THERMODYNAMIC INSIGHTS INTO METALLIC IRON-ASSISTED REDUCTION OF SPINEL FERRITES IN ZINC HYDROMETALLURGICAL RESIDUES

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Abstract. The thermodynamic feasibility of reduction-assisted dissolution of spinel-type ferrites ($ZnFe_2O_4$, $CuFe_2O_4$, and $CdFe_2O_4$) in zinc hydrometallurgical residues was investigated using metallic iron as a reducing agent. Gibbs free energy calculations revealed that the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ is spontaneous over the entire temperature range (298–1288 K), whereas $CuFe_2O_4$ reduction requires elevated temperatures (~580–600 K) to become thermodynamically favorable, identifying it as the rate-limiting reaction. An operational window of 600–650 K is recommended to achieve effective ferrite reduction while minimizing energy consumption and avoiding adverse solid-state effects. The formation of Fe^{2+} and divalent metal oxides improves subsequent acid leaching of zinc, copper, and cadmium, supporting efficient recovery of valuable metals from industrial residues. The study provides a thermodynamic basis for developing integrated hydrometallurgical processes for sustainable metal recovery and waste management.

Keywords: Ferrite reduction, zinc hydrometallurgical residues, metallic iron, Gibbs free energy, thermodynamic analysis, spinel ferrites, metal recovery, acid leaching.

Аннотация: Изучена термодинамическая возможность восстановления ферритов шпинельного типа ($ZnFe_2O_4$, $CuFe_2O_4$ и $CdFe_2O_4$) из цинковых гидрометаллургических отходов с использованием металлического железа в качестве восстановителя. Расчёты изменения свободной энергии Гиббса показали, что восстановление $ZnFe_2O_4$ и $CdFe_2O_4$ спонтанно во всем диапазоне температур (298–1288 K), тогда как восстановление $CuFe_2O_4$ термодинамически благоприятно только при повышенных температурах (~580–600 K), что определяет его как лимитирующую реакцию.

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Рекомендуемый температурный диапазон для эффективного восстановления ферритов составляет 600–650 K, что позволяет минимизировать энергозатраты и избежать неблагоприятных эффектов твердого состояния. Образование Fe^{2+} и двухвалентных оксидов металлов улучшает последующее кислотное выщелачивание цинка, меди и кадмия, способствуя эффективному извлечению ценных металлов из промышленных отходов. Исследование предоставляет термодинамическую основу для разработки интегрированных гидрометаллургических процессов устойчивого извлечения металлов и управления отходами.

Ключевые слова: Восстановление ферритов, гидрометаллургические отходы цинка, металлическое железо, свободная энергия Гиббса, термодинамический анализ, ферриты шпинельного типа, извлечение металлов, кислотное выщелачивание.

Annotatsiya. Tadqiqotda metallik temirni reduktor sifatida qo‘llagan holda tsink gidrometallurgik chiqindilaridagi spinel turidagi ferritlar ($ZnFe_2O_4$, $CuFe_2O_4$ va $CdFe_2O_4$)ning reduksiya yordamida eritilishining termodinamik imkoniyatlari o‘rganildi. Gibbs erkin energiyasi hisob-kitoblari $ZnFe_2O_4$ va $CdFe_2O_4$ ning 298–1288 K diapazonida spontanniy ekanligini, $CuFe_2O_4$ ning esa termodinamik jihatdan foydali bo‘lishi uchun yuqori harorat (~580–600 K) talab qilinishini ko‘rsatdi, bu esa uni jarayonning cheklovchi reaksiyasi sifatida belgilaydi. Ferritlarning samarali reduksiyasini ta’minlash va energiya sarfini kamaytirish uchun 600–650 K harorat oralig‘i tavsiya etiladi. Fe^{2+} va ikki valentli metall oksidlar hosil bo‘lishi tsink, mis va kadmiyning keyingi kislotali eritilish samaradorligini oshiradi va sanoat chiqindilaridan qimmatbaho metallarning samarali tiklanishini qo‘llab-quvvatlaydi. Tadqiqot integratsiyalashgan gidrometallurgik jarayonlarni ishlab chiqish uchun termodinamik asos yaratadi, bu esa metallarni tiklash va chiqindilarni boshqarishni barqaror qilishi mumkin.

Kalit so‘zlar: Ferrit reduksiyasi, rux gidrometallurgik chiqindilari, metallik temir, Gibbs erkin energiyasi, termodinamik tahlil, spinel ferritlar, metall tiklash, kislotali eritish.

Introduction.

The sustainable management of zinc hydrometallurgical residues has become an increasingly important issue for both environmental protection and resource recovery [1]. These residues, commonly known as leach cakes, are produced after the selective leaching of zinc plant wastes and typically contain significant amounts of valuable metals such as zinc, copper, cadmium, and iron in oxide forms [2]. Efficient utilization of these by-products is of great importance for minimizing hazardous waste generation and promoting the circular economy principles within the non-ferrous metallurgy sector [3].

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The main challenge in processing these residues lies in the low solubility of certain metallic compounds that persist in the solid phase after conventional acid leaching [4-5]. In particular, zinc, copper, cadmium, and iron often remain in the residue as spinel-type ferrites such as $ZnFe_2O_4$, $CuFe_2O_4$, and $CdFe_2O_4$ [6-8]. These compounds are known for their highly stable crystal structures and strong resistance to both acidic and alkaline dissolution [9]. Consequently, a considerable fraction of valuable metals remains unrecovered, which reduces the overall efficiency of hydrometallurgical extraction processes [10].

Despite numerous studies devoted to improving the leachability of ferrite-type compounds, most approaches rely on extreme process conditions or complex chemical reagents, which limit their industrial applicability [11-12]. The reduction of trivalent iron (Fe^{3+}) to divalent iron (Fe^{2+}) within the spinel lattice is a promising route to enhance dissolution, as it destabilizes the crystal structure and facilitates the subsequent acid leaching of the associated metal oxides. However, the thermodynamic feasibility and efficiency of such reduction-assisted leaching remain insufficiently explored, especially under practical process conditions and for locally generated zinc residues [13-14].

In the context of Uzbekistan's zinc production industry, large amounts of leach residues containing ferritic phases are accumulated annually. Their effective processing represents not only an environmental necessity but also a potential secondary source of valuable non-ferrous metals. Local zinc hydrometallurgical residues typically exhibit high concentrations of iron ferrites, making them ideal for studying reduction-based leaching strategies [15].

Therefore, the present study aims to perform a comprehensive thermodynamic analysis of the reduction-assisted dissolution of spinel-type ferrites found in zinc plant residues [16]. Metallic iron powder is proposed as a reducing agent to convert Fe^{3+} to Fe^{2+} species, thereby increasing the solubility of zinc, copper, and cadmium in sulfuric acid media. The findings of this study are expected to provide fundamental insight into the redox behavior of ferrite systems and to support the development of efficient hydrometallurgical processes for the recovery of valuable metals from zinc plant wastes [17-18].

Materials and Methods. The thermodynamic behavior of spinel-type ferrite compounds in contact with metallic iron was studied to evaluate the feasibility of reduction-assisted dissolution of zinc, copper, and cadmium ferrites in sulfuric acid media. The reactions considered in this study were as follows:

$$ZnFe_2O_4 + Fe = ZnO + 3FeO \quad (1)$$

$$CuFe_2O_4 + Fe = CuO + 3FeO \quad (2)$$

$$CdFe_2O_4 + Fe = CdO + 3FeO \quad (3)$$

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These reactions represent the reduction of trivalent iron (Fe^{3+}) within the ferrite lattice to divalent iron (Fe^{2+}), accompanied by the formation of more soluble divalent metal oxides (ZnO, CuO, CdO). Metallic iron was selected as the reducing agent due to its low cost, availability, and favorable redox potential relative to the Fe^{3+}/Fe^{2+} couple.

Standard thermodynamic parameters for all solid and oxide species were taken from the JANAF Thermochemical Tables, HSC Chemistry 9.0 database, and verified with values reported in the FactSage 8.2 thermodynamic database. The standard enthalpy of formation ($\Delta H°_{(298)}$), standard entropy ($S°_{(298)}$), and heat capacity (C_p) data were used to compute the Gibbs free energy ($\Delta G°$) as a function of temperature.

Thermodynamic calculations were carried out in the temperature range of 298–1273 K to simulate the conditions relevant to industrial leaching and roasting processes. The Gibbs free energy change ($\Delta G°$) for each reaction was calculated according to the following equation:

$$\Delta G^\circ{}_T = \Delta H^\circ{}_{298} - T\Delta S^\circ{}_{298} + \int_{298}^{T} \Delta C_p dT - T\int_{298}^{T} \frac{\Delta C_p}{T} dT \quad (4)$$

Where ΔC_p is the difference in heat capacities between products and reactants. The equilibrium constant K was determined using the standard thermodynamic relationship:

$$\ln K = -\frac{\Delta G^\circ{}_T}{RT} \quad (5)$$

Where R is the universal gas constant and T the absolute temperature. Negative values of $\Delta G°$ and large values of K indicate spontaneous and thermodynamically favorable reactions.

The temperature dependence of $\Delta G°$ and log K was analyzed to determine the stability domains of the products and to identify the temperature ranges at which the reduction of ferrites by metallic iron becomes feasible. Comparative assessment of reactions (1)–(3) allowed for the evaluation of the relative reducibility of $ZnFe_2O_4$, $CuFe_2O_4$, and $CdFe_2O_4$. All thermodynamic computations were performed using HSC Chemistry 9.0 software, supplemented with manual verification through classical thermodynamic equations.

Results and discussion. In order to organize a clear and consistent discussion, comparative thermodynamic analysis was carried out according to a certain sequence (algorithm). At this stage of the research, three main chemical reactions were selected, primarily aimed at reducing the trivalent iron in the above-mentioned ferrites to the bivalent state. The stoichiometric equations of these reactions, as well as the Gibbs free energy equations compiled accordingly, are presented in Table 1.

ISSN 3030-3907

Table 1.

Gibbs free energy equations for ferrite reduction reactions

№	Chemical reaction	Gibbs energy equation
1.	$ZnFe_2O_4 + Fe = ZnO + 3FeO$	ΔG1=-31.8-0.08462*T
2.	$CuFe_2O_4 + Fe = CuO + 3FeO$	ΔG2= 53.80-0.09257*T
3.	$CdFe_2O_4 + Fe = CdO + 3FeO$	ΔG3= -69.35-0.10177*T

Table 1 presents the Gibbs free energy equations derived for the solid-state reduction of zinc, copper, and cadmium ferrites by metallic iron. The obtained temperature-dependent expressions demonstrate that the spontaneity of each reaction increases with rising temperature, as indicated by the negative coefficients of the entropy term (–TΔS).

Among the studied systems, the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ (Equations 1 and 3) exhibits negative ΔG° values under standard conditions, suggesting that these reactions are thermodynamically favorable even at ambient temperature. In contrast, the $CuFe_2O_4$ reduction reaction (Equation 2) shows a positive Gibbs free energy ($\Delta G^\circ > 0$) at 298 K, implying that it is non-spontaneous at lower temperatures and becomes feasible only at elevated temperatures (above approximately 580 K).

Overall, the obtained Gibbs energy functions confirm that the application of metallic iron as a reducing agent can effectively destabilize ferrite spinels by converting Fe^{3+} to Fe^{2+}, thereby facilitating the liberation of Zn, Cu, and Cd as more soluble oxide forms in subsequent hydrometallurgical processing.

Table 2.

Variation of Gibbs free energy and equilibrium constants with temperature for ferrite reduction reactions

№	Temperature		Gibbs energy, kJ/mol			Equilibrium constant		
	T (K)	T (°C)	ΔG_1	ΔG_2	ΔG_3	K_1	K_2	K_3
1	298	25	-57,02	26,21	-99,68	1,0233	0,9895	1,0411
2	308	35	-57,86	25,29	-100,70	1,0229	0,9902	1,0401
3	318	45	-58,71	24,36	-101,71	1,0225	0,9908	1,0392
4	328	55	-59,56	23,44	-102,73	1,0221	0,9914	1,0384
5	338	65	-60,40	22,51	-103,75	1,0217	0,9920	1,0376
6	348	75	-61,25	21,59	-104,77	1,0214	0,9926	1,0369
7	358	85	-62,09	20,66	-105,78	1,0211	0,9931	1,0362
8	368	95	-62,94	19,73	-106,80	1,0208	0,9936	1,0355
9	378	105	-63,79	18,81	-107,82	1,0205	0,9940	1,0349
10	388	115	-64,63	17,88	-108,84	1,0202	0,9945	1,0343

ISSN 3030-3907

11	398	125	-65,48	16,96	-109,85	1,0200	0,9949	1,0338
12	408	135	-66,32	16,03	-110,87	1,0198	0,9953	1,0332
13	418	145	-67,17	15,11	-111,89	1,0195	0,9957	1,0327
14	428	155	-68,02	14,18	-112,91	1,0193	0,9960	1,0323
15	438	165	-68,86	13,25	-113,93	1,0191	0,9964	1,0318
16	448	175	-69,71	12,33	-114,94	1,0189	0,9967	1,0314
17	458	185	-70,56	11,40	-115,96	1,0187	0,9970	1,0309
18	468	195	-71,40	10,48	-116,98	1,0185	0,9973	1,0305
19	478	205	-72,25	9,55	-118,00	1,0184	0,9976	1,0302
20	488	215	-73,09	8,63	-119,01	1,0182	0,9979	1,0298
21	498	225	-73,94	7,70	-120,03	1,0180	0,9981	1,0294
22	508	235	-74,79	6,77	-121,05	1,0179	0,9984	1,0291
23	518	245	-75,63	5,85	-122,07	1,0177	0,9986	1,0288
24	528	255	-76,48	4,92	-123,08	1,0176	0,9989	1,0284
25	538	265	-77,33	4,00	-124,10	1,0174	0,9991	1,0281
26	548	275	-78,17	3,07	-125,12	1,0173	0,9993	1,0279
27	558	285	-79,02	2,15	-126,14	1,0172	0,9995	1,0276
28	568	295	-79,86	1,22	-127,16	1,0171	0,9997	1,0273
29	578	305	-80,71	0,29	-128,17	1,0169	0,9999	1,0270
30	588	315	-81,56	-0,63	-129,19	1,0168	1,0001	1,0268
31	598	325	-82,40	-1,56	-130,21	1,0167	1,0003	1,0265
32	608	335	-83,25	-2,48	-131,23	1,0166	1,0005	1,0263
33	618	345	-84,10	-3,41	-132,24	1,0165	1,0007	1,0261
34	628	355	-84,94	-4,33	-133,26	1,0164	1,0008	1,0259
35	638	365	-85,79	-5,26	-134,28	1,0163	1,0010	1,0257
36	648	375	-86,63	-6,19	-135,30	1,0162	1,0011	1,0254
37	658	385	-87,48	-7,11	-136,31	1,0161	1,0013	1,0252
38	668	395	-88,33	-8,04	-137,33	1,0160	1,0014	1,0250
39	678	405	-89,17	-8,96	-138,35	1,0160	1,0016	1,0249
40	688	415	-90,02	-9,89	-139,37	1,0159	1,0017	1,0247
41	698	425	-90,86	-10,81	-140,39	1,0158	1,0019	1,0245
42	708	435	-91,71	-11,74	-141,40	1,0157	1,0020	1,0243
43	718	445	-92,56	-12,67	-142,42	1,0156	1,0021	1,0242
44	728	455	-93,40	-13,59	-143,44	1,0156	1,0022	1,0240
45	738	465	-94,25	-14,52	-144,46	1,0155	1,0024	1,0238
46	748	475	-95,10	-15,44	-145,47	1,0154	1,0025	1,0237
47	758	485	-95,94	-16,37	-146,49	1,0153	1,0026	1,0235

ISSN 3030-3907

48	768	495	-96,79	-17,29	-147,51	1,0153	1,0027	1,0234
49	778	505	-97,63	-18,22	-148,53	1,0152	1,0028	1,0232
50	788	515	-98,48	-19,15	-149,54	1,0152	1,0029	1,0231
51	798	525	-99,33	-20,07	-150,56	1,0151	1,0030	1,0230
52	808	535	-100,17	-21,00	-151,58	1,0150	1,0031	1,0228
53	818	545	-101,02	-21,92	-152,60	1,0150	1,0032	1,0227
54	828	555	-101,87	-22,85	-153,62	1,0149	1,0033	1,0226
55	838	565	-102,71	-23,77	-154,63	1,0149	1,0034	1,0225
56	848	575	-103,56	-24,70	-155,65	1,0148	1,0035	1,0223
57	858	585	-104,40	-25,63	-156,67	1,0148	1,0036	1,0222
58	868	595	-105,25	-26,55	-157,69	1,0147	1,0037	1,0221
59	878	605	-106,10	-27,48	-158,70	1,0146	1,0038	1,0220
60	888	615	-106,94	-28,40	-159,72	1,0146	1,0039	1,0219
61	898	625	-107,79	-29,33	-160,74	1,0145	1,0039	1,0218
62	908	635	-108,63	-30,25	-161,76	1,0145	1,0040	1,0217
63	918	645	-109,48	-31,18	-162,77	1,0145	1,0041	1,0216
64	928	655	-110,33	-32,10	-163,79	1,0144	1,0042	1,0215
65	938	665	-111,17	-33,03	-164,81	1,0144	1,0042	1,0214
66	948	675	-112,02	-33,96	-165,83	1,0143	1,0043	1,0213
67	958	685	-112,87	-34,88	-166,85	1,0143	1,0044	1,0212
68	968	695	-113,71	-35,81	-167,86	1,0142	1,0045	1,0211
69	978	705	-114,56	-36,73	-168,88	1,0142	1,0045	1,0210
70	988	715	-115,40	-37,66	-169,90	1,0142	1,0046	1,0209
71	998	725	-116,25	-38,58	-170,92	1,0141	1,0047	1,0208
72	1008	735	-117,10	-39,51	-171,93	1,0141	1,0047	1,0207
73	1018	745	-117,94	-40,44	-172,95	1,0140	1,0048	1,0207
74	1028	755	-118,79	-41,36	-173,97	1,0140	1,0049	1,0206
75	1038	765	-119,64	-42,29	-174,99	1,0140	1,0049	1,0205
76	1048	775	-120,48	-43,21	-176,00	1,0139	1,0050	1,0204
77	1058	785	-121,33	-44,14	-177,02	1,0139	1,0050	1,0203
78	1068	795	-122,17	-45,06	-178,04	1,0139	1,0051	1,0203
79	1078	805	-123,02	-45,99	-179,06	1,0138	1,0051	1,0202
80	1088	815	-123,87	-46,92	-180,08	1,0138	1,0052	1,0201
81	1098	825	-124,71	-47,84	-181,09	1,0138	1,0053	1,0200
82	1108	835	-125,56	-48,77	-182,11	1,0137	1,0053	1,0200
83	1118	845	-126,41	-49,69	-183,13	1,0137	1,0054	1,0199
84	1128	855	-127,25	-50,62	-184,15	1,0137	1,0054	1,0198

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85	1138	865	-128,10	-51,54	-185,16	1,0136	1,0055	1,0198
86	1148	875	-128,94	-52,47	-186,18	1,0136	1,0055	1,0197
87	1158	885	-129,79	-53,40	-187,20	1,0136	1,0056	1,0196
88	1168	895	-130,64	-54,32	-188,22	1,0136	1,0056	1,0196
89	1178	905	-131,48	-55,25	-189,24	1,0135	1,0057	1,0195
90	1188	915	-132,33	-56,17	-190,25	1,0135	1,0057	1,0195
91	1198	925	-133,17	-57,10	-191,27	1,0135	1,0058	1,0194
92	1208	935	-134,02	-58,02	-192,29	1,0134	1,0058	1,0193
93	1218	945	-134,87	-58,95	-193,31	1,0134	1,0058	1,0193
94	1228	955	-135,71	-59,88	-194,32	1,0134	1,0059	1,0192
95	1238	965	-136,56	-60,80	-195,34	1,0134	1,0059	1,0192
96	1248	975	-137,41	-61,73	-196,36	1,0133	1,0060	1,0191
97	1258	985	-138,25	-62,65	-197,38	1,0133	1,0060	1,0191
98	1268	995	-139,10	-63,58	-198,39	1,0133	1,0061	1,0190
99	1278	1005	-139,94	-64,50	-199,41	1,0133	1,0061	1,0190
100	1288	1015	-140,79	-65,43	-200,43	1,0132	1,0061	1,0189

Table 2 summarizes the calculated Gibbs free energy (ΔG) and equilibrium constant (K_m) values for the reduction reactions of zinc, copper, and cadmium ferrites by metallic iron over the temperature range of 298–1288 K. The data reveal a clear temperature dependence of the reactions' thermodynamic favorability.

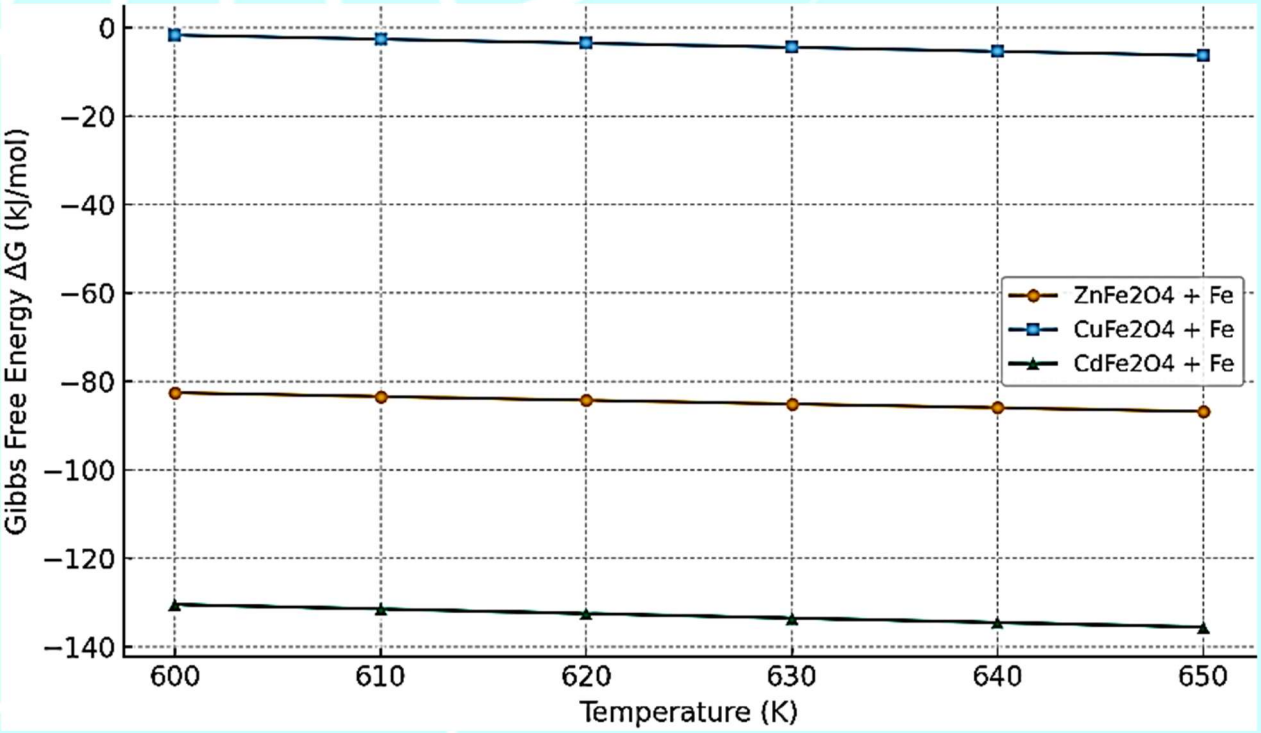


Fig.1. Influence of temperature on Gibbs energy during the reduction of ferrites with metallic iron

For $ZnFe_2O_4$ and $CdFe_2O_4$, the ΔG values remain negative across the entire temperature interval, indicating that these reactions are spontaneous at standard and

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elevated temperatures. Moreover, their equilibrium constants (K_1 and $K_3 > 1$) slightly decrease with temperature, suggesting that the reactions are strongly product-favored and thermodynamically stable even at higher temperatures.

In contrast, the $CuFe_2O_4 + Fe \rightarrow CuO + 3FeO$ reaction exhibits positive ΔG values at low temperatures, confirming its non-spontaneous nature near ambient conditions. However, as temperature increases, ΔG gradually decreases and crosses into the negative range near 580–600 K (Figure 1), where K_2 approaches unity ($K_2 \approx 1$) (Figure 2). This transition indicates that the reaction becomes thermodynamically feasible at moderate to high temperatures, consistent with the positive entropy change ($\Delta S > 0$) obtained from the Gibbs energy equation.

Overall, the observed trends confirm that temperature plays a decisive role in the stability and reducibility of ferrite spinels. The reactions involving Zn and Cd ferrites are thermodynamically more favorable than that of Cu ferrite, implying that the selective reduction of Zn^{2+} and Cd^{2+} species from mixed ferritic residues may occur preferentially during thermal or hydrometallurgical processing.

Among the three investigated reduction reactions, the $CuFe_2O_4 + Fe = CuO + 3FeO$ reaction can be identified as the limiting (rate-determining) reaction in the overall ferrite reduction system. This conclusion is supported by both the Gibbs free energy and equilibrium constant data.

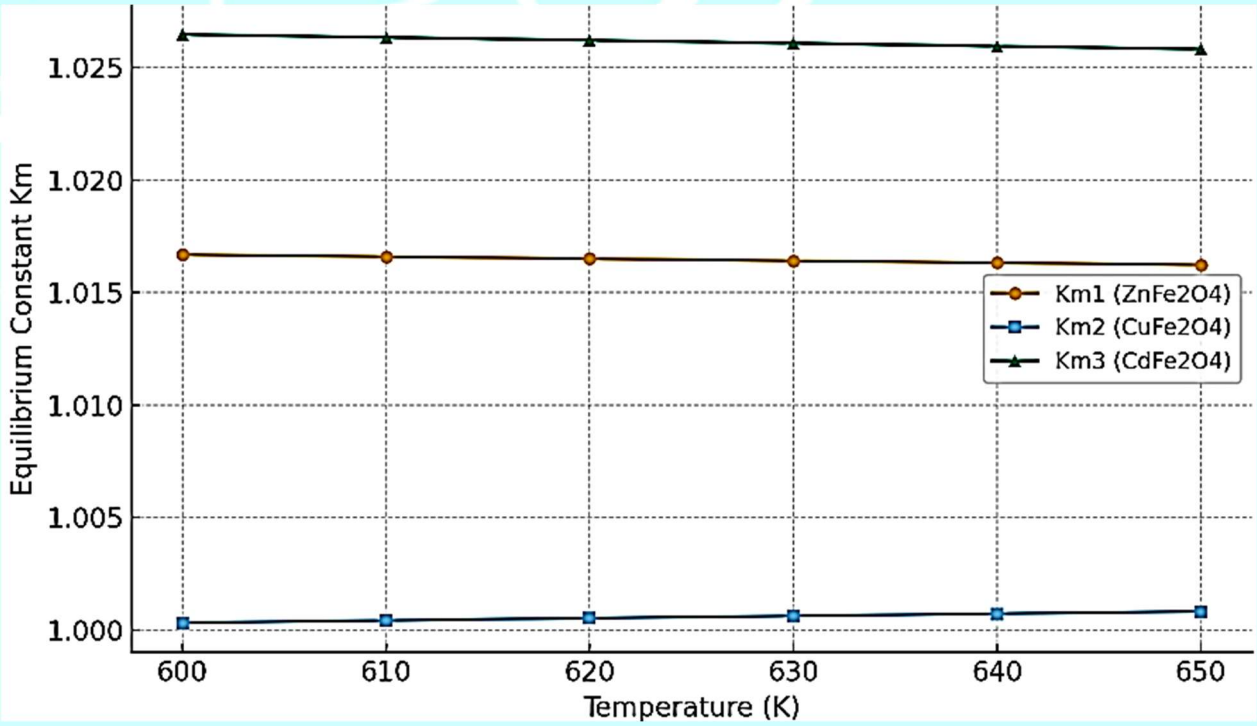


Fig.2. Influence of temperature on the equilibrium constant during the reduction of ferrites with metallic iron

At standard temperature (298 K), the $CuFe_2O_4$ reduction exhibits a positive Gibbs free energy value ($\Delta G° = +53.8$ kJ/mol), indicating that the process is non-spontaneous under ambient conditions. In contrast, the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ show negative $\Delta G°$ values (–31.8 and –69.35 kJ/mol, respectively), which

ISSN 3030-3907

means that they proceed spontaneously even without external energy input. As temperature increases, ΔG for the $CuFe_2O_4$ reaction gradually decreases and becomes negative only above approximately 580–600 K, where the equilibrium constant (K_2) approaches unity and then exceeds 1.

This thermodynamic behavior demonstrates that the $CuFe_2O_4$ reduction requires higher thermal activation to overcome its positive Gibbs free energy barrier. Consequently, it represents the thermodynamically least favorable step and thus acts as the limiting reaction that governs the overall reduction sequence of mixed ferrite phases in the residue.

In practical terms, this implies that during the reductive treatment of ferritic waste materials, the complete reduction of $CuFe_2O_4$ will occur only after the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ has already taken place. Therefore, the $CuFe_2O_4$ +Fe → CuO + 3FeO transformation determines the minimum operational temperature and energy requirement for effective spinel breakdown and subsequent metal recovery in hydrometallurgical processes.

The thermodynamic dataset in Table 2 and Figure 1 indicates that the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ by metallic iron is spontaneous across the entire examined temperature range (298–1288 K), whereas the reduction of $CuFe_2O_4$ is non-spontaneous at ambient temperature and becomes thermodynamically feasible only at elevated temperature. Consequently, the selection of an operational temperature must be driven by the requirement to render the Cu-ferrite reaction exergonic while avoiding unnecessary thermal penalties or deleterious microstructural changes to the solids.

From the calculated Gibbs energy functions and the tabulated values, the Cu-ferrite reaction $\Delta G_2(T)$ crosses zero between 580 and 600 K (≈307–327 °C). At temperatures slightly above this transition (for example 598–608 K in Table 2), ΔG_2 becomes modestly negative (≈ −1 to −2 kJ·mol^{-1}) and the corresponding equilibrium constant (K_2) reaches values close to unity and then exceeds 1. At the same temperature interval the Zn- and Cd-reduction reactions are already strongly exergonic (ΔG_1 and ΔG_3 remain highly negative), so the entire set of target reductions can proceed under a common thermal regime.

Balancing thermodynamic driving force, energy consumption, and potential adverse effects of high temperature (particle sintering, phase transformations, enhanced solid state diffusion that may retard productive leaching kinetics, and increased equipment/corrosion demands), we recommend an operating window of approximately 600–650 K (≈327–377 °C) as the optimal compromise for thermochemical pretreatment:

• Thermodynamic rationale. At ~600 K the Cu-ferrite reduction is marginally exergonic and the equilibrium shifts in favor of product formation; Zn- and Cd-

ISSN 3030-3907

ferrite reductions are already strongly favoured (large negative ΔG). This ensures that all three spinel phases are thermodynamically susceptible to reduction by metallic iron in the same thermal treatment.

• Kinetic and practical rationale. Temperatures near 600–650 K are high enough to accelerate solid-state reaction rates and interfacial redox exchange between metallic iron and the spinel lattice, yet remain below temperatures where extensive sintering, grain growth, or unwanted secondary phase formation are typically dominant in oxide systems. Operating in this window also limits energy consumption relative to much higher temperatures while providing sufficient driving force for conversion within industrially reasonable residence times.

• Process integration rationale. Producing Fe^{2+} (as FeO) and divalent metal oxides at ~600–650 K is advantageous for subsequent sulfuric acid leaching: the presence of Fe^{2+} and divalent metal oxides improves the leachability of Zn, Cu and Cd versus their ferritic (Fe^{3+}-containing) counterparts. Thus the recommended temperature window promotes downstream hydrometallurgical recovery efficiency without imposing excessive thermal costs.

Finally, it is important to emphasize that the thermodynamic recommendation should be validated experimentally under realistic process conditions. Key operational variables that will influence the practical optimum include: particle size and specific surface area of the cake, the stoichiometric ratio of metallic iron to ferrite phases (an iron excess is commonly advisable), ambient gas atmosphere (inert or mildly reducing to avoid unwanted oxidation of metallic iron), residence time, and heating/cooling rates. We therefore recommend pilot-scale trials within the 600–650 K window to determine the minimal temperature–time combination that achieves target conversion, followed by kinetic modelling to refine industrial setpoints.

Conclusion. The present study provides a comprehensive thermodynamic assessment of the reduction-assisted dissolution of spinel-type ferrites ($ZnFe_2O_4$, $CuFe_2O_4$, and $CdFe_2O_4$) in zinc hydrometallurgical residues using metallic iron as a reducing agent. The Gibbs free energy analysis demonstrates that the reduction of $ZnFe_2O_4$ and $CdFe_2O_4$ is spontaneous across the entire examined temperature range (298–1288 K), indicating their high thermodynamic susceptibility to $Fe^{3+} \rightarrow Fe^{2+}$ conversion. In contrast, $CuFe_2O_4$ exhibits positive Gibbs free energy at ambient temperature and becomes thermodynamically favorable only above approximately 580–600 K, identifying it as the rate-limiting reaction in the overall ferrite reduction sequence.

The thermodynamic data suggest that a thermal pretreatment in the range of 600–650 K provides an optimal compromise, ensuring the effective reduction of all three ferrite phases while minimizing energy consumption and avoiding

ISSN 3030-3907

excessive solid-state sintering or unwanted phase transformations. At this temperature window, Fe^{2+} generation and formation of divalent metal oxides (ZnO, CuO, CdO) enhance the subsequent acid leaching efficiency of valuable metals from residues.

Overall, the study confirms that metallic iron-assisted reduction is a viable thermochemical strategy to destabilize spinel ferrites in zinc plant residues. The findings establish a fundamental thermodynamic basis for designing integrated hydrometallurgical processes that improve the recovery of zinc, copper, and cadmium while supporting sustainable management of industrial wastes. Experimental validation under realistic process conditions is recommended to optimize operational parameters such as particle size, iron stoichiometry, atmosphere, and residence time, facilitating the translation of these thermodynamic insights into practical industrial applications.

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