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Modeling, Simulation, and Thermodynamic parameters: Nonlinear Studies of Co, Ni, and Cu Leaching processes

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Abstract: The leaching of Co, Ni, and Cu isotherms, kinetic modeling approaches, and thermodynamics features have been studied mathematically through the sulfuric acid chemical leaching process by solving the nonlinear equations using the MATLAB code. The chemical characterization of the ore sample was recorded as Al_2O_3(27%) > SiO_2 (13.5%) > Fe_2O_3 (12.3%) > MnO (8.4%) > CaO (6.5%) > MgO (4.7%), in addition to, Co, Ni, and Cu were assaying 1000, 730 and 1900 ppm, respectively. The effects of some parameters such as grain size, solid/liquid ratio, sulfuric acid concentration, contact time, and absolute temperature were investigated. The physical phenomena of the leaching process were determined by the shrinking core model which indicated that the particle size and the responding nucleus of metal ions decreased simultaneously; also, the dissolution rate of the reaction was identified as solid diffusion or mixed between chemical and solid for Cu ions and film diffusion reaction for both Co and Ni ions. The activation energy in the leaching process was evaluated to be 31.20, 15.02, and 13.31 kJ/mol for Co, Ni, and Cu respectively which denoted that the sulfuric acid leaching process was controlled by interfacial chemical reaction. Finally, temperature has a significant impact on the leaching process according to thermodynamic studies. The applied thermodynamic model called the floatotherm model including the Van't Hoff equation described the leaching process for Co, Ni, and Cu as a spontaneous reaction with an endothermic nature.

Keywords: Leaching process; Shrinking core model; Nonlinear kinetics; Conservation ratio; Gibbs free energy, ΔH and ΔS; Floatotherm model including Van't Hoff equation.

1 Introduction

Thermodynamics and kinetics are two essential concepts in many branches of science and engineering, and they play critical roles in many areas such as chemical engineering, metallurgy, biotechnology, food processing, and petroleum engineering. Kinetics may be viewed as a tool for analyzing the rate of chemical reaction and understanding how various processes are influenced whereas thermodynamics is commonly used to forecast and suggest chemical reaction paths, energy, products, and equilibrium conditions. Leaching is a solid-liquid reaction considered as the first and major step of numerous hydrometallurgical processes. Consequently, it is critical to understand processes and mathematical models for leaching kinetics. The most often used way for assessing leaching kinetics is to use the models found by Levenspiel in 1999 for fluid-particle processes. Modeling of aqueous electrolyte solutions obtained from the Leaching process is of immense importance to the development, analysis, design, and control of hydrometallurgical processes [1].

In the leaching process there are various phenomena exist in different scales, to understanding each phenomenon requires a proper choice of scale. The most common model

That can be applied in the leaching process is known as the Progressive conversion model which the solid high porosity enables the liquid phase to penetrate the particles easily. Consequently, the reaction occurs across the volume of the solid particles and the concentration of the non-leached metal compounds is still uniform through the unchanged porous matrix. The second one is the shrinking core model, which depends on the main assumption that the reaction starts from the particle surface and continues until the reaction reaches the particle center. The concept of shrinking the core in the leaching process may happen in three probabilities (Fig. 1); i) Solid phase (a dense solid layer obtained as a product of the reaction covering the non-leached core and the liquid agent needs to diffuse through it) is also known as underflow, ii) Liquid phase mainly solute-rich (the surface of the non-leached core has no solid product and the particle is leached and its size becomes smaller than initial: leached) is also

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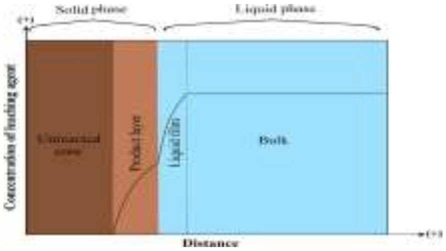

Fig.1: Schematic of leaching steps [2].

known as an overflow stream, iii) Solid-Liquid phase in between the previous phases [2]. When the solute concentrations in the underflow and overflow streams leaving a stage are equal, a solid-liquid stream has reached equilibrium. In hydrometallurgy, the leaching process is the initial stage in the recovery of metals from natural rock samples or secondary sources.

Cobalt is a ferromagnetic metal that is frequently employed in a variety of industrial industries. The most important ores that contain Co are sulphides and arsenides. The principal cobalt sulphide minerals are carrollite ($CuS.Co_2$ S_3) and linnaeite (Co_3S_4), while the chief arsenides are smaltite ($CoAs_2$), cobaltite (CoAsS) and skutterudite ($CoAs_3$). Co has been used to create alloys that are incredibly effective on the other hand because cobalt is a component of vitamin B12 which stimulates the synthesis of red blood cells living things only need very little amounts of metal much higher doses have deadly effects may result in nausea vomiting loss of appetite ringing in the ears nerve damage respiratory illnesses an abnormally large thyroid gland goiter and/or damage to the heart kidneys and/or kidneys. Cobalt and nickel frequently coexist in nature. Cobalt exists in compounds in the minerals of copper and nickel.

Nickel displays ferromagnetic characteristics at temperatures that are close to room temperature the majority of the nickel found on Earth is assumed to be in the planet's core the bulk of nickel is taken from one of two types of ore deposits laterites where the primary ore minerals are nickeliferous limonite and garnierite respectively and magmatic sulfide deposits where pentlandite Ni Fe_9S_8 is the predominant ore material. Today nickel is used in several industrial fields like as the steel industry because it was adapted as a material for electroplating because it does not readily oxidize or rust to produce rechargeable nickel-cadmium (Ni-Cd) batteries and the aerospace industry. It is a major consumer of nickel-based superalloys used to make turbine blades, discs, and other essential components of jet engines. Additionally, land-based combustion turbines, such as those used in electric power generation facilities, utilize nickel-base superalloys. Copper is considered one of the most important metals used in industry due to its electrical, thermal, optical, and catalytic properties [3]. In addition to, copper is quite biologically active, this is due to its tendency to form strong complexes in water or soil with organic ligands containing nitrogen or sulfur. It also forms complexes with some large macromolecules (proteins, nucleotides, etc.). It is found mainly in nature in the form of sulfide and oxide minerals such as malachite [Cu_2 $(OH)_2$ CO_3], azurite [$Cu_3(OH)_2(CO_3)_2$], tenorite (CuO), chrysocolla, bornite, brochantite, enargite, chalcopyrite, chalcocite, or covellite 3-5]. On the other hand, Copper is an essential trace mineral for humans, it is found in all body tissues: the liver, brain, heart, kidneys, and skeletal muscle. Red blood cells are produced by copper, which also supports neuron and immune system cells. It contributes to the creation of energy and aids in the body's ability to absorb iron and produce collagen. Although a deficiency is uncommon, it can cause cardiovascular disease and other issues. One of the significant factors in the leaching application process in the industrial scale that will be useful in a scale-up process is the information about the process mechanism, mathematical model, and constants' value related to that leaching process [6- 8].

The effectiveness of metal dissolving in the leaching agent seems to be influenced by the presence of different valence oxides. There are two frequent oxides of cobalt found are CoO and Co_3O_4, Cobalt (III) is the major form in which cobalt exists however it hardly dissolves in Sulfuric acid [3,4,9] and requires a reducing agent to convert it to a divalent state. In the case of Ni, the occurring oxides are NiO and Ni_2O_3 and sulfuric acid can dissolve NiO [5]. Oxides of the studied sample react with sulfuric acid in the leaching process, generating sulfates including, $CuSO_4$, $CoSO_4$, and $NiSO_4$ (Eq. 1-3) [9,10].

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \qquad (1)$$

$$CoO + H_2SO_4 \rightarrow CoSO_4 + H_2O \qquad (2)$$

$$NiO + H_2SO_4 \rightarrow NiSO_4 + H_2O \qquad (3)$$

Co, Ni, and Cu are now utilized as crucial components in the technical domains. Therefore, this study is aimed at modeling and simulating the leaching process of the metal ions as Co, Ni, and Cu using different concentrations of sulfuric acid. Meanwhile, find the reaction type and its rate including the evaluation of activation energy. The thermodynamic parameters were evaluated to determine more information about the occurred chemical reaction as heat transformation and spontaneity.

2 Experimental

2.1 Materials and Methods

The major oxides were measured by using the rapid silicate analysis method of Shapiro and Brannock (1962) to characterize the chemical composition of the studied sample [11]. The leaching process occurred by using the sulfuric acid method, and then estimation of Co, Ni, and Cu were achieved by atomic absorption spectrometer (model-969, Unicam) [12].

Table 1. Chemical major oxides of the studied sample (Wt.%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	ZnO	LOI
13.5	27	14.7	6.53	4.66	1.04	1.55	8.4	3.4	23.11

3 Results

The studied technological sample of the gibbsite-bearing shale was properly collected from the Um El Moghirat locality of Abu Zeneima, Egypt. The chemical composition is shown in table (1). Besides that, it assays 1000, 730, and 1900 ppm for Co, Ni, and Cu, respectively [12].

The study in which observational data was modeled by a function that was a nonlinear combination of the model parameters based on one or more independent variables used, and the data fitted using a successive approximations approach with many trials using the MATLAB software. Nonlinear models are currently the preferable choice not just for accuracy needs, but also for broadening the model's application. The emphasis on accuracy during model simulation results in the effective implementation of the system criteria [13].

3.1 Solid/ Liquid ratio –Grain Size effect

The relation of the conversion ratio “$X=[(C_0-C_e)/C_0]$: C_0 is initial concentration and C_e is equilibrium concentration” for Co, Ni, and Cu against the solid-liquid ratio factor and the grain size factor plotted in 3D by using the MATLAB program as shown in Fig. 2. The leachability increased by increasing of the solid/ liquid ratio to record their maximum values at 1/3 for Cu and Ni, whereas at 1/4 for Co. On the other hand, the effect of particle size factor has a significant role in the leaching process where the smaller the particle grain size used; the highest leachability obtained. Lower particle sizes (−80 mesh: Ni, −175 mesh: Cu and Co) led to improved liberation, according to the obtained data, which obeys the theoretical assumption that the higher the surface-to-volume ratio, which results in a faster leaching rate, the smaller the particle size, was supported by the leaching efficiencies. The general model of this relation is expressed by a nonlinear exponential equation as shown in Eq. (4). There are two analogy pseudo-first-order (PSO1st) reactions were occurred, which exhibit an increase of both grain size and solid/liquid factors that play as leaching antagonism effect.

$$f(GS,SL) = 1\text{-}Aexp(gGS+sSL) \qquad (4)$$

where, A is a function of overall conversion, g and s represented as the contribution of grain size and solid/liquid ratio respectively, (Table 2).

Table 2. Parameters affecting leaching grain size and solid /liquid function.

	A	***G***	***S***	***R***^{2}
Co	0.01732	0.02996	0.0002162	0.9992
Ni	3.07E-11	0.08444	0.3 998	0.9999
Cu	0.02156	1.211e-06	2.33	0.9870

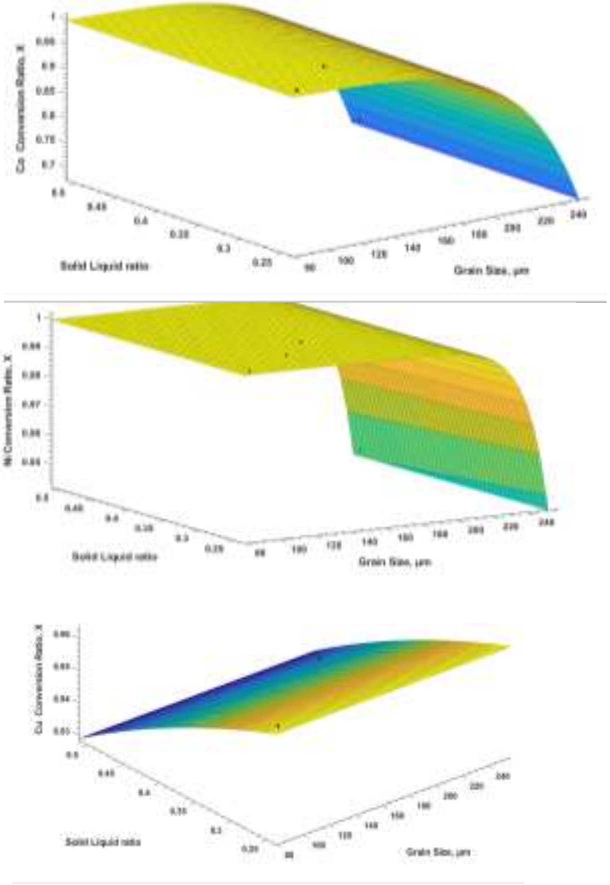

Fig. 2. 3D graphs including combined effects of factors on the leaching process: (a) solid/liquid ratio and (b) grain size *vs.* conversion ratio “***$X=[(C_0-C_e)/C_0]$***”

3.2 Time–Temperature effect

The effect of temperature is a vital factor that affects upon the leaching behavior of the reaction rate of metal ions (Co, Ni, and Cu) from its ore. The increasing temperature during the leaching process enhances the oxidizing power of the reaction, [where the used H_2SO_4 is considered an oxidizing agent] as well as the formation of sulfide components is oxidized to a predominant sulfate complex in a soluble form. The most renowned equation that may be used to stand for the time and temperature connection of the chemical reaction rate is the Arrhenius equation. It focuses on the mechanical behavior of the metal in conjunction with its surrounding components as a homogenous material.

Because it is difficult to define the observed departure from linearity in multistep reactions of idealized chemical networks, modeling of the experimental data from leaching processes is regarded as the most significant way of predicting the mechanisms of the diverse systems [14]. May be an occurrence of a transitional state established as a soluble state by sulfating of some elements of the ore sample (i.e., ferrous oxide) at a relatively low temperature is due to the rapid decomposition of ferric sulfate generating SO_2 gases in the early stage that is beneficial for the sulfation of cobalt, nickel, and copper [15].

Svante Arrhenius suggested the following equation (Eq. 5) based on collision theory in a gaseous state in the end of the 19th century to explain the relationship between a basis rate coefficient and temperature in a chemical reaction.

$$k = Ae^{-Ea/RT} \qquad (5)$$

where k is the coefficient of the chemical reaction rate, A is the frequency factor (pre-exponential factor), R is the ideal gas law constant, and T is the absolute temperature. The energy acquired to initiate a chemical reaction is known as activation energy Ea. Independent of the reaction model; the pre-exponential component may be evaluated. After determining the activation energy and pre-exponential factor, the reaction model may be rebuilt in tabular form, to which an explicit version of the reaction model can be fitted. It should be noted that the activation energy of the reaction is considered the only factor dependent on conversion that is adequate to correctly forecast the substance's behavior. Both Ar and Ea constants were calculated by solving the nonlinear form of the Arrhenius equation (Eq. 6) using MATLAB program for the expected pseudo 1st order reaction (Table. 3) the simulation result presented in Fig. (3) for Co and Cu, but in the case of Ni leaching achieved directly an efficiency reached ≥ 99%.

$$f(t,T) = Xm-(Xm*exp(t*(-Ar*exp(-Ea*1000/(8.314*T))))) \qquad (6)$$

where, Ar, Ea, and Xm are Arrhenius constant, activation energy, and maximum conversion fraction that equals $\max[(C_0-C_e)/C_0]$ respectively. The extension of the leaching time to 8 h was greatly beneficial to Cu and to a lesser extent for Ni as their leaching became complete. In a trial to improve the leaching efficiency of Co, a second series of leaching experiments was performed at 8 and 12 h to be compared with a similar experiment at 4h. indicated the improvement of the leaching efficiency of Co to 90.6% at 8 hrs.

Table 3. Parameters affecting leaching time and absolute temperature include Arrhenius, activation energy, and maximum conversion fraction.

	Ar	***Ea***	***Xm***	R^2
Co	1.935E+04	31.2	0.3427	0.99757
Cu	19.32	13.31	1	0.9838

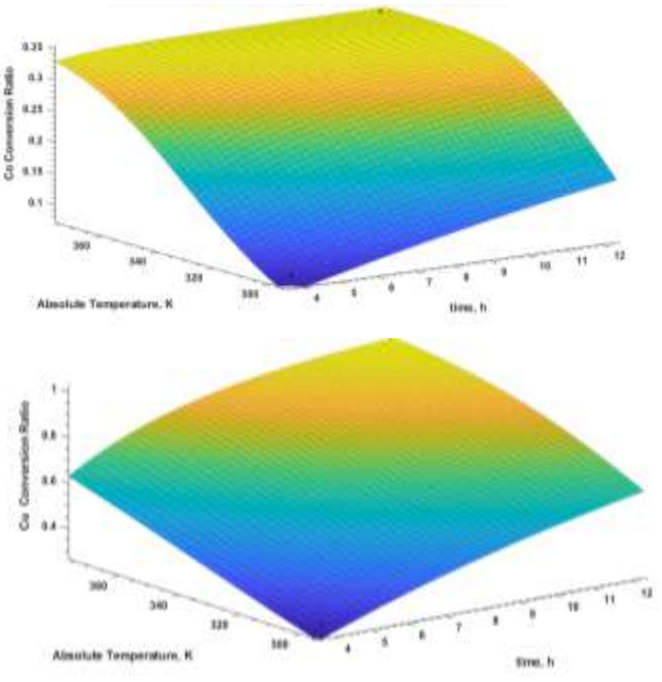

Fig. 3: 3D graphs including combined effects of factors on the leaching process: (a) time and (b) absolute temperature *vs.* conversion ratio "$X=[(C_0-C_e)/C_0]$".

3.3 Acid Concentration effect

The three-dimensional relation between the remained fraction "Xr = 1-X" from conversion ratio "X" for metal (Co, Ni, and Cu) ions and the used acid concentration (AC: 100, 200, and 400 g/L) during different absolute temperatures (T: 300, 320, 340, and 360 Kelvin) was demonstrated in Fig (4). Acid concentration (sulfuric acid) plays a critical role in the leaching process. The influence of sulfuric acid concentration upon the quantity of cobalt, nickel and copper leached from the ore sample was studied by varying its concentration from 100 to 400 g/L at room temperature (25°C) and constant solid/ liquid ratio (1/2) with -250µm as grain size for four hours exhibiting 8.4 and 31.5% leaching efficiency for Co and Ni at 400 g/L and the maximum leaching efficiency of Cu (30.7%) was achieved at 200g/L. On the other hand, the effect of time factor upon the leaching process varying from 4 to 12 hours studied. The suggested simulation model obeys to an Analogy Pseudo 1st order reaction including Arrhenius. The parameters affecting leaching process by different sulfuric acid concentrations at different absolute temperatures were demonstrated in Table (4) by applying Eq (7) that including Arrhenius. Increase in Ni dissolution can be interpreted as due to increased acid strength.

The almost stable leaching efficiency of Cu by acid increase from 200 to 400 g/l might be due to their presence in more than one mode of occurrence. The case of Co might be due to its oxidation state in the ore where it is most probably present in its weakly soluble trivalent state (Co^{3+}) and would require a reducing agent as Fe^{2+} that is already present in the sample constituents to be amenable for leaching. By increasing the acid concentration, Cu leaching efficiency attained up to 93 % suggesting possible dissolution of crednerite at these conditions. The leaching efficiency of Co has significantly increased (69%) to more than double its value at 400 g acid/L.

$$f(AC,T)=1-(a*exp(AC*(Ar*exp(-Ea*1000/(8.314*T))))) \qquad (7)$$

where a is another function of overall conversion, Ea is an activation energy of the reaction, and Xr is equals 1-X.

It is worthy of note that various leaching percent of Co, Ni and Cu indicate that there are oxides with different valances. The most of Ni ions seem to exist in the form of Ni_2^+.

Table 4. Parameters affecting leaching acid concentration and absolute temperature.

	Ar	**Ea**	**a**	**R^2**
Co	86.62	31.2	0.03577	0.9926
Ni	86.62	15.63	0.2487	0.9985
Cu	0.1513	13.31	0.1776	0.9975

3.4 Shrinking core model kinetics

Yagi and Kunii established the Shrinking Core Model for gas-solid combustion systems, but it has also been effectively applied to non-combustion systems combining liquids and solids [16–19]. A concept of the shrinking core model is based upon states that both the particle size and the responding core diminish at the same time. It is based on several assumptions as the metal ion particles are mostly spherical with a uniform radius, reversible isotherm, the effective diffusivity remains constant, and pseudo-steady state approximation is finally valid [1]. The basic reaction of the leaching process can consider as follows (Eq.8):

$$A_{Liquid} + bB_{Solid} \rightarrow cC_{Product} \quad (8)$$

Here, A is the leaching agent in the liquid, B is the reactive chemical component in the solid, C is the product(s) and b and c are the stoichiometric coefficients. The rate of leaching reaction per unit surface of the metal ion core "R_C" according to the previous assumptions can stated to the leaching rate of the metal ions (Co, Ni, and Cu) of interest is expressed as Eq (9)

$$R_c = \frac{M}{S_e}\frac{dN}{dt} \quad (9)$$

where, M is the molar mass of the metal ions, N is the metal ions particles amount (in moles), and S_e is the surface area of the unreacted metal ion particles.

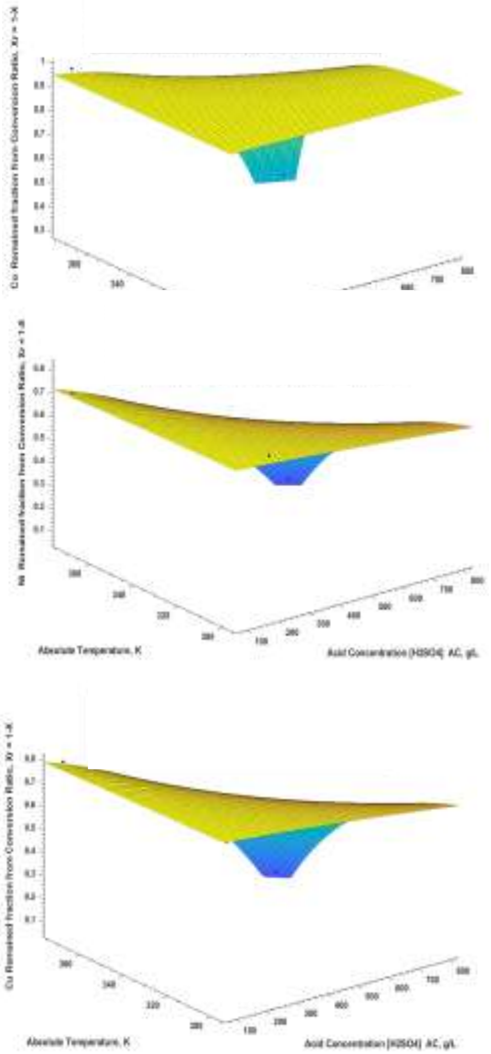

Fig. 4: 3D graphs including combined effects of factors on the leaching process: (a) acid concentration and (b) temperature *vs.* remained fraction from conversion ratio "***X_r=1-X***"

Eq (9) can be detailed with particle density and radius parameters as follows Eq (10):

$$R_c = -\frac{M}{(4\pi r_t^2)}\frac{d}{dt}\left(\frac{4\pi r_t^2 \rho}{3M}\right) \qquad (10)$$

where, ρ is the particle density of the metal ions and r_t is the radius of the unreacted metal ion particle at any time (t>0).

The leaching model of metal ions in mathematical form can be written as shown below Eq (11):

$$1-(1-X)^{1/3} = k_o exp(\frac{Ea}{RT})t \qquad (11)$$

Where R is the universal gas constant in KJ.mol^{-1}, E_a is the activation energy in kJ/mol., k_o is the pre-exponential term varies for each leaching system, and T is the temperature in Kelvin. The suggested model's performance was evaluated and fitted from the experimental data presented by Hazek et al, [12] using MATLAB-2021a code Eq (12). Generally, the shrinking core models are confined to three types of reactions: chemical reaction control, diffusion-reaction control, and film diffusion control (Fig. 5).

$$f(Xf,T)=((1/k_F)*Xf+(1/k_D)*(1-3*(1-Xf).\wedge\{(2/3)\}+2*(1-Xf))+(1/k_C)*(1-(1-Xf)\wedge\{(1/3)\}))*(exp(Ar*exp(-E*1000/(8.314*T)))) \qquad (12)$$

To examine the impact of an absolute temperature on the leaching rate, only film diffusion reaction is commonly considered for Co and Ni ions at elevated temperatures where $k_C > k_D > k_F$ and $k_C < k_D > k_F$ respectively, as shown in Table (5). On the other hand, the exhibited reaction of Cu ions is exactly the contrary, which $k_C > k_D < k_F$ that showing the achieved reaction of the leaching process controlled may be by solid diffusion or mixed reaction between the chemical and solid diffusion reactions were at the same value of the reaction rate.

Table 5. Parameters of the suggested reaction type in the leaching process.

	Ar	**Ea**	**k_C**	**k_D**	**k_F**	**R^2**
Co	1.935E +04	31.2	0.9816	0.7805	0.3389	0.9999
Ni	52.02	15.63	2.939E +05	3.312E +05	0.1144	0.9865
Cu	19.32	13.31	0.2899	0.2741	0.4727	0.9999

3.5 Thermodynamic Model

The experimental data reflect the chemistry principles of the leaching process, but a thermodynamic model may easily describe a whole system through a precise expression known as Gibbs free energy " ΔG". The spontaneity of the leaching chemical reaction was determined by observing the change of ΔG and its value if $\Delta G < 0$ or $\Delta G > 0$ indicating to a spontaneous or nonspontaneous reaction [20]. The modeling revealed that when temperature rises, the change in Gibbs free energy reaches greater negative values for the predominance of the reactions, making them more likely to occur spontaneously. The positive values of enthalpy "ΔH" represented that the leaching process occurred in an endothermic nature so thermodynamic results expressed that temperature has a great influence on sulfuric acid leaching. The expected mechanism of leaching reaction reactions and the calculated values of ΔS, ΔG, and ΔH have been presented in Table (5). Enthalpy and entropy were calculated from Eq (13), then substituted their values into Eq (14) to evaluate the Gibbs free energy and determine the spontaneity of the leaching reaction (Fig. 6).

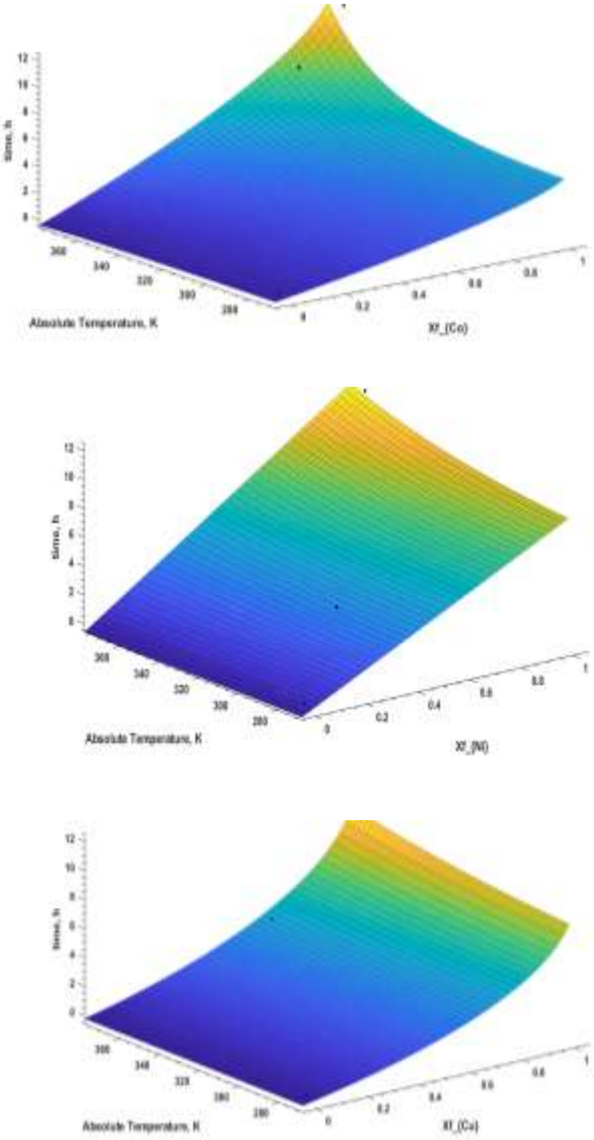

Fig. 5: 3D graph showing Shrinking Core Model including pseudo 1st order reaction with Arrhenius.

$$f(T,Xr) = qm*(exp(-DH*1000/(8.314*T)+DS/8.314))*Xr\wedge n/(1+(exp(-DH*1000/(8.314*T)+DS/8.314))*Xr\wedge m)\wedge g \qquad (13).$$

$$\Delta G=\Delta H-T*\Delta S/1000 \qquad (14)$$

Table 6: Thermodynamics parameters for the metals leaching process.

Metal	Reaction Mechanism	q_m (mmol/g)	ΔH (kJ/mol.)	ΔS (J/mol.K)	ΔG (kJ/mol.)						m	n	g	R^2
					298 K	308 K	323K	348K	363K	373K				
Co	$Co + H_2SO_4 \rightarrow CoSO_4 + H_2$	0.1118	16.03	3.521	-17.079	-17.114	-17.167	-17.255	-17.308	-17.343	0.9497	1.018	1.761	0.9806
Ni	$Ni + H_2SO_4 \rightarrow NiSO_4 + H_2$	0.5424	17.39	2.842	-18.237	-18.265	-18.308	-18.379	-18.422	-18.45	0.7857	0.5075	1.762	0.9871
Cu	$Cu + H_2SO_4 \rightarrow CuSO_4 + H_2$	0.1315	13.9	2.994	-14.792	-14.822	-14.867	-14.942	-14.987	-15.017	0.9556	0.5102	1.558	0.9944

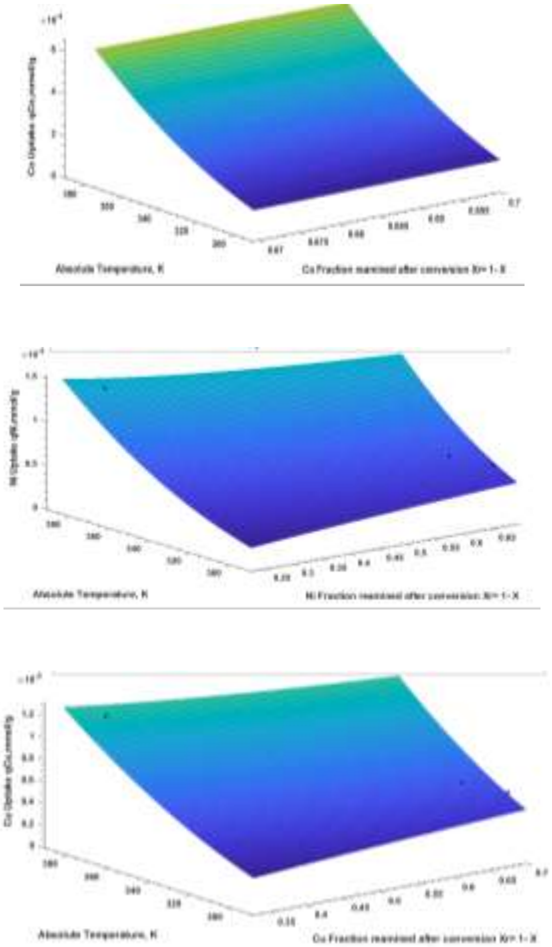

Fig. 6: 3D graph showing General an isotherm model: Floatotherm including Van't Hoff.

5 Conclusion

The three most significant metals that have a substantial impact on various commercial and industrial fields are cobalt, nickel, and copper. Leaching is the first stage of hydrometallurgical technology where the ore is treated with chemicals such as acid and alkaline solutions to transfer the metal into the soluble phase.

Due to high efficiency and reasonable price of Sulfuric acid was a rational choice. The parameters: sample grain size, acid concentration, solid/liquid, time, and temperature, affected the leaching process of cobalt, nickel, and copper from the studied ore sample were determined to study the nonlinear kinetic models and thermodynamic profile using MATLAB-2021 program. The type of reaction was shown from the 3D relation between the remained fraction of conversation ratio against absolute temperature and sulfuric acid concentration as analogy pseudo 1st order reaction including Arrhenius. Furthermore, the shrinking core model predicted that the leaching rate of the occurred reaction was identified as solid diffusion or mixed between chemical and solid diffusion reaction for Cu ions and film diffusion reaction for both Co and Ni ions. Based on the study of the thermodynamic model of the leaching process, the thermodynamic quantities i.e., ΔH, ΔG and ΔS were computed and discussed for the system the leaching viability of metal ions: Co, Ni, and Cu in the H_2SO_4 took place spontaneously with an endothermic nature.

References

[1] N. A. Kawady, E. Abd El Gawad, and A. E. Mubarak. Modified grafted nano cellulose-based bio-sorbent for uranium (VI) adsorption with kinetics modeling and thermodynamics. Korean J. Chem. Eng., 39(2), 408-422, 2022. DOI: 10.1007/s11814-021-0886-1

[2] F. Faraji, A. Alizadeh, F. Rashchi and N. Mostoufi. Kinetics of leaching: a review, Rev Chem. Eng. 2020. DOI: 10.1515/revce-2019-0073.

[3] R. Hubli, J. Mittra, A. Suri. Reduction-dissolution of cobalt oxide in acid media: a kinetic study. Hydrometallurgy, 44, 1– 2, 1997. https://doi.org/10.1016/S0304-386X(96)00036-9

[4] C. Vu, K. Han, F. Lawson. Leaching behavior of cobaltous and cobalt-cobaltic oxides in ammonia and in acid solutions. Hydrometallurgy, 6, 1–2, 1980. https://doi.org/10.1016/0304-386X(80)90009-2

[5] N. Al-Mansi, N. Abdel Monem. Recovery of nickel oxide from spent catalyst. J. Waste Manag, 22, 1, 2002. DOI: 10.1016/s0956-053x(01)00024-1

[6] M. Jaishnkar, T. Tseten, N. Anbalagan, B. B. Mathew, K. N. Beeregowda. Toxicity, mechanism and health effects of some heavy metals: REVIEW ARTICLE,

Interdiscip Toxicol, 7(2): 60–72, 2014. DOI: 10.2478/intox-2014-0009.

[7] E. Gomez, S. Pane, E. Valles. Electrodeposition of Co–Ni and Co–Ni–Cu systems in sulphate–citrate medium. Electrochimica Acta, 51, 146–153,2005. DOI:10.1016/j.electacta.2005.04.010 .

[8] Y. Geng, Y. Bana, B. Wangf, K. Song, Y. Zhang,Y. Jiae, B. Tiana, Y. Liua and A. A. Volinsky. A review of microstructure and texture evolution with nanoscale precipitates for copper alloys. Journal of Materials Research and Technology, 9(5):11918–11934, 2020. DOI.org/10.1016/j.jmrt.2020.08.055

[9] Z. Takacova, T. Havlik, F. Kukurugya, D. Orac. Cobalt and lithium recovery from the active mass of spent Li-ion batteries: Theoretical and experimental approach. Hydrometallurgy,163,2016 https://doi.org/10.1016/j.hydromet.2016.03.007

[10] L. Tao, L. Wang, K. Yang, X. Wang, L. Chen and P. Ninga. Leaching of iron from copper tailings by sulfuric acid: behavior, kinetics and mechanism. RSC Adv., 11, 5741, 2021.

[11] L. Shapiro, W. Brannock (1962) Rapid analysis of silicates, carbonates, and phosphate rocks. U.S Geol. Surv. Bull., Vol. 114 A

[12] M.N. Hazek, F. Y. Ahmed, M.A. Kasaby and R.M. Attia. Sulfuric acid leaching of polymetallic Abu Zeneima gibbsite-shale. Hydrometallurgy, 90, 34–39, 2008. https://doi.org/10.1016/j.hydromet.2007.09.009

[13] F. Joseph Henry. Modeling Lake Michigan Nearshore Carbon and Phosphorus Dynamics. Theses and Dissertations, 871, 182-193, 2015. https://dc.uwm.edu/etd/871.

[14] V. H. Carvalho-Silva, N. D. Coutinho, V. Aquilanti. Temperature Dependence of Rate Processes Beyond Arrhenius and Eyring: Activation and Transitivity. Frontiers in Chemistry, 7(380), 2019. DOI: 10.3389/fchem.2019.00380.

[15] S. Qiangchao, C. Hongwei, M. Xiaoyong, L. Yanbo, L. Guangshi, X. Qian and L. Xionggang. Efficient Synchronous Extraction of Nickel, Copper, and Cobalt from Low–Nickel Matte by Sulfation Roasting–Water Leaching Process Scientific Reports, 10:9916, 2020. |https://doi.org/10.1038/s41598-020-66894-x

[16] S. Yagi and D. Kunii. Fluidized-solids reactors with continuous solids feed—I: Residence time of particles in fluidized beds. Chemical Engineering Science, vol. 16, Number 3-4, pp 364-371. 1961. https://doi.org/10.1016/0009-2509(61)80043-2

[17] S. Yagi and Kunii, D. Fluidized-solids reactors with continuous solids feed—II: Conversion for overflow and carryover particles. Chemical Engineering Science, vol. 16, Number 3-4, pp 372-379. 1961. https://doi.org/10.1016/0009-2509(61)80044-4

[18] S. Yagi and D. Kunii. Fluidized-solids reactors with continuous solids feed—III : Conversion in experimental fluidized-solids reactors. Chemical Engineering Science, vol. 16, Number 3-4, pp 380 – 391, 1961. https://doi.org/10.1016/0009-2509(61)80045-6

[19] A. D. Souza, P. S. Peina, E. V. O. Lima, C. A. daSilva and V. A. Leão. Kinetics of sulphuric acid leaching of a zinc silicate calcine. Hydrometallurgy vol. 89, pp 337-345. 2007.

[20] Z. Takacova, T. Havli. Thermodynamic aspects of the extraction of Co and Li from the active mass of LiBs. Material,69(9),339-343,2015. jglobal.jst.go.jp/en/detail?JGLOBAL_ID=201502202499099764.