Gold Leaching from an Oxide Ore Using Thiocyanate as a Lixiviant: Process Optimization and Kinetics

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ABSTRACT: Thiocyanate (SCN\textsuperscript{−}) is a promising alternative to cyanide as a lixiviant for gold extraction and is 1000 times less toxic than cyanide. In this study, the following leaching parameters were tested to optimize the gold recovery for the first time from an oxide ore using the response surface methodology: initial thiocyanate concentration (10–500 mM), initial Fe\textsuperscript{3+} concentration (10–500 mM), and pulp density (10–50% w/v). The maximum gold recovery (96%) was achieved with 500 mM thiocyanate, 100 mM Fe\textsuperscript{3+}, and 50% pulp density at 25 °C and pH = 2 for 24 h. A kinetic study on the optimum leaching condition showed that it followed the shrinking core model, in which the rate-controlling mechanism was the diffusion process. These results are discussed in the context of the published literature.

1. INTRODUCTION

Gold is in high demand due to its many applications, for example, in electronics, computers, investments, and medicines. Cyanidation has been used to extract gold from ores for more than 100 years, even though cyanide is highly toxic and lethal to humans, other terrestrial animals, and aquatic organisms.\textsuperscript{1} With increasing exploitation over time, the average gold grade has decreased in deposits worldwide, leading to an exponential increase in cyanide consumption.\textsuperscript{2} Consequently, alternative gold leaching lixiviants such as thiosulfate, thiourea, and thiocyanate (SCN\textsuperscript{−}) have been proposed.\textsuperscript{1,3–5} It should be mentioned that in the Goldstrike mine, Nevada, of Barrick Gold Corp., thiosulfate is currently used as an alternative lixiviant for gold extraction on a large scale.\textsuperscript{6} Moreover, thiourea had been employed for gold leaching from the stibnite concentrate in the New England Antimony mine, New South Wales, and also from the copper concentrate in the Val d’Or Mine, Quebec.\textsuperscript{6} Thiourea and thiocyanate have not yet made any significant inroads in the gold mining industry. Compared with that of thiourea and thiosulfate, thiocyanate leaching in gold leaching is lower, which is cost-effective, and it has better stability than thiourea in various media and is 0.1% as toxic as cyanide.\textsuperscript{1,7,8}

First investigated in 1905,\textsuperscript{3} gold dissolution in ferric thiocyanate solution primarily yields stable and soluble dithiocyanato-aurous (Au(SCN)\textsuperscript{2−}) and tetrathiocyanato-auric (Au(SCN)\textsubscript{4}\textsuperscript{−}) species (eqs 1 and 2)

\begin{align*}
\text{Au} + 2\text{SCN}^- + 2\text{Fe}^{3+} & = \text{Au(SCN)}_2^- + 2\text{Fe}^{2+} \\
\text{Au} + 4\text{SCN}^- + 3\text{Fe}^{3+} & = \text{Au(SCN)}_4^- + 3\text{Fe}^{2+}
\end{align*}

The viability of thiocyanate leaching was confirmed in 1989,\textsuperscript{9} and subsequent studies have reported gold recovery ranging from 93% (oxide concentrate in 0.6 M NH\textsubscript{4}SCN in the presence of glycine and 0.05 M Fe\textsuperscript{3+}, pH 2) to 95% (hard arsenopyrite in 0.4 M KSCN, pH 2–5).\textsuperscript{11,14} Many studies have investigated thiocyanate leaching using 99.9% pure gold discs instead of gold-bearing ores and those evaluating gold-bearing ores often use sulfide ores. The most influential gold leaching parameters appear to be initial thiocyanate and oxidant (ferric) concentrations,\textsuperscript{5,12–14} and pulp density.\textsuperscript{15} In thiocyanate leaching, the Fe\textsuperscript{3+}/SCN\textsuperscript{−} ratio plays an important role to...
maximize gold dissolution, e.g., a ratio between 2 and 20 is ideal for a sulfide gold ore and a ratio <1 is ideal for an oxide gold ore. Temperature appears to be less important: the gold dissolution and leaching rate do not change when the temperature is increased from 25 to 55 °C.

For the first time, we focus on thiocyanate leaching of gold from an oxide ore using the response surface methodology (RSM) to determine optimal leaching conditions for maximum gold recovery. It is a popular tool to investigate interactions among leaching parameters and maximize gold recovery because it is cost-effective, rapid and highly accurate. First, pilot studies were designed to quantify the effects of initial thiocyanate, ferric concentrations and pulp densities on gold leaching from an oxide ore. Based on a model equation from Design Expert 7 (DX7) statistical software, the optimal conditions for maximum gold recovery were determined. Subsequently, leaching was carried out under optimal conditions, and the measured and predicted gold recoveries were compared to validate the model.

The coexistence of thiocyanate resonances and production of intermediate thiocyanate species in the leaching solution complicates kinetic investigations. Further, different sample types (e.g., pure gold disc vs gold-bearing ore) show different kinetics. To contribute to the relatively scant literature on the kinetics of thiocyanate leaching and to improve the efficiency of the leaching process, gold dissolution, thiocyanate oxidation, thiocyanate consumption, and the effect of other ions were evaluated to determine the rate-controlling step.

2. RESULTS AND DISCUSSION

2.1. Characterization. X-ray diffraction patterns indicate that the ore and leachate contained mainly quartz (SiO₂). Clinochlore [(Mg,Fe)₆(Si,Al)₄O₁₀(OH)₈], dolomite [CaMg(CO₃)₂], magnesite [Mg₀.₉₈Fe₀.₁₁CO₃], and albite (NaAlSi₃O₈) were also detected as intensity peaks in both diffraction patterns (Supporting Information Figure S1). After leaching under optimal conditions (initial SCN⁻, initial Fe³⁺, and pulp density values of 0.5 M, 0.1 M, and 40%, respectively), the clinochlore, magnesite, and dolomite peaks decreased, indicating that some elements (e.g., Mg and Al) dissolved during leaching. The particle size distribution did not differ between the original oxide ore and the leaching residues (data not shown). Some rod-shaped structures were observed on the surface of leaching residues rather than the ore, which may be associated with the dissolution of dolomite indicated by X-ray diffraction patterns (Supporting Information Figure S2).

2.2. Pilot Studies. The initial thiocyanate concentration had a positive effect on gold recovery (Figure 1a), as did the initial ferric concentration, though to a lesser degree (Figure 1b). By comparison, increasing the pulp density improved the
gold recovery at low thiocyanate and ferric concentrations (10 mM) but had a diminished effect at higher lixiviant and oxidizer concentrations (225 mM), although the overall gold recovery was higher (Figure 1c).

2.3. Statistical Evaluation and Process Optimization.

The range of the three influential parameters was defined based on the literature and pilot studies, and 20 experiments were designed using the D-optimal RSM technique (Table 1).

Table 1. D-Optimal Matrix for Influential Parameters A–C and One Response Variable

| experiment | A: pulp density (%) | B: initial SCN\(^{-}\) (mM) | C: initial Fe\(^{3+}\) (mM) | Au recovery (%) |
|------------|---------------------|--------------------------|--------------------------|-----------------|
| 1          | 10                  | 500                      | 500                      | 82.4            |
| 2          | 30                  | 10                       | 255                      | 25.4            |
| 3          | 50                  | 10                       | 10                       | 34.4            |
| 4          | 10                  | 500                      | 10                       | 82.6            |
| 5          | 50                  | 255                      | 500                      | 76.5            |
| 6          | 10                  | 255                      | 10                       | 41.6            |
| 7          | 50                  | 500                      | 500                      | 91.0            |
| 8          | 10                  | 10                       | 500                      | 2.6             |
| 9          | 50                  | 500                      | 10                       | 83.1            |
| 10         | 30                  | 500                      | 500                      | 85.0            |
| 11         | 10                  | 255                      | 255                      | 90.3            |
| 12         | 10                  | 10                       | 10                       | 0               |
| 13         | 40                  | 377.5                    | 255                      | 83.1            |
| 14         | 50                  | 500                      | 10                       | 39              |
| 15         | 10                  | 500                      | 10                       | 90.0            |
| 16         | 10                  | 10                       | 500                      | 0               |
| 17         | 30                  | 10                       | 10                       | 0               |
| 18         | 50                  | 10                       | 10                       | 3.5             |
| 19         | 10                  | 10                       | 10                       | 0               |
| 20         | 50                  | 10                       | 500                      | 7.0             |

A two-way analysis of variance (ANOVA) was run to define the most effective parameter (\(\alpha = 0.05\)). The multiple linear regression model explains thiocyanate leaching under defined conditions (Table 2).18 Only the initial SCN\(^{-}\) concentration linear regression model is significant, and the interactions between the parameters are negligible. The \(R^2\) value for the model (Table 3) is higher than the threshold of 0.7, indicating a reliable model.19 Further, the predicted and adjusted \(R^2\) values are in good agreement, differing by less than the threshold of 0.2. The signal-to-noise ratio is above the threshold of 4, indicating an adequate signal. DX7 software also provides the normal probability of the empirical model for the response, which follows a normal distribution.

Table 2. ANOVA Output for the Multiple Linear Regression Model for Au Recovery

| source              | sum of squares | degrees of freedom | mean square | \(F\)   | \(p\) (prob > \(F\)) |
|---------------------|----------------|--------------------|-------------|---------|----------------------|
| model               | 21999.43       | 3                  | 7333.14     | 19.23   | <0.0001              |
| A: pulp density     | 3.56           | 1                  | 3.56        | 9.342 \(10^{-3}\) | 0.9242              |
| B: initial SCN\(^{-}\) | 21120.56     | 1                  | 21120.56    | 55.39   | <0.0001              |
| C: initial Fe\(^{3+}\) | 384.39        | 1                  | 384.39      | 1.01    | 0.3303               |
| residual            | 6100.38        | 16                 | 381.27      | 1.41    | 0.3695               |
| lack of fit         | 4617.10        | 11                 | 419.74      | 1.41    | 0.3695               |
| pure error          | 1483.28        | 5                  | 296.66      | 1.41    | <0.0001              |
| corr total          | 28099.82       | 19                 |             |         |                      |

The equation for the model (eq 3) shows that all variables had a positive effect on gold recovery, while thiocyanate concentration has the highest coefficient, which indicates that it is the most effective parameter compared to the other two.

\[
\text{Au recovery} = 5.8 + 0.024 \times \text{pulp density (\%)} + 0.16 \times \text{initial SCN}^{-} \text{(mM)} + 0.02 \times \text{initial Fe}^{3+} \text{(mM)}
\] (3)

The perturbation diagram comparing the effect of the three parameters at their middle levels in the design space (Figure 2) also shows that the initial SCN\(^{-}\) concentration affected gold recovery the most, which is consistent with the proposed model equation.

Three-dimensional response surface diagrams allow visualization of the effect on the response of two parameters at the same time, while the third parameter is fixed at its mid-level. From blue to red contour lines, the gold recovery increased to a maximum of 91% with the increasing initial SCN\(^{-}\) concentration and pulp density (Figure 3a) and the increasing initial Fe\(^{3+}\) and SCN\(^{-}\) concentrations (Figure 3b). Lower gold recovery was achieved with combinations of increasing initial Fe\(^{3+}\) concentration and pulp density (Figure 3c).
The combined effect of initial SCN$^-$ and Fe$^{3+}$ concentrations (Figure 3b) is considered to define the optimal condition. However, a higher pulp density and lower reagent concentrations could be more cost-effective. Thus, the optimal leaching conditions were identified using model suggestions that would meet the objective of maximizing gold recovery at the highest pulp density and lowest reagent concentrations. Experiments were carried out under four optimal conditions, and the results were compared with the predicted gold recovery using eq 3 (Table 4). A gold recovery of 96% was achieved at initial conditions of 500 mM SCN$^-$, 100 mM Fe$^{3+}$, and 50% pulp density.

2.4. Kinetic Study. During the leaching period, the gold dissolution rate was high until $\sim$2 h and then slowed (Figure 4). This can be explained by auto-reduction, whereby spontaneous reduction of Fe$^{3+}$ to Fe$^{2+}$ oxidizes SCN$^-$ to produce the metastable intermediate products (SCN)$_2$ and (SCN)$_3^-$ (eqs 4 and 5).12

$$2\text{SCN}^- + 2\text{Fe}^{3+} = (\text{SCN})_2 + 2\text{Fe}^{2+}$$

Figure 3. Combined effect on the gold recovery of (a) initial SCN$^-$ concentration and pulp density at 255 mM Fe$^{3+}$, (b) initial Fe$^{3+}$ and SCN$^-$ concentrations at 30% pulp density, and (c) initial Fe$^{3+}$ concentration and pulp density at 400 mM SCN$^-$. 

ACS Omega 2021, 6, 17183−17193
concentration decreases, leading to slower gold leaching.13 Solution ORP decreases, Au(SCN)$_2^-$ leaching process (Supporting Information Figure S3). As rapidly formed as the predominant gold species early in the leaching period (Figure 4). As a result of fast auto-reduction at high ORP, Au(SCN)$_4^-$ is produced, decreasing the gold dissolution rate.6,14 Gradual formation of a stable passive layer of AuSCN on the gold surface, decreasing the gold dissolution rate.9,13

Initially, iron precipitated as Fe(OH)$_3$. This hypothesis is supported by the observation that after pH adjustment to around 2, the total iron concentration slightly increased from 3.9 to 4.5 g/L. It is also postulated that Fe$^{3+}$ accumulation in the system decreases the solution ORP.

Table 4. Optimal Conditions for Thiocyanate Gold Leaching at the Highest Pulp Density and Lowest Reagents Concentration

| experiment | pulp density (% w/v) | initial SCN$^-$(mM) | initial Fe$^{3+}$(mM) | measured | predicted |
|-----------|----------------------|----------------------|----------------------|----------|-----------|
| 1         | 50                   | 500                  | 150                  | 90       | 90        |
| 2         | 40                   | 500                  | 100                  | 91       | 89        |
| 3         | 50                   | 500                  | 300                  | 94       | 93        |
| 4         | 50                   | 500                  | 100                  | 96       | 89        |

Figure 4. Gold recovery and ORP changes at optimal leaching conditions: 500 mM initial SCN$^-$ concentration, 100 mM initial Fe$^{3+}$, and 40% pulp density at 300 rpm.

3SCN$^-^+$ + 2Fe$^{3+}$ = (SCN)$_3^-^-+$ + 2Fe$^{2+}$  \hspace{1cm} (5)

These intermediate thiocyanate species can act as oxidants and complexants to accelerate SCN$-$ oxidation and gold dissolution. As leaching proceeds, intermediate species, especially (SCN)$_2$H$^+$, are likely hydrolyzed, leading to higher thiocyanate consumption and slower gold dissolution (eq 6):

3(SCN)$_2$H$^+$ + 4H$_2$O = 5SCN$^-$ + HCN + SO$_4^{2-}$ + 7H$^+$  \hspace{1cm} (6)

In addition, when iron-bearing thiocyanate species such as FeSCN$^2+$ and Fe(SCN)$_2^-$ are produced, the free thiocyanate concentration decreases, leading to slower gold leaching.13

The oxidation–reduction potential (ORP) of the slurry decreased throughout the leaching period (Figure 4). As a result of fast auto-reduction at high ORP, Au(SCN)$_3^-^-$ is formed as the predominant gold species early in the leaching process (Supporting Information Figure S3). As solution ORP decreases, Au(SCN)$_2^-$ is formed at a lower rate, leading to the adsorption of AuSCN [Au(s) + SCN$^-$] and gradual formation of a stable passive layer of AuSCN on the gold surface, decreasing the gold dissolution rate.6,14

The total iron concentration decreased rapidly during the first 3 h of leaching and then plateaued (Figure 5). This change was driven by the reduction of Fe$^{3+}$ to Fe$^{2+}$ early in the leaching process. One hypothesis is that when the ore was added to the solution, the pH rapidly increased to around 4, and iron precipitated as Fe(OH)$_3$. This hypothesis is supported by the observation that after pH adjustment to around 2, the total iron concentration slightly increased from 3.9 to 4.5 g/L. It is also postulated that Fe$^{3+}$ accumulation in the system decreases the solution ORP.

2.4.1. Rate-Controlling Step. The shrinking core model (SCM) has been widely used to describe leaching kinetics. The particle cores shrink, but the particle size remains constant. Generally, particle dissolution in leaching solutions is a heterogeneous reaction. In this case, the following steps in series can be identified during the leaching: diffusion of the leaching agent through the thin liquid film surrounding the particle, diffusion of the leaching agent through the solid product layer, and the reaction on the surface of the unreacted core. Therefore, based on the SCM, the following steps can be identified:20

1 Leachant diffusion to the particle
2 Chemical reaction on the surface of the particle

The overall leaching rate is controlled by the slower step. If both steps control the dissolution rate, the SCM is a mixed control model. To investigate which step(s) controls the reaction rate, the results were plotted based on standard SCM equations, eqs 7–9 for leachant diffusion, chemical reaction, and mixed control, respectively (Figure 6), where the Y axis in Figure 8 indicates the left side of the following equations

1 $-3(1-X)^{2/3} + 2(1-X) = k_d t$  \hspace{1cm} (7)
2 $1 - (1-X)^{1/3} = k_f t$  \hspace{1cm} (8)
3 $(1 - 2/3X) - (1-X)^{2/3} + B(1 - (1-X)^{1/3}) = k_m t$  \hspace{1cm} (9)

where X represents the reacted fraction of Au at time t. The rate constants $k_d$, $k_f$, and $k_m$ are for diffusion, chemical reactions, and mixed control, respectively. In the mixed control equation, B is the ratio of $k_f/k_d$. In Figure 6, the $R^2$ value for diffusion ($R^2 = 0.98$) is slightly higher than that of the chemical reaction ($R^2 = 0.95$). Therefore, the leaching process more likely follows a diffusion-controlled model, which is consistent with the literature.6,21 The thiocyanate gold leaching process seems to have three stages. The initial leaching stage is when the solution potential is high, and Au(SCN)$_2^-$ is produced rapidly. In the next stage, when the solution potential decreases gradually, Au(SCN)$_3^-^-+$ is produced moderately and results in the formation of a stable passivation layer of AuSCN [Au(s) + SCN$^-$] on the gold surface in the final stage of leaching.6,9,14 The passive layer of the latter stage limits the diffusion of species to and from the gold surfaces. Consequently, diffusion of the leaching agent through the
passivation layer is assumed as the rate-controlling step in the system.

It should be noticed that the $R^2$ value for the chemical reaction equation is also higher than 0.9 ($R^2 = 0.98$), which means that the chemical reaction of the leachant on the gold surface can also contribute to the leaching rate. The amount of free thiocyanate for gold complex formation can be considered as an important parameter in the chemical reaction step. As has been mentioned before, at the beginning of the leach, when the ORP of the solution is high and the predominant species is $\text{Au(SCN)}_4^{-}$, more SCN$^-$ ions are required for the formation of gold–thiocyanate complexes. In addition, the intermediate species, $(\text{SCN})_3^-$ and $(\text{SCN})_2^-$, and Fe–SCN complexes also consume more free thiocyanate, which contributes to the thiocyanate loss and limits the chemical reaction on the particle surfaces.

2.5. Thiocyanate Consumption. One of the challenges to commercializing non-cyanide gold leaching reagents is their high consumption rate, which was observed during the first 4 h of leaching (Figure 7). This high consumption was in part due to the formation of thiocyanate intermediate species, predominantly $\text{Au(SCN)}_4^-$, at a high ORP, which means that four SCN$^-$ ions are required for each complex. As leaching proceeds, the ORP decreases and $\text{Au(SCN)}_2^-$ becomes the predominant species, with a concomitant decrease in the thiocyanate consumption rate. Approximately 60% of the initial thiocyanate available at the end of the 24 h leach could be recovered by recycling the leach solution in the process circuit.

2.6. Effects of Other Metal Ions on Thiocyanate Gold Leaching. Among other metals present in leach solutions that could compete with Au to form complexes with thiocyanate, Cu was present at the highest concentration (Figure 8) and under the optimized leaching conditions was probably present as $\text{Cu(SCN)}_2^{(aq)}$. At high concentration ($>13$ g/L Cu), the predominant Cu species, $\text{CuSCN(s)}$, precipitates as a solid, resulting in thiocyanate loss. It is recommended that Cu is pre-leached in sulfuric acid at a pH of 1–3 from the Cu-bearing gold ore to limit this loss. The effect of the relatively high total Fe concentrations in the leach solution (Figure 8) depends on whether it is in the ferric or ferrous state. Barbosa-Filho and Monhemius achieved the highest gold recovery in gold thiocyanate leaching tests when 5–10% of the total Fe was $\text{Fe}^{2+}$, slightly lowering the ORP of the leach slurry and helping with moderate auto-reducing rates. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be controlled by adding manganese dioxide ($\text{MnO}_2$). Therefore, dissolution of Mn in solution has a positive effect on leaching efficiency. Mg was also present at relatively high concentrations (Figure 8). However, Mg ions do not form a complex with thiocyanate, and Mg($\text{SCN)}_2$ salt readily dissolves in leaching solutions; thus, its presence does not have a deleterious effect on thiocyanate gold leaching. Zn and As were present at lower concentrations (Figure 8), and their impact on gold leaching is expected to be negligible. Ag appears to have the highest potential to contribute to thiocyanate consumption because it forms stronger complexes than Fe and Cu. However, the Ag concentration in the experimental oxide ore—and thus in the pregnant leach solution—was very low (Figure 8).

2.7. Fourier Transform Infrared Analysis. Thiocyanate is an ambidentate ligand: it has two electron structures (SCN$^-$ and NCS$^-$) and thus has the ability to attach to the central atom at either the S or N atom. Moreover, bridge-type complexes may be formed with metals, in which both S and N atoms donate electrons. According to the hard and soft acid–base theory, SCN$^-$ is a soft base ion and NCS$^-$ is a hard base ion. Soft metals such as Au and Ag have an affinity to bond

Figure 6. Kinetics of thiocyanate gold leaching fitted to three standards equations for the SCM at optimal conditions: 500 mM initial SCN$^-$ concentration, 100 mM initial Fe$^{3+}$ concentration, and 40% pulp density at 300 rpm.

Figure 7. Thiocyanate consumption at optimal leaching conditions: 500 mM initial SCN$^-$ concentration, 100 mM initial Fe$^{3+}$ concentration, and 40% pulp density at 300 rpm.
with S which is more covalent, and hard metals such as Fe, Mn, Cu, Zn, and Ni preferentially bond with N that is more ionic.22,30

The peaks in the Fourier transform infrared spectra around 3300 cm\(^{-1}\) in thiocyanate and pre- and post-leach solutions (Figure 9) correspond to symmetric and asymmetric stretching vibrations of water, respectively.31 For thiocyanate, the broad band between 2200 and 2020 cm\(^{-1}\) likely represents the double or triple bond CN vibration band,32 which could correspond to the CN vibration bands of M-NCS, M-SCN, and M-NCS-M that occur at 2100–2050, 2130–2085, and 2165–2065 cm\(^{-1}\), respectively.33 The sharp band at 1635 cm\(^{-1}\) is ascribed to conjugated vibration and stretching of C≡N,35,38 which shifts slightly to 1637 cm\(^{-1}\) in the pre-leach solution and back to 1635 cm\(^{-1}\) after 24 h leaching.34–36 The band at 1103 cm\(^{-1}\) in the pre-leach solution is attributed to the C–N single bond, which shifts after 24 h leaching to 1101 cm\(^{-1}\).34,37 The peak in the pre-leach solution at 2062 cm\(^{-1}\) can be assigned to the vibration band of C≡N.35,38–40 Consequently, it can be assumed that after Fe addition as an oxidant, the predominant form of thiocyanate is NCS\(^{-}\), which can easily coordinate with the hard metals such as Zn and Mn. After 24 h leaching, the C≡N vibration band shifts to a slightly lower wavenumber (2060 cm\(^{-1}\)), which suggests that these bands are only slightly affected by the presence of the ore because the gold and silver (as soft metals) concentrations in the ore are low relative to that of hard metals such as Fe.

3. LITERATURE COMPARISON

Table 5 compares the results of the present work with thiocyanate gold leaching studies from the literature. Two studies used high-purity gold discs, and the results cannot be generalized to thiocyanate gold leaching from more complex ores or concentrates. As mentioned above, a key challenge is the high thiocyanate consumption due to complexation with other ions. Most reports investigated the effect of copper and iron on leaching efficiency but neglected the effects of other ions associated with gold-bearing minerals. In addition, some studies used reagents such as thiourea41 and glycine10 to reduce reagent consumption. Recently, the synergistic effect of thiourea and thiocyanate on gold extraction from activated carbon ashes in the presence of H\(_2\)O\(_2\) as the oxidant has been

![Figure 8. Dissolved concentration of metals ion at optimal leaching conditions: 500 mM initial SCN\(^{-}\) concentration, 100 mM initial Fe\(^{3+}\) concentration, and 40% pulp density at 300 rpm.](https://doi.org/10.1021/acsomega.1c00525)

![Figure 9. Infrared spectra for thiocyanate and the optimal leaching solution (500 mM initial SCN\(^{-}\) concentration, 100 mM initial Fe\(^{3+}\) concentration, and 40% pulp density at 300 rpm) before and after 24 h leaching.](https://doi.org/10.1021/acsomega.1c00525)
investigated. In this study, 0.13 M thiourea and 0.78 M thiocyanate extracted 89% gold in 100 min; the leaching rate is significant, while the reagent concentration is still higher than that in the present article.\(^1\) Generally, it can be concluded that the gold concentration, ore type, and ore mineral composition affect thiocyanate consumption and optimum leaching conditions. Overall, the results of the present study, high gold recovery, and optimal leaching conditions represent unique contributions to the literature by using the design of experiments approach, conducting leaching experiments on the oxide ore rather than the high-purity gold disc and more common sulfide ores, not adding a synergist to reduce the reagent consumption, employing a high pulp density, and evaluating leaching kinetics along with effect of different metal ions.

4. MATERIALS AND METHODS

4.1. Oxide Gold Ore. The oxide ore used for leaching experiments originated from the province of Ontario, Canada. Ore samples were vacuum-dried, pulverized to an 80% passing size of 60 μm, and split with a riffle splitter to obtain an even distribution for particle size analysis (Supporting Information Figure S4). Aqua regia digestion followed by inductively coupled plasma optical emission spectrometry (ICP–MS) was done on an ore sample to analyze the metallic composition of the oxide ore (Table 6). Gold can be recovered from this ore using conventional cyanidation.

4.2. Analytical Methods. The metallic composition of the oxide ore sample was analyzed using ICP–MS (PerkinElmer ELAN 9000/NexION). Qualitative X-ray diffraction analysis was conducted to characterize the mineral composition of fresh ore samples and leaching residues with a Philips X’Pert Pro powder diffractometer and X’Pert HighScore Plus software (v. 3.0e, Malvern Panalytical, Netherlands). Particle size analysis of the ore and residues was done using a Mastersizer 3000 laser diffraction particle size analyzer (Malvern Panalytical, Netherlands). The surface morphology of ore samples before and after leaching was examined with a scanning electron microscope (Quanta 650, Thermofisher Scientific, USA).

At specified intervals during leaching, Eh and pH were measured with an Accumet XL600 Eh and pH meter. An atomic adsorption spectroscope (ThermoScientific ICE 3000) with an air–acetylene flame was used to measure the gold and total dissolved Fe concentrations in leaching solutions and residues. The Fe\(^{2+}\) concentration during leaching (eqs 1 and 2) was analyzed by colorimetric titration using 0.01 N ceric sulfate as the titrant and Ferroin solution as the end-point indicator (orange–red to pale blue). Fe\(^{3+}\) was calculated by subtracting Fe\(^{2+}\) from the total dissolved Fe. Thiocyanate concentrations during leaching were analyzed by the Volhard method,\(^6\) an argentometric titration in which 0.0192 N AgNO\(_3\) diluted in 5% HNO\(_3\) is added to the solution; Ag\(^+\) reacts with SCN\(^-\), changing the dark red solution to white or colorless. Au–SCN complexes are stronger than other SCN complexes in solution;\(^25\) therefore, the residual thiocyanate measured by titration is the amount that was not involved in gold extraction. Thiocyanate consumption was determined by subtracting the residual concentration from the initial thiocyanate concentration. Concentrations of other metals in the ore and residues were assayed in the pregnant leach solution obtained after 12, 24, and 48 h of leaching by ICP–MS (Agilent). To determine the mode of bonding of the thiocyanate structure in the solution, Fourier transform infrared spectra of thiocyanate, the
leaching solution before ore addition (a mixture of thiocyanate and ferric), and the leaching solution after 24 h leaching (a mixture of thiocyanate, ferric, and the ore sample) were recorded in the 500–4000 cm⁻¹ range at a resolution of 4 cm⁻¹ by the attenuated total reflectance spectroscopy instrument (Platinum ATR, Bruker, Netherlands).

4.3. Design of Experiments Methodology. Design of experiments is a useful method to determine the optimal condition of a process based on the variation of effective parameters in a minimal number of leaching experiments. The software provides a perturbation diagram showing interactions and numerical relationships between the parameters. Twenty runs were set using DX7 software (State-Ease Inc., Minneapolis, USA) to determine the optimum conditions to achieve the highest gold recovery.45

4.4. Leaching Procedure. Leaching solutions were prepared with pure (98%) sodium thiocyanate (Alfa Aesar) as the lixiviant and iron(III) sulfate (Alfa Aesar) as the oxidant in deionized water; 10% (v/v) sulfuric acid was used to adjust the solution pH to 2. Pilot studies were conducted by modifying the initial thiocyanate and ferric concentrations and pulp densities of the leach slurry. The slurry was mixed at 300 rpm on a magnetic stirrer. Leaching experiments were carried out at 25 °C for 24 h unless otherwise noted. Kinetic experiments were performed using 500 mM SCN⁻ and 100 mM Fe³⁺. The pulp density was kept at 40% to minimize foam formation during mixing. The stirring speed was 300 rpm, and the leaching solution was acidified to pH 2 with 10% v/v sulfuric acid. Slurry samples were collected at specified time intervals. Each 10 mL sample was centrifuged at 5500 rpm for 5 min for solid–liquid separation, and the supernatant was filtered through a sterile 0.45 μm syringe filter for atomic adsorption spectroscopy to measure Au, total Fe, and Cu. The filtrate was collected for Volhard and ferrous titrations. At the end of each leaching experiment, the final slurry was filtered using a vacuum pump attached to a Buchner funnel/bottle, and the filtrate (gold pregnant solution) was collected for ICP–MS. The residue retained on the filter was generously washed with deionized water to remove the residual soluble gold. The resulting “cake” was oven-dried at 60 °C for 24 h, crushed with a mortar and pestle, and analyzed.

5. CONCLUSIONS

The results of the present study show that the RSM technique can rapidly determine the optimal conditions for gold leaching. The initial thiocyanate concentration more strongly affected gold recovery than the initial ferric concentration, and the effect of pulp density was negligible. The optimized conditions—incorporating cost-effectiveness, operational considerations, and Au recovery—for initial thiocyanate and ferric concentrations and pulp density were 500 mM, 100 mM, and 50% (w/v), respectively, resulting in approximately 96% Au recovery at pH 2, 25 °C, and 300 rpm stirring speed.

Kinetic analysis indicated that optimum thiocyanate leaching followed the SCM, and the process was a diffusion-controlled process. Some thiocyanate consumption was attributed to the formation of complexes with Cu. The main thiocyanate structure in the leaching solution was N-thiocyanate, which tends to form complexes with hard metal ions. Comparison between the present work and the reported studies showed that the present study is promising for gold recovery from gold-bearing oxide ores. The recovery of gold from the pregnant leach solution is a part of future investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.1c00525.

X-ray diffraction patterns of the oxide ore and residue after 24 h leaching under optimal conditions (500 mM initial SCN, 100 mM initial Fe³⁺, and 40% pulp density at 25 °C); scanning electron micrographs of the oxide ore before leaching at 1000× and 500× magnification and leaching residues at 1000× and 500× magnification; Eh–pH diagrams for the Au–SCN–H₂O system at SCN⁻ and Au concentrations of 100 mM and 2 ppm, respectively, at 25 °C, and particle size distribution of the oxide ore sample used in this study (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC), McEwen Mining Inc., and Barrick Gold Corp. through the Collaborative Research and Development grant CRDPJ 532307-18.
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