

## The kinetic study of refractory silver ore in acidified potassium chloride - hypochlorite media

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**Abstract:** In this study, the dissolution of refractory silver ore samples obtained from the Kütahya Gümüşköy region in the HCl/NaOCl and KCl system was investigated. Chemical and morphological analyzes of the sample show that the ore consists mainly of quartz, dolomite, barite and clay. Silver is dispersed as free fine particles or locked in barite and quartz minerals. The leaching tests were carried out under ambient conditions with direct contact of the solvent reagent with the sample. Reaction temperature, time, and KCl concentration were examined as leaching parameters to elucidate their effects on silver extraction. The results obtained in leaching tests indicated that the dissolution of silver occurs very quickly, almost linearly, within the first minute of the reaction. After this point, the dissolution rate decreases and reaches equilibrium after 10 minutes. It was found that increasing both temperature and KCl concentrations have a positive effect on extraction. These effects become more evident in the first stage, especially at high salt concentrations (1 M). The experimental results showed that the highest silver extraction of 53.15% was obtained under the following conditions: Temperature of 85°C, leaching time of 10 min, concentrations of 0.5 M and 0.1 M for KCl and NaOCl, respectively, the solid ratio of 30%, and particle size ( $d_{80}$ ) 15  $\mu\text{m}$ . The kinetics of AgCl dissolution was specifically studied using aforementioned leaching system as well. The reaction rates, kinetic orders and activation energies were calculated. Correspondingly, a general kinetic model describing leaching systems based on shrinking core was proposed as a rate-controlling model for the dissolution mechanism.

**Keywords:** silver extraction, potassium chloride, sodium hypochlorite, dissolution kinetics, reaction order, activation energy

### 1. Introduction

Gold and silver are two important noble metals that have attracted attention since historical times. Both metals have wide usage in investment, jewellery, decoration and high-tech industries due to their excellent physical and chemical properties. The ideal method for enrichment of fine particle size gold/silver is to dissolve it with suitable solvents without reacting with other minerals. In the early periods, dissolution with aqua regia or collecting it by creating amalgam with mercury were the basic processes employed in gold and silver enrichment. In later stages, with the development of the cyanidation process in 1887, the cyanidation method (Merrill Crowe or later Carbon-in-Pulp) has gradually become the most widely accepted method from the early 19<sup>th</sup> century to the present day. Although the amalgamation process has been continued up to the 1960s to recover large gold particles, today, it was abandoned in many areas outside Africa due to the harmful nature of mercury (Habashi, 1993). Within this process change, undoubtedly fast reaction kinetics, excellent performance against a wide variety of ores, low process cost, process simplicity and wide application experience have been the most important factors for the application of cyanidation as a basic enrichment method. However, cyanide is a toxic reagent.

One of the problems encountered in classical cyanidation practice in addition to posing a potential risk to the environment, is the low recovery efficiency in refractory ores compared to easily dissolving

resources. The nature of the challenges for refractory ores mainly resultant from (a) physical interlocking in silicates and oxides, (b) chemical interlocking of gold compounds in pyrite and arsenopyrite, (c) reactive gangue mineralogy, which includes leached minerals and pre-stripped materials; carbonaceous substance. Therefore, such ores or concentrates require pre-treatment or an oxidation process before and along with the dissolution process to ensure desired contact of the reagent and the valuable grain (Au/Ag). The oxidation process can be carried out using pressure, heat or chemicals. The choice of appropriate technology for processing of such ores varies depending on the structure and content of the ore. While Sherrite pressure oxidation is preferred in an acid or alkaline environment to oxidize gold-containing sulfides in many applications, chemical oxidation is seen as an advantageous process as it can easily oxidize all silver-related sulfides at the end of the process. In this process, sulfate is formed instead of elemental sulfur, which causes passivation of mineral surfaces. In the study conducted by Pangum et al., 1996. pressure oxidation was employed as pretreatment step and it was reported that this stage positively affects the overall recovery. The ore was roasted at 650°C and then leached with cyanide. The authors reported that 98% of the gold could be recovered with a 24-hour leaching process. It has also been suggested that simultaneous oxidation and dissolution of gold in an autoclave using the  $O_2/H_2SO_4/HCl/NaCl$  system as an alternative to NaCN could also be considered with relatively lower recovery rate.

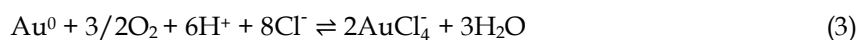
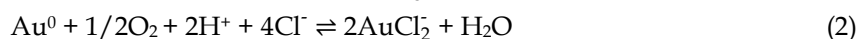
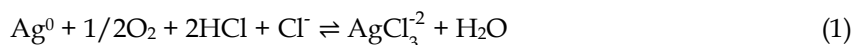
Another possible complication for the next few decades is the low recovery encountered in preg robbing low grade complex ores that will be used as the main sources instead of high-grade ores. During the cyanidation process, carbonaceous materials or possible preg-robbing materials such as pyrite, copper sulphides, quartz and layered silicates negatively affect gold recovery due to their ability to adsorb gold from the cyanide leach solution. These ores often exhibit a complex structure because the ultrafine particles do not easily separate from the gold (Adams, 2005; Vaughan, 2004). Preliminary separation of these minerals using flotation, use of selective surfactant or roasting similar to refractory ores can be listed as the main techniques recommended to solve this problem (Owusu et al., 2021). This issue has more recently well reviewed by Sung et al., 2022. In this study, the sources and mechanisms of preg-robbing, their effect on recovery were discussed together with current/ promising new methods to mitigate preg-robbing.

As indicated above, cyanide is a toxic reagent, it is requiring a strict control in order to prevent its harmful effect on environment, is therefore the use of the cyanidation process has restricted in many countries today. Where cyanidation is not restricted, increased regulations scrutiny for new gold projects under intense pressure from environmental activists, is a serious concern for mining companies. Based on the literature research, it is seen that the use of thiourea, thiosulfate, thiocyanate, halide ( $Cl_2$ ,  $Br_2$ ,  $I_2$ ) or chloride and its derivatives under oxidative conditions are the solvents that attract the most attention as alternative options to the cyanide method. Using thiourea ( $NH_2CSNH_2$ ) as a gold/silver extraction agent is one of the promising options. The reaction is fast and the extraction efficiency is high under optimum conditions (Up to 99%). The usage of under acidic conditions is seen as an advantage for refractory ores. Despite its proven effectiveness, thiourea is available in very few full-scale operations. Being expensive compared to cyanide, using larger quantities and having more processing steps are stated as disadvantages that prevent its commercial adoption. On the other hand, although the acceptable gold leaching rates reported for the use of thiosulphate with ammonia and copper offer an alternative process to traditional cyanide leaching, high reagent consumption continues to be one of the factors limiting its widespread use. More information on the usage of thiourea and thiosulfate for gold extraction can be found a review paper published by Yanti et al., 2023.

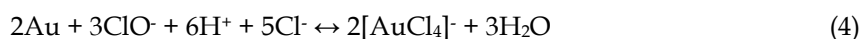
Apart from these, although the use of halide systems, especially chlorine, to dissolve gold predates cyanidation, these systems have regained importance among alternative solvents in recent years. Earlier examples of these include the "Plattner Process", which was used for the recovery of gold from ores as early as 1848, and the "Patera Process", especially for silver ores. The "Plattner Process" is basically the solubility of  $AuCl_3$  with chlorinated water acidified with dilute sulfuric acid, and then precipitated with iron sulphate. In the Patera Process, the ore was roasted with sodium chloride to convert silver into silver chloride and then leached with water to remove base metals. Both processes became obsolete for the recovery of Au/Ag from easily soluble ores at the beginning of this century with the introduction of the cyanidation process (Habashi, 1993).

In fact, gold/silver dissolves much faster with chlorine than with cyanide. However, the presence of low concentrations of sulphides or other reactive components in the ore can make reagent consumption excessive and can be reduced dissolved complex ions ( $\text{Au}[\text{Cl}_4]^-$ ) back to metallic gold depending on the process conditions. These have emerged as the main factors limiting its application as an alternative reagent compared to cyanide for easily soluble ores, therefore its applications are mostly restricted to the electrorefining of gold. However, in recent years, due to the increasing environmental opposition against the NaCN, development of some possible pretreatment stages for removal of sulfur and carbonates, and its more workability for refractory or complex ores has led to a renewed interest in chlorinated systems. In a previous research study conducted by the United States Bureau of Mines within the scope of improving the recovery of precious metals from refractory ores, the proposed method adding carbon after initial chlorination and continuing chlorination, can be given as a promising example for returning to the chlorination practices (Greaves et al., 1990). The results were considered interesting as they showed over 90% efficiency. This result was an incentive for various studies on production by chlorination in the following years. In this context, one of the applications that has attracted attention in recent years, as well as the use of chloride solutions after pressurized oxidation, is the ability to dissolve gold/silver and refractory sulphides simultaneously by using acidic chloride solutions directly in the presence of potential oxidants such as hypochlorite, bromate, hydrogen peroxide, ozone and ferric salts.

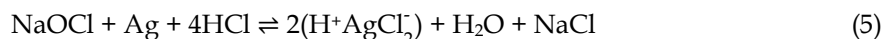
In the chlorination process, silver is oxidized to  $\text{Ag}^+$  by the air ( $\text{O}_2$ ) supplied to the environment and forms a complex with free chlorine and dissolves as  $\text{AgCl}_2^-$ ,  $\text{AgCl}_3^{2-}$ . The general solubility reactions of chlorine for gold and silver are expressed as in Equations (1), (2) and (3) (Puvvada and Murthy, 2000).



Depending on the properties of aqueous solutions, chlorine gas can occur mainly in three types of oxidizing forms; aqueous chlorine,  $\text{Cl}_2$  (aq), hypochlorous acid (HOCl) and hypochlorite ion ( $\text{OCl}^-$ ). These species can also be produced by adding sodium hypochlorite (NaOCl) or calcium hypochlorite ( $\text{Ca}(\text{ClO})_2$ ) to an aqueous solution. For this reason, many researchers in the literature have directed to use the chloride-hypochlorite method in the enrichment of refractory and complex ores (Hilson et al., 2006; Hasab et al., 2013; Li et al., 2016; Aylmore, 2016). Chlorine are strong oxidizing agents. As reaction (4) shows, chlorine readily dissolves elemental gold into gold (III)-chloro complex,  $[\text{AuCl}_4]^-$ . In the presence of chloride ions, provided the pH is less than 2.



A similar dissolution reaction for Ag can be given as followed (Olteanu et al., 2014).



The equilibrium reactions indicated that the stability of the complex ions is the most important factor on the recovery. In this context, chloride concentration and pH of the solution have been the factors that studied intensively in the literature. It was noted that low pH and the increased presence of chloride ions can greatly reduce the re-dissolution potential of gold/silver. This issue was experimentally investigated by Murphy and Lagrange, 1998 using Raman spectroscopy data evaluating the speciation of gold chloride complexes with pH. It was reported that both gold and chloride concentrations are the efficient factors on the stability of the various chloro-hydroxy species. At low gold concentrations, hydrolysis of  $[\text{AuCl}_4]^-$  is becoming possible at lower pH values. This is especially getting more visible in the absence of excess chloride ( $\Sigma\text{Cl} = 4\Sigma\text{Au}$ ) concentration. The study conducted by Baghalha et al., 2007 also supports this result. It was reported that the  $\text{OCl}^-$  concentration in the solution is important and should be equal to or greater than  $10\text{g}/\text{dm}^3$  in order to ensure optimum conditions in gold recovery using chloride/hypochlorite from oxide ore at room temperature. The ambient pH another parameter that must tightly be controlled for both dissolution kinetics and maximum recovery. In another recent study by Harjanto et al., 2019, direct chlorite leaching was noted as a recommended method as an alternative to amalgamation to extract gold in small-scale industries. In this study, the addition of NaCl and other solvents; HCl and  $\text{H}_2\text{O}_2$  were optimized using the Taguchi Method. It has been suggested

that under optimum conditions more than 78% of the gold can be extracted within 3 hours. In addition to NaCl, there are also studies in literature to use different chloride salts such as KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, FeCl<sub>3</sub> and CuCl<sub>2</sub>. For example, in a recent study by (Lampinen et al., 2017), the dissolution mechanism and kinetics of gold in copper chloride solution was investigated. Experimental studies carried out using concentrated chloride (3 M) solutions with copper ion concentration in the range of 0.02–1.0 M and temperature of 65–95 °C were showed that gold dissolution increases proportionally with the increase in temperature and cupric ion concentrations up to 0.5 M. Under these conditions the dissolution of gold mainly obey mixed control. More recently, an environmental comparison of one-stage direct application of chloride leaching for refractory ores versus leaching after conventional pressure oxidation reported by Rinne et al., 2021 can be considered an interesting study in that it includes a simulation-based life cycle assessment. It was found that application of pressure oxidation for refractory gold ores is environmentally more attractive for highly refractory ores however, for partially refractory sulfide ores direct leaching could be more beneficial depending on the leaching conditions.

Although gold and silver exhibit nearly similar properties, compared to gold, silver has a significant difference, especially in terms of the diversity of its industrial uses. While gold is mostly used in relatively protected areas for investment and decoration purposes, silver is used as a primary consumption material in medicine with its natural antibacterial properties, and in military, electronics, water treatment, composites and photography industries due to its stainless and excellent thermal and conductive properties. This situation causes the demand for silver to increase due to the increasing industrialization potential of the countries. In this context, supply limitations shift the production from primary easily soluble sources to refractory or complex ores and even to secondary sources due to the gradual decrease in easily soluble ore resources. This necessitates the development of alternative extraction methods other than cyanide to meet the ever-increasing demand. Currently an around six hundred million ounces of silver is mined each year, while industry consumes about eight hundred and seventy million ounces. Which clearly indicate is tightening of the market (<https://www.mining.com/silver-is-now-even-more-precious-than-gold-do-you-own-any>).

In conclusion, considering the applications given above, it is clear that the direct acidic chlorination process is one of the promising applications, especially for the recovery of refractory ores. However, it seems that the studies mostly focus on gold recovery and the studies on silver are quite limited. Considering the increasing silver demand of the industry, it is important to increase knowledge on this subject, especially the mechanism and kinetics of silver recovery by chlorination method. As indicated above in direct acid leaching with different salts can be use such as NaCl, CaCl<sub>2</sub> or KCl. Within these, although NaCl is one of the most preferred substances in a recent study performed by Li et al, it was suggested that KCl is more effective with an order of KCl>CaCl<sub>2</sub>>NaCl. Even though the authors did not provide any explanatory support on this issue; According to Pearson's acid-base definition, the diameter match between "Ag" and "K" ions is more suitable than "Ag" and "Na" ions, which can be considered as the support behind this motivation. (Ölmez and Yılmaz, 2010). Therefore, different from the previous one (Canveren and Karagüzel, 2021), in this study the dissolution kinetics of silver ore in oxidizing sodium hypochlorite and acidified KCl solution were investigated and discussed as detail.

## 2. Materials and methods

### 2.1. Materials

The sample used in experiments was obtained from an open pit mine in the Kütahya Gümüşköy region. Before leaching tests, the sample was first subjected to crushing (below 4 mm in the primary jaw crusher) and grinding (agate mill) processes to ensure a particle size of -15 µm. The phase analyses of the samples were carried out using XRD (Panalytical Empyrean) with a nickel filtered Cu K $\alpha$  radiation. According to XRD patterns given at Fig. 1, main minerals found in the sample were quartz, dolomite and barite.

The Chemical analyses of representative ground sample performed by X-ray fluorescence spectrometer, XRF (PANalytical -Axios-max) and standard spectrophotometric atomic absorption (AAS) and ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) methods was supports the XRD results. As can be seen in Table 1, the feed sample was predominantly consisting of

SiO<sub>2</sub> and followed by other oxides; CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, BaO, K<sub>2</sub>O and ZnO. The silver content of sample was determined as 85 ppm.

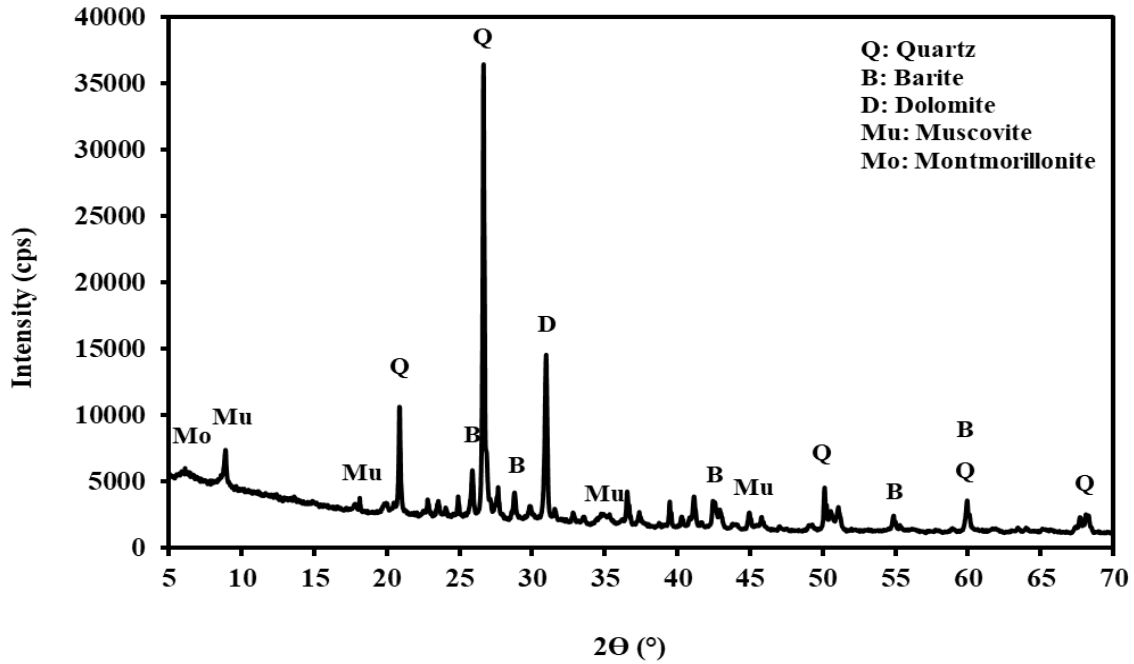


Fig. 1. XRD diffractogram of Gümüşköy silver ore

Table 1. Chemical analysis results of Gümüşköy ore

Oxide (XRF)	%	Element (ICP)	ppm
SiO <sub>2</sub>	44.03	Ag	85
CaO	8.66	Cu	73
Al <sub>2</sub> O <sub>3</sub>	9.49	Pb	4854
MgO	4.56	Zn	13785
Fe <sub>2</sub> O <sub>3</sub>	4.53	Fe	20910
BaO	3.88	Mn	3642
K <sub>2</sub> O	3.71	Ni	33
ZnO	2.25	Sb	1977
SbO <sub>2</sub>	0.37	As	3855

More advanced scanning electron microscopy (SEM) studies were performed to better characterize the sample. The SEM images and polished sections of the sample are given in Fig. 2. Their energy-dispersive X-ray (EDX) intensities can be seen at Table 2 and Table 3 respectively. The results in Fig. 2 indicate that the silver was distributed in barite and silicate minerals such as quartz and clay because of the presence of Si and Al elements. These results also agree with the literature that silver was encapsulated in barite, quartz, chalcedony, and dolomite matrices (Dinçer, 1997; Arık, 2002).

Table 2. The X-Ray (EDX) analysis on silver ore (Fig 2a)

Selected Area 1		Selected Area 2	
Element	%	Element	%
O	1.51	O	4.69
Al	0.40	Al	3.51
Si	3.12	Si	11.01
Si	15.23	S	13.13
Ag	6.86	Ag	5.31
Ba	72.88	Ba	62.35

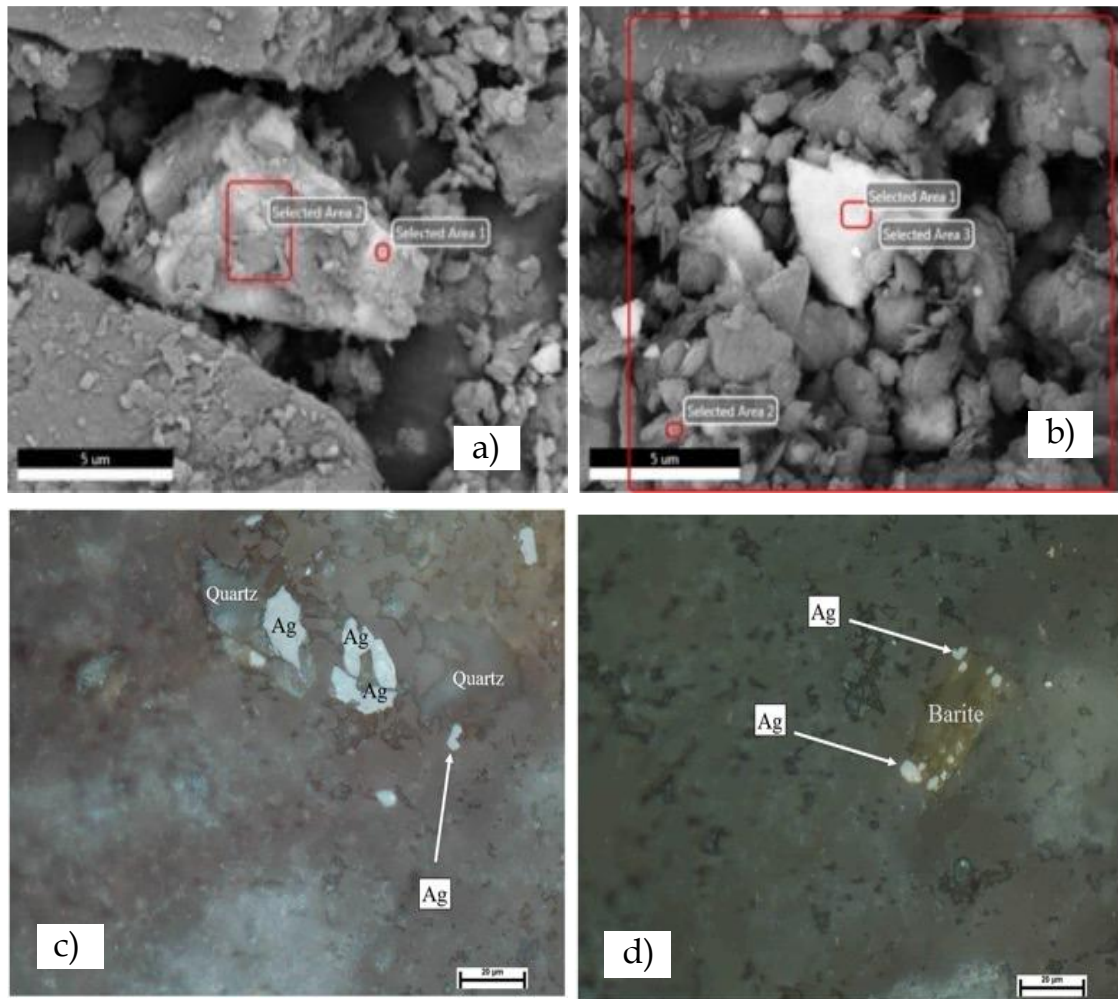


Fig. 2. Scanning electron microscope (SEM) images (a-b), polished sections of silver ore (c-d)

Table 3. The X-Ray (EDX) analysis on silver ore (Fig 2b)

Selected Area 1		Selected Area 2		Selected Area 3	
Oxide	%	Oxide	%	Oxide	%
Al <sub>2</sub> O <sub>3</sub>	0.21	Na <sub>2</sub> O	1.58	Na <sub>2</sub> O	0.15
SiO <sub>2</sub>	3.97	MgO	7.97	MgO	2.34
SO <sub>4</sub>	31.15	Al <sub>2</sub> O <sub>3</sub>	9.24	Al <sub>2</sub> O <sub>3</sub>	8.45
AgO	0.10	SiO <sub>2</sub>	29.77	SiO <sub>2</sub>	49.85
K <sub>2</sub> O	0.09	SO <sub>4</sub>	7.79	SO <sub>4</sub>	6.93
CaO	0.25	AgO	3.90	AgO	1.34
BaO	63.82	K <sub>2</sub> O	2.55	K <sub>2</sub> O	3.74
Fe <sub>2</sub> O <sub>3</sub>	0.41	CaO	16.31	CaO	7.63
		BaO	14.51	BaO	13.92
		Fe <sub>2</sub> O <sub>3</sub>	6.38	Fe <sub>2</sub> O <sub>3</sub>	5.66

## 2.2. Method

Leaching experiments were carried out in a 500 cm<sup>3</sup> three-necked, round-bottom glass reactor placed on a temperature-controlled magnetic stirrer supported by an air pump used to supply oxygen to the system (Fig. 3). A condenser was attached to the reactor to avoid evaporating any reactor content. Leaching tests were conducted in a leach system consisting of 0.25M HCl and 0.1M NaOCl. Varying

amount of KCl were added to the leach, to evaluate the impact of concentration on the leach kinetics, from 0.25 to 1.0 M. In each test, a 100-g samples with 15 microns  $d_{80}$  was added into the solution that had previously been adjusted to desired temperature (25, 45, 65 and 85 °C). The solid/liquid ratio and the air flow was kept as constant with 30% and 0.5 bar respectively. The solutions were then continuously stirred at a fixed stirring speed of 600 rpm. To evaluate the effects of test parameters on dissolution, 15 ml samples were removed from the reactor at predetermined time; filtered, and their silver concentrations were analyzed by atomic absorption spectrometry. Metal extractions were calculated based on the analysis of leaching solid residues. pH and Eh were measured with Hanna HI 9125 pH/ORP meter both before and after the leaching experiments. The entire operation parameters used in the experiments are presented in Table 4.



Fig. 3. Experimental set-up

Table 4. Experimental parameters for the pressure leaching experiments

Parameters	Quantity
Sample amount	100 g
Particle size	$d_{80}$ : 15 $\mu\text{m}$
pH	4-7
Eh	0.6-1.2 V
Stirring speed	600 rpm
KCl	0.25-0.5-1 M
Temperature	25-45-65-85 °C
NaOCl	0.1 M
Solid ratio	30 %
HCl	0.25 M
Oxygen	0.5 bar

### 3. Results and discussion

#### 3.1. Effect of KCl concentration

In the leaching tests with the studied ore, effective parameters such as time-dependent KCl concentration and reaction temperature were examined in detail, and the results obtained were interpreted by kinetic analysis. The results of leaching tests at KCl concentrations of 0.25, 0.5 and 1 M under a constant temperature of 298 K, NaOCl of 0.1 M, initial pH: 4 and ORP: 1.2 V are given in Fig. 4.

As discussed previously, for the HCl + NaOCl and KCl system, under oxidative conditions,  $\text{Ag}^0$  in the ore sample is expected to transform into a stable complex silver ion ( $\text{AgCl}_2^-$ ) as given in reaction 5



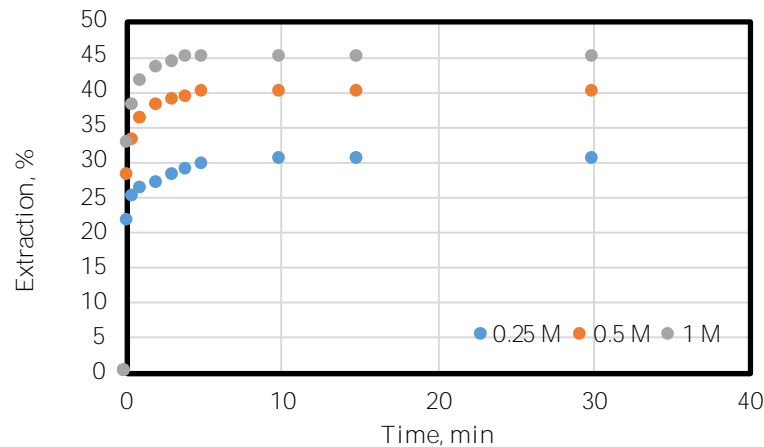


Fig. 4 Effect of KCl concentration on Ag dissolution at 298 K

and pass into the leach solution. As can be seen in Fig. 4, this transformation occurs very quickly, almost linearly, within the first 1 minute of reaction and after this point, the dissolution rate decreases and reaches equilibrium after 10 minutes. Although similar behavior was observed for all KCl concentrations, it can be noted that increasing KCl concentrations have a positive effect on recovery. The Ag recoveries for 0.25 M, 0.5 M and 1 M KCl concentrations were calculated as 30%, 40% and 45%, respectively. This can be explained as the positive effect of increasing chloride concentration on the forward progress of the dissolution reaction. These results are confirmed with the previous study conducted by Puvvada and Murthy 2000, for selective metal recovery from chalcopyrite concentrate using chloride/hypochlorite medium. The recovery of silver was found to increase from 20% to 45% when the NaCl concentration was varied from 25 to 200 g/dm<sup>3</sup> at the end of 4 h of leaching. In addition, it can also be suggested that the increase in concentration positively affects the time to reach final equilibrium concentrations. It was determined that the processing time decreased as the concentration values increased. The low dissolution rate observed in the extension phases can be attributed to the formation of the rate-limiting diffusion barrier after the end of the initiation period. This phenomenon indicates that the dissolution mechanism consists of more than one stage and the existence of rate-limited diffusion stages. This can be explained by the presence of easily dissolved free Ag grains in the ore sample and the close influence of the ambient potential on the stability of dissolved ions.

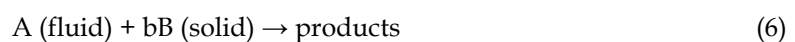
### 3.2. Effect of solution temperature

The effect of temperature, 290–358 K, on the dissolution of Ag samples, according to the salt (KCl) concentration of the leaching reagent, is presented in Fig. 5.

It reveals that the extraction recovery of silver increases with increasing temperature for all relevant salt concentrations. This effect becomes more evident in the first stage, especially at high salt concentrations (1 M). Silver recovery in the initial period of the reaction for 1 M KCl at 85 °C is calculated as approximately 45%, while for lower concentrations of 0.5 M and 0.25 M, these rates are limited to 35% and 30%, respectively. Additionally, the silver recovery increased up to 53% 1 M KCl at 85 °C after 10 minutes, and reached a plateau, and there was no change in the recovery up to 30 minutes. On the other hand, for lower KCl concentrations 0.5 M and 0.25 M silver recoveries were 53.15% and 49%, respectively, at 85 °C. Considering the optimum leaching conditions, it can be noted that the optimum parameters were as follows: Temperature of 85 °C, leaching time of 10 min, concentrations of 0.5 M and 0.1 M for KCl and NaOCl, respectively, the solid ratio of 30%, and particle size ( $d_{80}$ ) 15  $\mu\text{m}$ .

### 3.3. Kinetic Analysis

In extractive metallurgy the dissolution reaction, taking place between a fluid and a solid, can be written in its simplest form as follows (Shon and Wadsworth, 1979):





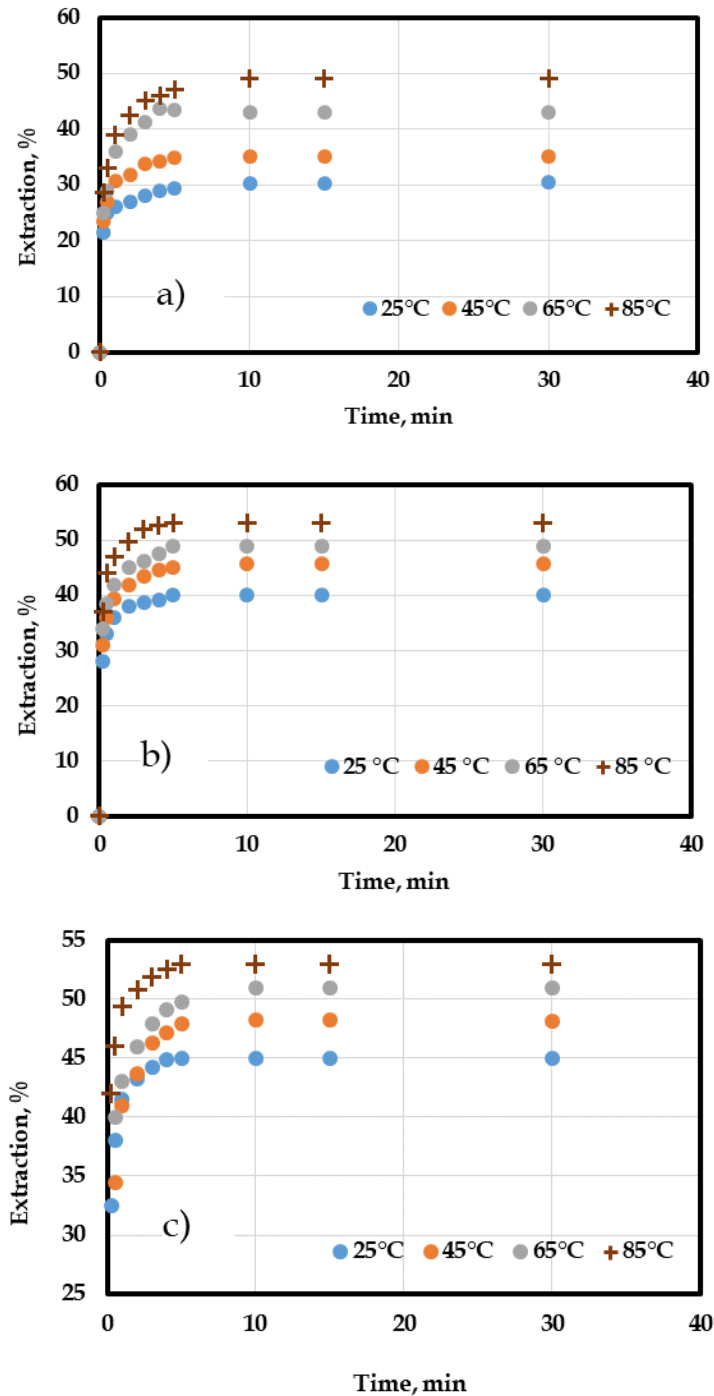


Fig. 5. Calculated Ag recoveries according to solution temperature and KCl concentrations, 0.25 M (a), 0.5 M (b) and 1 M (c)

Under this general definition, if the reaction performed on pure oxide minerals the reaction rate expressed as a controlled by chemical surface reaction or diffusion through a limiting boundary film. For these conditions, which are mostly observed for readily soluble oxide ores, if the dissolution reaction occurs on grain surfaces, the reaction rate is mainly controlled by the linear rate and the equation can be given as follows.

$$1-(1-\alpha)^{1/3} = kt \quad (7)$$

where  $\alpha$  is the reaction reacted,  $k = Ck_t/r_0$  time<sup>-1</sup>. The conversion is defined as the ratio of the amount of silver dissolved to the initial amount of silver at time  $t$ ,  $C$  is the concentration of fluid. Considering the dissolution reaction of silver in oxidative and acidic states given in Equation 5, solid product

formation is not expected. However, the equilibrium reaction discussed previously depends on reactant product concentrations and can be reversible. This will require the reconversion of dissolved silver ions into metallic silver. Apart from the reverse dissolution reaction, the dissolution of other minerals rather than silver due to the reaction processes and their possible precipitations on the reacting surface may also cause the formation of a diffusion layer. Thus, the reaction rate decreases due to the diffusion of the solvent reagent through this diffusion layer. This situation, which is encountered in many hydrometallurgical applications, especially in refractory ores, can be explained by the shrinking core model, which consists of an unreacted shrinking core and a diffusion layer surrounding it, as given in Fig. 6.

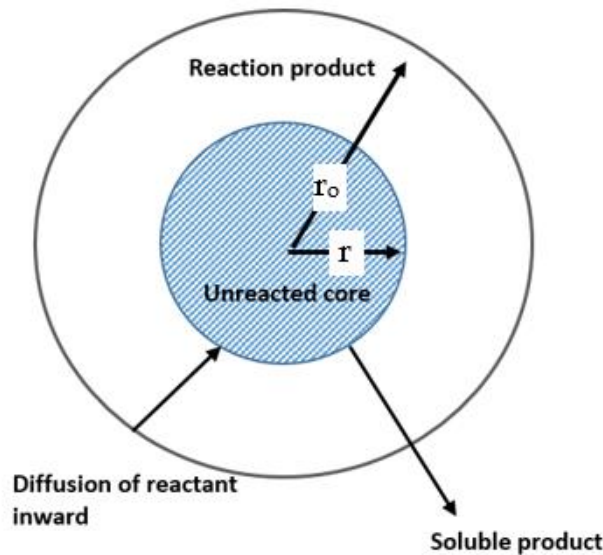


Fig. 6. Particle reacting topochemically with diffusion through remanent structure or products of reaction as the rate limiting step

In this case, the overall process can be identified within to following steps; external mass transfer, diffusion of the leaching agent through the thin liquid film surrounding the particle, diffusion of the leaching agent through the product layer, chemical reaction at the interface between the unreacted and completely reacted zones.

According to the assumption that the shape of the solid is spherical and does not change during the reaction, their mathematical expression is;

$$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = \frac{6bDc_t}{qR^2} = kt \quad (8)$$

where  $b$  is a coefficient of the solid,  $k$  is the reaction rate constant,  $D$  is the diffusion coefficient,  $\rho$  is the molar density, and  $R$  is the radius of the solid particle. The calculated rate constants; that is,  $K_s$  and  $K_p$ , as surface and diffusion regions, and the correlation coefficients calculated for  $KCl$  concentrations using Equations 7 and 8 are given in Tables 5, 6 and 7, respectively.

Table 5. The calculated rate constants and regression coefficients ( $R^2$ ) for 1 M  $KCl$  concentration

Temperature	1 <sup>st</sup> Stage				2 <sup>nd</sup> Stage	
	$k_s$	$r^2$	$k_p$	$r^2$	$k_p$	$r^2$
25 °C	0.3129	0.8258	0.0384	0.9125	0.0006	0.9693
45 °C	0.3599	0.8595	0.0504	0.9501	0.0007	0.9823
65 °C	0.3950	0.7749	0.0592	0.9550	0.0008	0.9824
85 °C	0.4260	0.7942	0.0686	0.8638	0.0008	0.9301

Table 6. The calculated rate constants for 0.5 M KCl concentration

Temperature	1 <sup>st</sup> Stage				2 <sup>nd</sup> Stage	
	$k_s$	$r^2$	$k_p$	$r^2$	$k_p$	$r^2$
25 °C	0.2800	0.8477	0.0311	0.9440	0.0003	0.8294
45 °C	0.3110	0.8390	0.0381	0.9273	0.0006	0.9750
65 °C	0.3395	0.8201	0.0501	0.9639	0.0007	0.9945
85 °C	0.3817	0.8620	0.0590	0.9535	0.0008	0.9563

Table 7. The calculated rate constants and correlation coefficients for 0.25 M KCl concentration

Temperature	1 <sup>st</sup> Stage				2 <sup>nd</sup> Stage	
	$k_s$	$r^2$	$k_p$	$r^2$	$k_p$	$r^2$
25 °C	0.2060	0.8336	0.0173	0.9241	0.00007	0.9131
45 °C	0.2254	0.8249	0.0205	0.9122	0.0003	0.9593
65 °C	0.2433	0.8337	0.0238	0.9225	0.0013	0.9288
85 °C	0.2817	0.8345	0.0314	0.9215	0.0014	0.9754

The regression coefficients calculated for the surface and diffusion model given in Tables 5, 6 and 7 showed that the  $R^2$  values obtained for the diffusion model were more reliable. Tables indicated that in the first stage, reaction rates for all KCl concentrations were faster than that of the ongoing process. However, the model moved away from the linear form even at the first stage. Therefore, it can be suggested that in the HCl/NaOCl and KCl system, the entire dissolution reaction of silver is controlled by the diffusion of fluid to the reacted diffusion layer around the unreacted shrinking core model. As indicated above, this can be attributed to the presence of easily dissolved free Ag grains in the ore sample and the close influence of the ambient potential on the stability of dissolved ions.

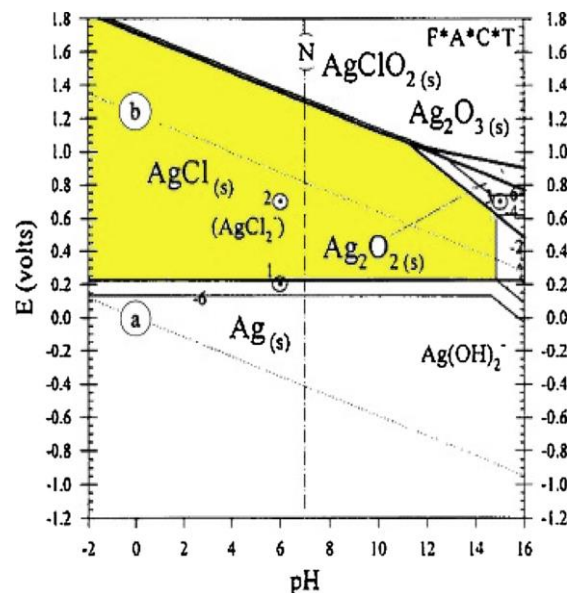


Fig. 7. Pourbaix diagram for Ag in chloride media Source: Masilela and Ndlovu, 2019.

Ag can exist in different forms in aqueous chloride solution (Fig. 7). As in the experience getting dissolution processes using aqua regia, the factor affecting the silver recovery efficiency in dissolved silver complexes is the stabilization of dichlorosilver ( $\text{AgCl}_2^-$ ) ion. In early paper released by Vifials et al., 1995 for gold dissolution. It was pointed out that chlorine concentration and pH are the effected factors that influence the recovery. For  $\text{pH} < 1.5$  the reaction rates were insensitive to pH however, for

pH > 1.5 the rates decrease progressively until the pH is 4. This effect was attributed to the change in the distribution of chlorine species. In the studies conducted at different chloride concentration the fraction reacted amount, was found to be increased as the concentration increased. A recent study by Nam et al., 2008, aiming to recover silver from waste material, also supports this result. The authors reported that for the chloride-hypochlorite leaching method, Ag dissolution is closely related to the stability of the complex ion formed as a result of the leaching process and the dissolution kinetics is controlled by shrinking core model. Especially, the occurrence of  $\text{Au}(\text{OH})_3$ , slow down the dissolution. In addition, although the solubility of barite to barium and sulfate ions in water is low ( $2.47 \text{ mg/dm}^3$  ( $25^\circ\text{C}$ , solubility product  $K_{\text{sp}} = 10^{-9.9}$ ), researchers in the literature have reported that its solubility can be increased in acidic environment (HCl), especially in the presence of K or Na chloride (Monnin and Galinier., 1988; Zhen-Wu et al., 2016):



If such dissolution occurs in oxidative conditions, the reaction of  $\text{Ba}^{2+}$  with oxygen occurs under ambient conditions, resulting in the formation of Barium oxide, which consists of colorless cubic or hexagonal crystals. On the other hand, it is clear that members of the jarosite subgroup may also occur in this case. Although strong acidic conditions and relatively high temperature ( $\geq 90^\circ\text{C}$ ) are required for the formation of jarosite/jarosite subgroups, considering the literature information, the formation of jarosite is also possible at room temperature ( $25^\circ\text{C}$ ) (Brown., 1970; Duoqiang et al., 2008; Bigham et al., 2010). In the recent study published by Caneren and Karagüzel., 2021 jarosite formation was reported under pressure and high temperature conditions for similar dissolution processes, which supports the possible jarosite formation. When these results are evaluated, the main requirement for jarosite formation appears to be the provision of an  $\text{Fe}^{3+}$  bearing, acidic environment (pH < 3). However, once minerals are formed, they easily decompose when removed from their stable regions. Therefore, the continuation of the formation reaction conditions and the stability of the resulting product will be very important. In the precipitation reaction in which no neutralizing agent is added, precipitation will continue until the equilibrium acid concentration is reached, at which point the net precipitation of jarosite will cease. The SEM image of leaching waste and EDX analysis results are given in Fig. 8.

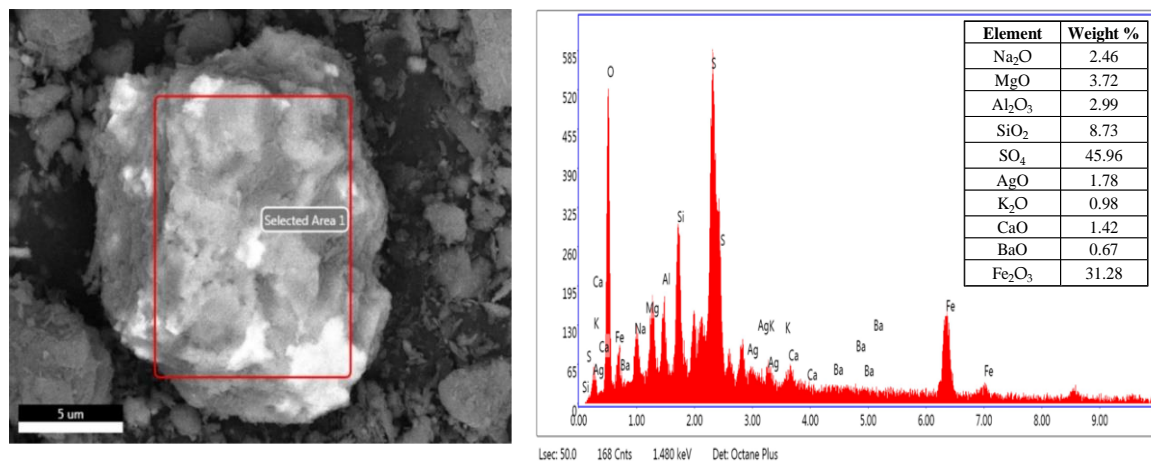


Fig. 8. SEM image and EDX results of the leaching residue experimented at  $25^\circ\text{C}$  in 1M KCl, 0.25M HCl and 0.1M NaOCl solutions (Chemical formula of jarosite:  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ )

These results support the possibilities discussed above. However, the increases in silver ion concentration passing into the solution in step two suggest that the formed K-jarosite is not very stable. Under these assumptions, plots of  $1 - 2/3 \alpha - (1 - \alpha)^{2/3}$  as a function of time for Ag samples according to concerning KCl concentrations given at Fig. 8 confirm the shrinking core model is valid for a diffusion-controlled process. Fig. 9 also reveals that increase in temperature is positively affect the reaction rates. This effect was more evident in the first stage for 1 and 0.5 M KCl concentrations, while for 0.25 M KCl, it getting more pronounced then after  $45^\circ\text{C}$  at the second stage compared to other concentrations.

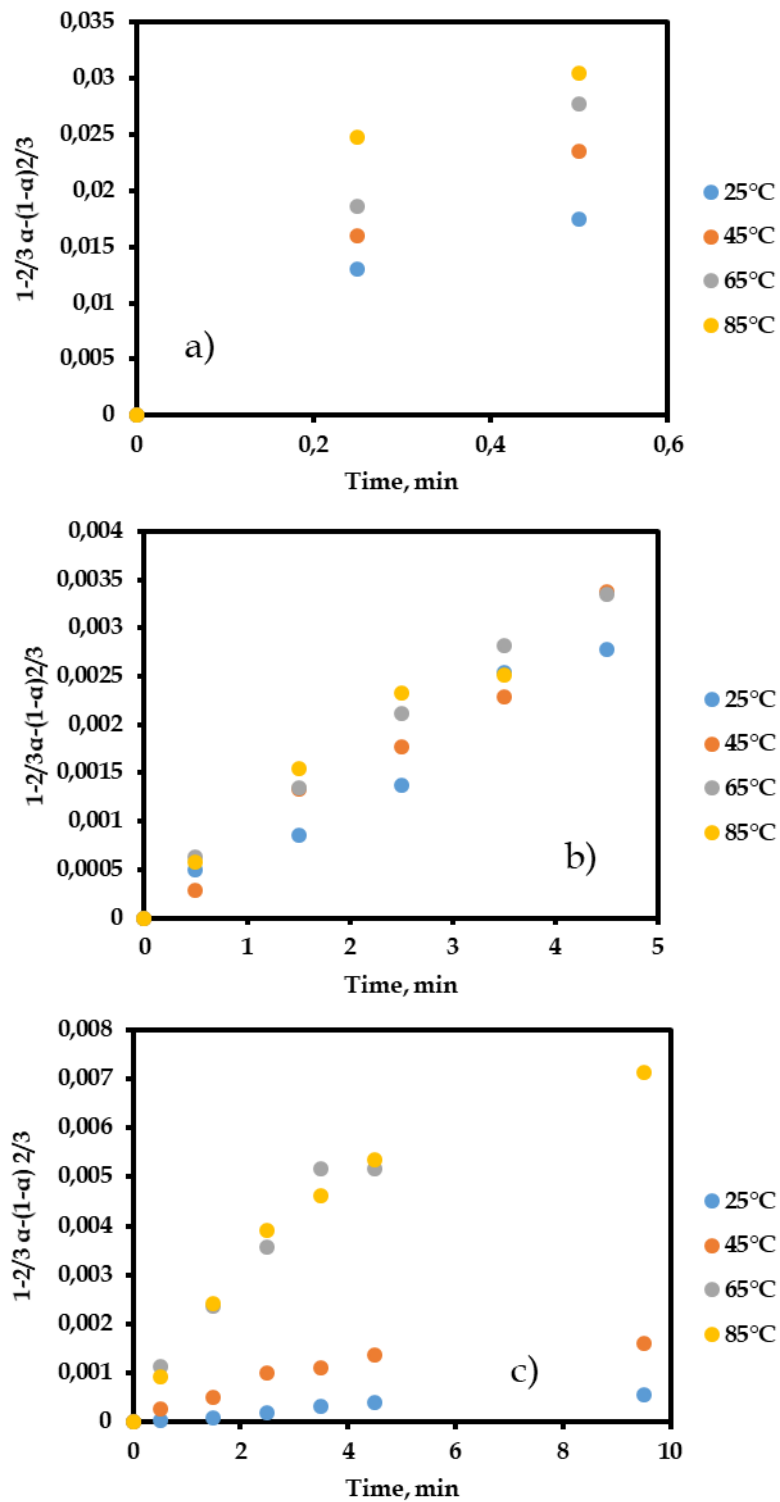


Fig. 9. Plot of  $1 - \frac{2}{3}\alpha - \frac{(1-\alpha)^2}{3}$  for Ag samples as a function of time: (a) 1 M KCl (b) 0.5 M KCl, and (c) 0.25 M KCl

The activation energies of the dissolution reactions were calculated by using a linear form of the Arrhenius equation given as:

$$\ln k = \ln A - (E/RT) \quad (10)$$

where A is the exponential coefficient, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. Arrhenius plots with using Kp for first and second sages are given at Fig. 10.

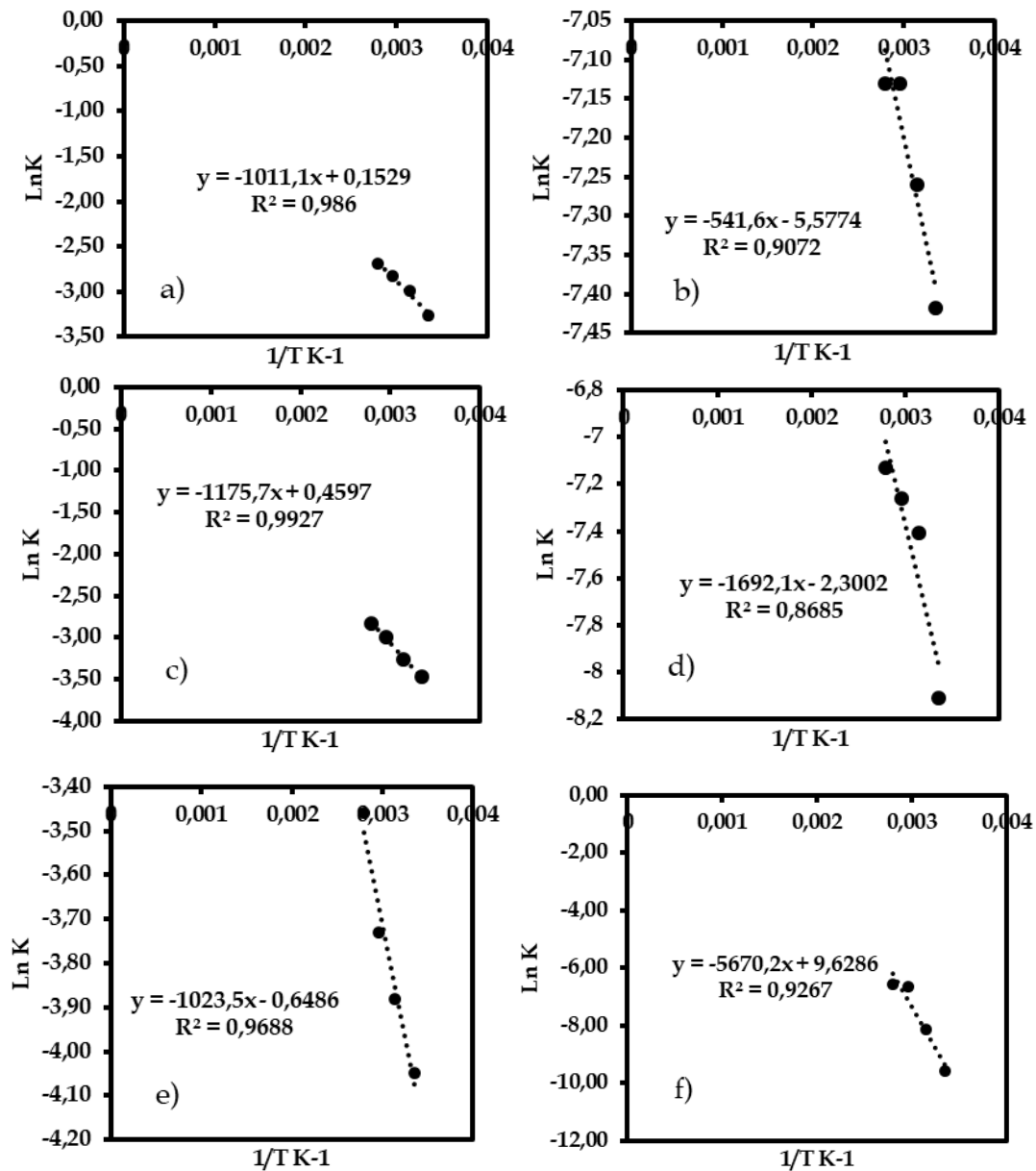


Fig. 10. Arrhenius plot for the dissolution of Ag samples showing the effect of temperature on k: (a), (b) 1 M KCl first and second stages, (c), (d) 0.5 M KCl first and second stages, and (e), (f), 0.25 M KCl first and second stages

For the temperature range of 290–358 K, activation energies for 1M, 0.5 and 0.25 M KCl concentrations in the first stage, where the main dissolution is occurred, were calculated as 8434, 9807, 8537 J mol<sup>-1</sup>, respectively. In the second stage, analysis results show that the dissolution reaction occurs in a diffusion-controlled manner. Unlike the first stage, activation energies decrease as the KCl concentration increases. 4517, 14113.9, 47293 J mol<sup>-1</sup>.

This result shows a similarity with the recent study by Li et al., 2018. In this study, cyanidation waste was subjected to selective leaching with chloride after a pre-oxidation performed in a tube furnace. The authors note that the activation energy of silver is approximately 8.97 kJ/mol, indicating that dissolution can be characterized by diffusion control.

#### 4. Conclusions

In this study, the silver dissolution in HCl/NaOCl and KCl solution was investigated as an alternative to NaCN leaching. The leaching tests performed at various parameter levels (temperature 25 °C -85 °C and KCl concentrations 0.25 M -1 M) showed that;

- The optimal leaching conditions are found as 0.5 M KCl, 10 minutes of stirring time, 85 °C of temperature, 0.1 M of NaOCl concentration, 0.25 M of HCl concentration, 30% of solids ratio and particle size ( $d_{80}$ ) 15  $\mu\text{m}$ ,
- Under the optimum conditions, the silver extraction from refractory ore is 53.15%,
- The dissolution process occurs very quickly within 0.5 minutes,
- Although this high dissolution rates are thought that the reaction progresses with dissolution from the solid grain surface during this period, kinetic calculations show that a diffusion process occurs with the shrinking core or formation of new products in this process, which reduces the reaction rate,
- It is seen that increasing the reagent concentration has a positive effect on the reaction rate for the first part.
- After than the first stage, it is seen that the dissolution reaction (rate) slows down very much, especially for high concentration and temperature increases. For low KCl concentrations, dissolution in this part continues for increased contact times. For this reason, for 0.25 M KCl the reaction rate constant was calculated as higher than 0.5 M and 1 M. For increasing concentrations, the reaction rate nearly constant and decreases because most of the dissolution reaction is completed in the first period.

### Acknowledgments

The authors gratefully acknowledge Eti Silver Mining Industry Co., Ltd. for providing the raw material and laboratory supports.

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