	1,0789
18	315	42	1,54	-15,72	-198,10	0,9994	1,0060	1,0786
19	316	43	1,45	-15,75	-198,03	0,9994	1,0060	1,0783
20	317	44	1,35	-15,78	-197,97	0,9995	1,0060	1,0780
21	318	45	1,26	-15,80	-197,90	0,9995	1,0060	1,0778
22	319	46	1,16	-15,83	-197,84	0,9996	1,0060	1,0775
23	320	47	1,06	-15,86	-197,77	0,9996	1,0060	1,0772
24	321	48	0,97	-15,88	-197,71	0,9996	1,0060	1,0769
25	322	49	0,87	-15,91	-197,64	0,9997	1,0060	1,0767
26	323	50	0,78	-15,93	-197,58	0,9997	1,0060	1,0764
27	324	51	0,68	-15,96	-197,51	0,9997	1,0059	1,0761
28	325	52	0,59	-15,99	-197,44	0,9998	1,0059	1,0758
29	326	53	0,49	-16,01	-197,38	0,9998	1,0059	1,0756
30	327	54	0,40	-16,04	-197,31	0,9999	1,0059	1,0753
31	328	55	0,30	-16,06	-197,25	0,9999	1,0059	1,0750
32	329	56	0,21	-16,09	-197,18	0,9999	1,0059	1,0748
33	330	57	0,11	-16,12	-197,12	1,0000	1,0059	1,0745
34	331	58	0,02	-16,14	-197,05	1,0000	1,0059	1,0743
35	332	59	-0,08	-16,17	-196,98	1,0000	1,0059	1,0740
36	333	60	-0,17	-16,19	-196,92	1,0001	1,0059	1,0738

37	334	61	-0,27	-16,22	-196,85	1,0001	1,0059	1,0735
38	335	62	-0,36	-16,25	-196,79	1,0001	1,0059	1,0732
39	336	63	-0,46	-16,27	-196,72	1,0002	1,0058	1,0730
40	337	64	-0,55	-16,30	-196,66	1,0002	1,0058	1,0727
41	338	65	-0,65	-16,33	-196,59	1,0002	1,0058	1,0725
42	339	66	-0,74	-16,35	-196,52	1,0003	1,0058	1,0723
43	340	67	-0,84	-16,38	-196,46	1,0003	1,0058	1,0720
44	341	68	-0,93	-16,40	-196,39	1,0003	1,0058	1,0718
45	342	69	-1,03	-16,43	-196,33	1,0004	1,0058	1,0715
46	343	70	-1,12	-16,46	-196,26	1,0004	1,0058	1,0713
47	344	71	-1,22	-16,48	-196,20	1,0004	1,0058	1,0710
48	345	72	-1,31	-16,51	-196,13	1,0005	1,0058	1,0708
49	346	73	-1,41	-16,53	-196,07	1,0005	1,0058	1,0706
50	347	74	-1,50	-16,56	-196,00	1,0005	1,0058	1,0703
51	348	75	-1,60	-16,59	-195,93	1,0006	1,0058	1,0701
52	349	76	-1,69	-16,61	-195,87	1,0006	1,0057	1,0699
53	350	77	-1,79	-16,64	-195,80	1,0006	1,0057	1,0696
54	351	78	-1,88	-16,66	-195,74	1,0006	1,0057	1,0694
55	352	79	-1,98	-16,69	-195,67	1,0007	1,0057	1,0692
56	353	80	-2,07	-16,72	-195,61	1,0007	1,0057	1,0690
57	354	81	-2,17	-16,74	-195,54	1,0007	1,0057	1,0687
58	355	82	-2,26	-16,77	-195,47	1,0008	1,0057	1,0685
59	356	83	-2,36	-16,80	-195,41	1,0008	1,0057	1,0683
60	357	84	-2,45	-16,82	-195,34	1,0008	1,0057	1,0681
61	358	85	-2,55	-16,85	-195,28	1,0009	1,0057	1,0678
62	359	86	-2,64	-16,87	-195,21	1,0009	1,0057	1,0676
63	360	87	-2,74	-16,90	-195,15	1,0009	1,0057	1,0674
64	361	88	-2,83	-16,93	-195,08	1,0009	1,0057	1,0672
65	362	89	-2,93	-16,95	-195,01	1,0010	1,0057	1,0670
66	363	90	-3,02	-16,98	-194,95	1,0010	1,0056	1,0668
67	364	91	-3,12	-17,00	-194,88	1,0010	1,0056	1,0665
68	365	92	-3,22	-17,03	-194,82	1,0011	1,0056	1,0663
69	366	93	-3,31	-17,06	-194,75	1,0011	1,0056	1,0661
70	367	94	-3,41	-17,08	-194,69	1,0011	1,0056	1,0659

71	368	95	-3,50	-17,11	-194,62	1,0011	1,0056	1,0657
72	369	96	-3,60	-17,13	-194,56	1,0012	1,0056	1,0655
73	370	97	-3,69	-17,16	-194,49	1,0012	1,0056	1,0653
74	371	98	-3,79	-17,19	-194,42	1,0012	1,0056	1,0651
75	372	99	-3,88	-17,21	-194,36	1,0013	1,0056	1,0649
76	373	100	-3,98	-17,24	-194,29	1,0013	1,0056	1,0647

Thermodynamic analysis of the reactions presented in Table 2 provides a comprehensive understanding of the selective leaching behavior of zinc sulfide (ZnS) under different physicochemical conditions. The calculated Gibbs free energy equations clearly indicate how temperature influences the spontaneity and feasibility of each reaction.

The first reaction, $ZnS(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2S(g)$, describes the direct dissolution of zinc sulfide in an acidic medium without any oxidizing reagent. The corresponding Gibbs free energy equation, $\Delta G_1 = 31.5 – 0.09511T$, shows that the Gibbs energy value decreases with increasing temperature, implying that higher thermal energy slightly favors the process. However, the positive initial ΔG value (31.5 kJ/mol) at standard conditions means that the reaction is non-spontaneous at lower temperatures and requires additional energy input to proceed. This indicates that the dissolution of ZnS in acid alone is thermodynamically unfavorable, as the sulfide mineral structure remains highly stable in the absence of an external oxidant.

The second reaction, $ZnS(s) + MnO_2(s) \rightarrow ZnO(s) + MnO(s) + S(s)$, represents a redox interaction occurring between two solid phases. The Gibbs energy expression, $\Delta G_2 = –7.5 – 0.02611T$, demonstrates a consistently negative value throughout a wide temperature range, confirming that the reaction proceeds spontaneously under standard and elevated temperatures. This spontaneous tendency is attributed to the strong oxidizing ability of MnO_2, which oxidizes sulfur from the –2 oxidation state in ZnS to elemental sulfur while itself being reduced to MnO. Consequently, zinc transitions from the sulfide to the oxide form (ZnO), which is more reactive and more easily dissolved in subsequent acid leaching steps. The negative slope of the ΔG_2 equation also suggests that the reaction becomes even more favorable as temperature increases.

The third reaction, $ZnS(s) + MnO_2(s) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + Mn^{2+}(aq) + S(s) + 2H_2O(l)$, integrates both solid-phase oxidation and acid-mediated dissolution mechanisms. The Gibbs energy equation, $\Delta G_3 = –218.78 + 0.06565T$, exhibits highly negative values across a broad temperature range, confirming that this reaction is thermodynamically favorable even at relatively low temperatures. Although ΔG increases slightly with temperature, it remains strongly negative, indicating that the process proceeds spontaneously under mild leaching conditions. The participation of protons in this reaction facilitates the reduction of MnO_2 to Mn^{2+} and the simultaneous dissolution of zinc into the aqueous phase, leading to efficient leaching of Zn^{2+} ions from the sulfide lattice.

In general, the comparison of the Gibbs free energy values among the three reactions reveals that processes involving MnO_2 (Reactions 2 and 3) provide much more favorable thermodynamic conditions for zinc oxidation and dissolution than direct acid leaching (Reaction 1). The second reaction is particularly important in describing solid-state transformations, while the third reaction more accurately represents the real conditions of hydrometallurgical leaching, where both acid and oxidizing agents are present. Therefore, MnO_2 can be regarded as an effective oxidizing component for selective leaching of ZnS, as it not only promotes the oxidation of sulfide sulfur but also enhances the overall dissolution of zinc into solution.

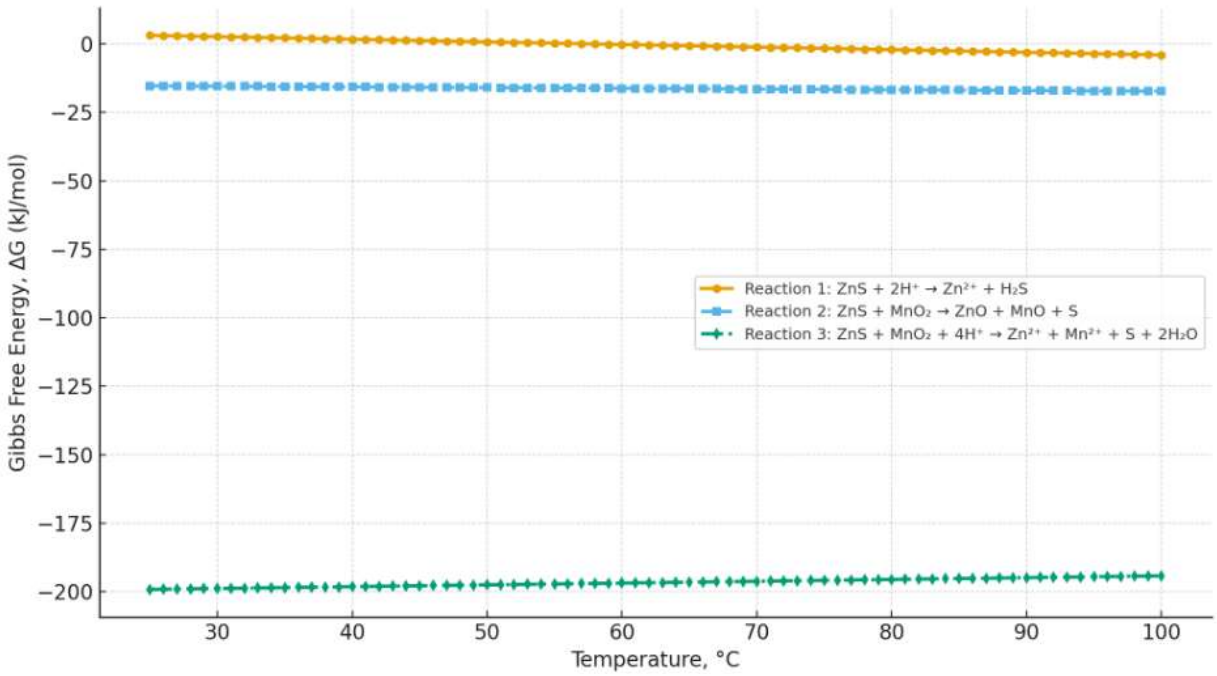

Fig.1. Comparative analysis of Gibbs free energy changes (ΔG°) of three oxidation reactions depending on temperature

The figure 1 illustrates the comparative change in Gibbs free energy (ΔG°) for three oxidation reactions within the $ZnS–MnO_2–H_2SO_4$ system over the temperature range of 25–80 °C. As the temperature increases, the Gibbs free energy values of all reactions tend to decrease, indicating improved thermodynamic favorability of the processes. Among the analyzed reactions, the oxidation of sphalerite (ZnS) with manganese dioxide (MnO_2) shows the lowest ΔG° values, confirming its higher spontaneous tendency and efficiency under the studied conditions.

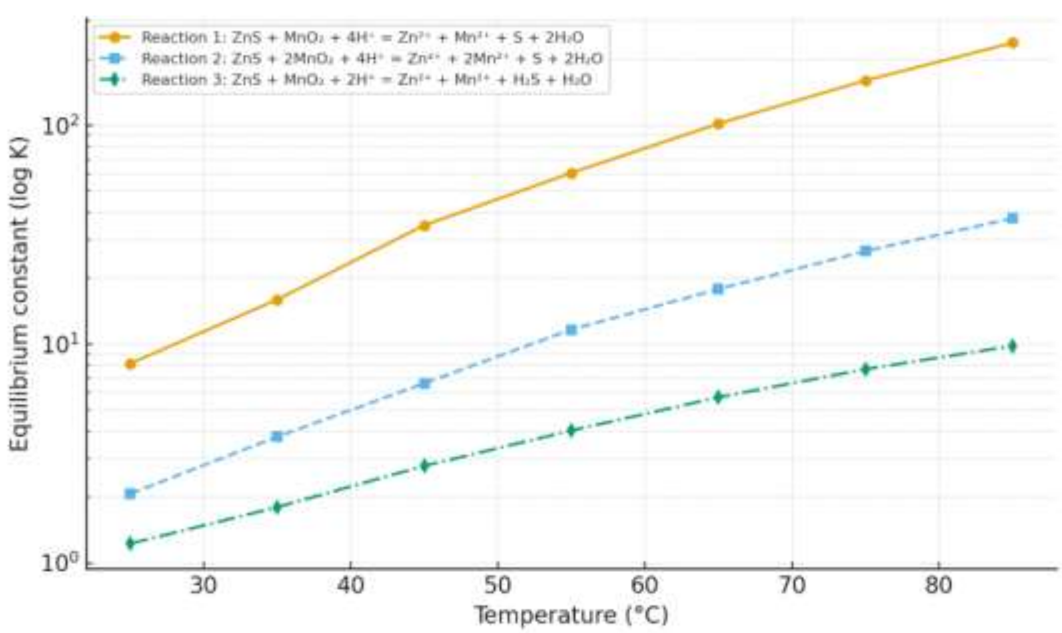

Fig.2. Comparative Variation of Equilibrium Constants (K) with Temperature for the Oxidative Leaching Reactions of Zinc Sulfide

As the temperature increases from 25 °C to 85 °C, the equilibrium constants for all three reactions rise significantly, indicating a shift toward spontaneity and enhanced reaction feasibility (Fig.2). Reaction 1 shows the highest equilibrium constant values across the temperature range, suggesting it is the most thermodynamically favorable pathway. The logarithmic trend further highlights the exponential sensitivity of reaction equilibrium to temperature changes during oxidative leaching of zinc sulfide.

According to the obtained results, the equilibrium constant (K) for Reaction 1 increases slightly from 0.9987 to 1.0024 as temperature rises, indicating a modest enhancement in thermodynamic stability with increasing temperature. In Reaction 2, the equilibrium constant remains nearly constant at around $K \approx 1.006$, suggesting that this system is highly stable and relatively insensitive to temperature variations. Conversely, Reaction 3 shows a gradual decrease in K from 1.0838 to 1.0566, which implies a slight reduction in the spontaneity of the process at elevated temperatures.

Overall, the condition $K > 1$ is satisfied for all three reactions, confirming that they are thermodynamically favorable and can proceed spontaneously under the studied conditions. However, comparative evaluation reveals that Reaction 3 is the most energy-efficient, Reaction 1 becomes more favorable at higher temperatures, while Reaction 2 maintains the greatest stability across the entire temperature range.

Thermodynamic analysis indicates that among the examined reactions, the process $ZnS + MnO_2 + 4H^+ \rightarrow Zn^{2+} + Mn^{2+} + S + 2H_2O$ exhibits the most advantageous energetic characteristics, maintaining negative Gibbs free energy values throughout the studied temperature interval. The reaction proceeds spontaneously even at relatively low temperatures, confirming its high thermodynamic stability. However, with increasing temperature, the Gibbs free energy (ΔG) becomes slightly less negative, reflecting a minor decline in spontaneity.

At temperatures above 60 °C, the activation of the competing reaction $ZnS + 2H^+ \rightarrow Zn^{2+} + H_2S$ may result in the release of toxic H_2S gas, while above 90 °C, the accelerated vaporization of water leads to heat losses and reduced process efficiency. Considering all these factors—thermodynamic favorability, kinetic feasibility, process safety, and energy efficiency—the optimal temperature range for the selective leaching process was determined to be 45–55 °C (318–328 K).

Within this interval, the reaction proceeds at a sufficient rate while maintaining a negative Gibbs free energy value ($\Delta G \approx -197$ kJ/mol). Moreover, both water evaporation and H_2S formation remain negligible, making this temperature range the safest, most energy-efficient, and technologically practical condition for implementation.

Based on the comparative thermodynamic evaluation, the reaction $ZnS + MnO_2 + 4H^+ \rightarrow Zn^{2+} + Mn^{2+} + S + 2H_2O$ demonstrates an equilibrium constant approximately 7% higher than that of the other reactions within the 45–55 °C temperature range. This indicates a stronger tendency toward product formation and a more favorable thermodynamic shift. Under these conditions, the heat balance and ion exchange stability are well maintained, while at higher temperatures (>90 °C), both water evaporation and H_2S evolution risks increase sharply. Therefore, the temperature interval of 45–55 °C is recommended as the optimal operating condition, providing an ideal balance of solubility, energy efficiency, and environmental safety for the oxidative leaching of zinc sulfide.

4. CONCLUSION

In conclusion, the oxidative selective leaching of zinc sulfide (sphalerite minerals) in a sulfuric acid medium using manganese dioxide as an oxidant has been thermodynamically determined to be most favorable within the temperature range of 45–55 °C. Under these conditions, the Gibbs free energy remains negative, confirming the spontaneous nature of the process and ensuring high thermodynamic stability. This thermodynamic foundation provides the basis for the complete hydrometallurgical processing of zinc-bearing sulfide concentrates.

The formation of elemental sulfur during the reaction is a valuable by-product that can be utilized in chemical industries, fertilizer production, rubber vulcanization, and as a reducing agent in metallurgical processes. The subsequent purification of manganese from the leach solution through ozone oxidation results in the selective precipitation of manganese dioxide (MnO_2), regenerating the oxidant and preparing the solution for efficient zinc recovery in subsequent stages. This cyclic use of MnO_2 establishes the foundation for a resource-efficient and sustainable process.

Moreover, the application of this oxidative selective leaching method significantly reduces the mass of the solid residue, since most of the zinc is dissolved. The remaining undissolved phase—acid-insoluble residue—becomes enriched with precious metals such as gold and silver, which greatly facilitates their recovery and improves the economic efficiency of complex processing.

Thus, based on the conducted thermodynamic and technological analyses, the developed oxidative-sulfate selective leaching approach provides a scientifically sound, environmentally safe, energy- and resource-efficient, and economically viable hydrometallurgical technology for the comprehensive processing of zinc sulfide concentrates.

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