Combined leaching of Carlin-type gold deposit in Guizhou by potassium chlorate and bleaching powder

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Abstract

Cyanidation has been considered an effective process for extracting gold from gold-bearing ores for over 100 years. However, this process also has several disadvantages including it being toxic, inefficient, and unsuitable for leaching gold from carbonaceous gold ores containing organic and inorganic carbons. Moreover, it is not feasible for the extraction of gold from refractory gold ores, which are increasingly being used. Therefore, there is an urgent need to find an environmentally friendly and efficient leaching method to improve the extraction rate of gold from refractory gold ores. This study discusses using potassium chlorate and bleaching powder for combined leaching of refractory gold ore. Compared with other leaching methods, this method does not require the pre-oxidizing of the refractory gold ore. Moreover, the optimal reaction temperature required for the reaction is lower, thus achieving efficient and environmentally friendly leaching of refractory gold ore. To improve on the method, we used response surface methodology (RSM). RSM can quickly determine the quadratic function connection between the response value and each component and optimize the experimental settings to precisely forecast the experimental findings, saving a significant amount of time and money. This study presents a response surface approach based on a thermodynamic analysis of gold-bearing mineral oxidation to analyze the primary composite design experiment. The response surface model uses four components and three levels of potassium chlorate concentration, bleaching powder addition, reaction temperature, and reaction pH. The model gives 0.16 mol l⁻¹ potassium chlorate, 37.5 g bleaching powder, 25 °C reaction temperature, and reaction pH of 13 as the optimal conditions for leaching gold using potassium chlorate and bleaching powder. Under these conditions, the gold leaching rate can reach 90.84%. In addition, the following parameters influence combined gold leaching in decreasing order: bleaching powder dose, reaction temperature, potassium chlorate concentration, and reaction pH. The results show that potassium chlorate and bleaching powder combined is advantageous for leaching of Carlin-type gold ore in Guizhou. It provides a high leaching rate. There is no need for pre-oxidation of gold ore. It is a simple inexpensive process that can be operated at a low optimum reaction temperature. Thus, it is a feasible method in industrial applications and provides a new way for gold leaching.

1. Introduction

Gold, a rare and valuable metal, is a reserve, investment and significant material in the jewelry, electronics, and aerospace industries, among other disciplines [1–3]. As the world’s gold mines continue to be exploited [4, 5], easy-to-separate gold resources are being depleted, and massive amounts of refractory gold are becoming essential raw materials for the gold manufacturing sector [6, 7].

Owing to its high selectivity for gold and silver over other metals and its relatively low cost, cyanidation has been considered an effective process for extracting gold from gold-bearing ores for over 100 years [8–11]. Currently, many gold mines use cyanidation for gold extraction.
However, this process also has several disadvantages. First, the cyanide used in the leaching process is highly toxic, and its residues, which are generated during gold extraction, cause severe environmental pollution [12, 13]. Second, the dissolution rate of gold in cyanide is low; therefore, the process is inefficient [14]. Third, cyanidation is unsuitable for leaching gold from carbonaceous gold ores containing organic and inorganic carbons [15]. Dissolved aurocyanide complexes are removed from the solution through adsorption by carbonaceous matter, making the extraction of gold difficult or reducing the extraction rate [16]. Finally, direct alkaline cyanidation is ineffective for gold extraction from high-arsenic and high-sulfur refractory gold ores, which usually contain sulfidic minerals such as pyrite, arsenopyrite, and chalcopyrite [17, 18]. Gold particles are typically included or finely disseminated in sulfidic minerals, making extracting gold even after the ore is finely ground difficult. As sulfidic minerals are usually dense and insoluble in water, dissolved oxygen and leaching agents cannot diffuse to the surface of the gold particles during leaching. In addition, many sulfide minerals must react in a high-temperature environment, and many metal impurities are involved in the reaction. This increases the leaching cost and reaction energy consumption and forms a passivation layer on the surface of the gold particles, reducing the gold extraction rate [19]. Pretreatment is generally carried out before gold leaching to improve the gold extraction rate effectively. However, pretreatment pollutes the environment, requires complex processes, increases extraction costs, and cannot achieve satisfactory results. Therefore, extensive studies have been conducted in finding an environmentally friendly and efficient leaching method for improving the gold extraction rate of refractory gold ores.

With large-scale exploitation and utilization of mineral resources, the amount of free-milling gold ore has gradually decreased [20]. Thus, many countries are increasingly using refractory gold ores [21]. Furthermore, arsenic- and carbon-containing, high-sulfur, ultra-fine-grain gold ores have become the main focus for gold extraction; however, traditional cyanidation is not a feasible process for such refractory ores. Pretreatment is generally performed before gold leaching to improve the gold extraction rate. The basic principle of pretreatment involves the disruption of sulfidic mineral crystals to increase the chance of interaction between cyanide and gold. The main pretreatment methods for refractory gold ores include chemical oxidation [22], pressure oxidation [23], biological oxidation, and roasting oxidation. However, pretreatment often results in environmental pollution; moreover it involves complicated processes and increased extraction costs, and may fail to achieve satisfactory results [24]. Therefore, there is an urgent need to find an environmentally friendly and efficient leaching method to improve the extraction rate of gold from refractory gold ores.

After decades of effort, several non-cyanide alternative chemicals, such as thiourea, thiosulfate, perchlorate, thiocyanate, iodine, and chloride, have been proposed [25–28]. Nevertheless, most of them are still at the laboratory scale. Remarkably, an improved chlorination process for gold recovery was developed in our recent study, which is efficient and inexpensive.

Guizhou Province, an important gold resource of China, has abundant Carlin-type gold deposits. Therefore, this study used potassium chlorate and bleaching powder to leach refractory gold ore in Guizhou. Using potassium chlorate as a strong oxidant can efficiently dissociate gold-loaded sulfides from ores. Conversely, it can also be used as a leaching agent to provide Cl− synergistic inexpensive and non-toxic leaching powder for the non-cyanide leaching of gold. Compared with other leaching methods, this method does not require the pre-oxidizing of the refractory gold ore. Moreover, the optimal reaction temperature required for the reaction is lower, thus achieving efficient and environmentally friendly leaching of refractory gold ore.

Many studies have employed an orthogonal experimental design to improve data; however, orthogonal experiments require many experiments. Hence, the number of experiments is considerable, particularly if there are many affecting elements and levels. Conversely, the response surface methodology (RSM) can quickly determine the quadratic function connection between the response value and each component. Moreover, it can optimize the experimental settings to precisely forecast the experimental findings, saving a significant amount of time and money. Consequently, RSM is widely utilized in metallurgy, chemistry, biology, food, and other industries.

The viability of simultaneous leaching of potassium chlorate and bleaching powder was demonstrated using thermodynamic analysis. Finally, the optimum process parameters and importance ranking of the influencing factors of gold leaching for the combined leaching of refractory gold ore in Guizhou were determined using RSM.

2. Experiment

2.1. Experimental instruments and reagents

The main instruments used in the test were an A3AFG flame atomic absorption spectrophotometer, 202-ABS electrothermal constant-temperature drying oven, PHS-3C precision pH meter, GWA-UN4-S30 ultrapure water tank, and X-Pert PRO XRD diffractometer.
The main reagents used in the test were potassium chlorate, bleaching powder, hydrochloric acid, nitric acid, sodium chloride, sodium fluoride, anhydrous ethanol, tartaric acid, and thiourea (all reagents are analytical grade).

2.2. Experimental materials
The gold ore used in this experiment was obtained from Zijin Mining, Guizhou Province, China. It is a dark gray, thick block broken by a jaw crusher, ground in a conical ball mill, sieved to a 74 μm fraction, accounting for 92%, mixed, and then bagged for later usage using the grid sampling method. Table 1 lists the major chemical composition of the ores.

2.3. Experimental method
The ore powder was broken, ball-milled, sieved, dried, and blended ahead of time, and 50 g was inserted into a 500 ml beaker. The prepared leaching agent was introduced into a thermostatic water bath and agitated at 400 rpm. The pulp was filtered using medium-speed qualitative filter paper after leaching, and the filter cake was weighed after drying. The mineral gold concentration, before and after leaching, was evaluated using foam plastic enrichment flame atomic absorption spectrometry [29, 30]. The leaching rate was estimated, and the gold recovery was calculated using equation 1 as follows:

Table 1. Main chemical compositions of ores (%).

| Chemical composition | Al₂O₃ | Pb | S | Fe | Zn | C | Au | Mn | As | SiO₂ | CaO | MgO |
|----------------------|-------|----|---|----|----|---|----|----|----|------|-----|-----|
| Content              | <0.01 | <0.05 | 1.65 | 2.99 | 0.10 | 9.46 | 15.03g/t | 0.15 | 0.14 | 8.78 | 24.6 | 13.9 |

Table 2. Standard redox potential $E^0$ value of metal sulfide.

| MeS   | FeS  | Ni₃S₂ | NiS  | CoS  | ZnS  | CdS  | CuFeS₂ | FeS₂ | Cu₂S | CuS  |
|-------|------|-------|------|------|------|------|--------|------|------|------|
| pHₘₐₓ| 3.94 | 3.35  | 2.80 | 1.71 | 1.07 | 0.174 | −1.10  | −1.19 | −3.50 | −3.65 |
| pHₘᵢₙ| 1.78 | 0.47  | 0.45 | −0.83 | −1.60 | −2.60 | −3.80  | −5.26 | −8.04 | −7.01 |
| $E^0$(V) | 0.066 | 0.097 | 0.145 | 0.22 | 0.26 | 0.33 | 0.41   | 0.42  | 0.56  | 0.59  |
where $M_i, M_0, W_i,$ and $W_0$ are the mass of the leached sample at a specific time interval (g), mass of the raw sample (g), concentration of gold in the leached sample at specific time intervals (g/t), and concentration of gold in the raw sample (g/t), respectively.

\[ \text{Aurecovery} = \left( 1 - \frac{M_i \times W_i}{M_0 \times W_0} \right) \times 100 \]  

(1)

### 3. Experimental principles

#### 3.1. Thermodynamic analysis of gold-bearing mineral oxidation

The main gold-bearing minerals in refractory gold ores in Guizhou are pyrite and arsenopyrite. Fine gold particles are primarily encapsulated in pyrite and arsenopyrite, and a small amount is encapsulated in other metal sulfides. Therefore, maximizing the dissociation of the above metal sulfides and destroying the encapsulated gold carrier is the key to improving the gold leaching rate.

Table 2 lists the standard redox potential of metal sulfides common in ores. In the table, the redox potential of metal sulfides and the difficulty of oxidation gradually increase from left to right.

The redox potential reflects the macroscopic redox properties of all substances in an aqueous solution. The higher the redox potential, the stronger the oxidation. Conversely, the lower the redox potential, the stronger
is the reducibility. Positive and negative potentials indicate that the solution shows a specific oxidation and reduction, respectively.

As shown in figure 1, the redox potential of Fe^{3+}/Fe^{2+} is higher than that of other metal sulfides, except Ag_2S, and the redox potential of Cl_2/Cl^- is significantly higher than that of metal sulfides, indicating that both can oxidize and decompose such base metal sulfides.

### 3.1.1. Thermodynamic analysis of S-H_2O system

When the leaching process is carried out under acidic conditions, the element is precipitated to form a film of sulfur, which hinders the oxidation of pyrite and arsenopyrite by the solution, as shown in figure 2. When pH > 7, the stable area of elemental sulfur is very small. The sulfur element in the system mainly exists in the form of S^{2-}, HS^-, HS^-, or SO_4^{2-} in the solution. Therefore, under alkaline conditions, the S element in pyrite and arsenopyrite will eventually be converted into SO_4^{2-}.

### 3.1.2. E-pH diagram of FeS_2-H_2O system

To further explore the oxidative decomposition process of the main gold-bearing minerals (gold minerals pyrite and arsenopyrite) in gold deposits, E-pH diagrams of the FeS_2-H_2O and FeAsS-H_2O system at 298.15 K were drawn, and the E-pH diagram of the FeS_2-H_2O system is shown in figure 3.

As shown in figure 3, the redox potential of FeS_2 is higher, and the oxidative decomposition of FeS occurs prior to FeS_2. Therefore, increasing the potential or pH of the solution can cause the Fe in FeS_2 to enter the solution in the form of Fe^{2+} and Fe^{3+}. S is leached in the form of S^{2-}, H_2S, or SO_4^{2-}.

In an alkaline solution, using oxygen as an oxidant to oxidize pyrite, the following reaction occurs:

\[
4\text{FeS}_2(s) + 16\text{OH}^- (aq) + 15\text{O}_2(g) \\
= 8\text{SO}_4^{2-} (aq) + 4\text{Fe(OH)_3} (aq) + 2\text{H}_2\text{O(l)}
\]  

(2)

According to the thermodynamic data, Gibbs free energy of the reaction (\(\Delta_rG^\theta\)) is \(-1582.44\) kJ mol\(^{-1}\), indicating that the reaction has a strong tendency and can proceed spontaneously.

### 3.1.3. E-pH diagram of FeAsS-H_2O system

It can be seen from figure 4 that at higher oxidation potentials, As mainly exists in the form of HAsO_4^{2-} and AsO_4^{3-} in the solution, sulfur mainly exists in the form of SO_4^{2-}, and Fe mainly exists in the form of goethite.

In an alkaline solution, arsenic pyrite is oxidized using oxygen. The reaction is as follows:

\[
2\text{FeAsS}(s) + 10\text{OH}^- (aq) + 7\text{O}_2(g) \\
= 2\text{AsO}_4^{3-} (aq) + 2\text{SO}_4^{2-} (aq) + 2\text{Fe(OH)_3} (aq) + 2\text{H}_2\text{O(l)}
\]  

(3)

The thermodynamic data show that \(\Delta_rG^\theta\) is \(-1258.57\) kJ mol\(^{-1}\) indicating that the reaction can be carried out spontaneously. The gold-coated arsenopyrite will be converted into ionic AsO_4^{3-} and SO_4^{2-}, and because of the formation of colloidal Fe(OH)_3, some gold will be adsorbed by Fe(OH)_3, resulting in a decrease in gold leaching rate.

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Figure 4. E-pH diagram of FeAsS-H_2O system (298.15 K).
3.1.4. Thermodynamic analysis of Au-H₂O system

The chemical properties of gold are relatively stable, and leaching generally requires both oxidants and leaching agents to play a role. If the oxidant has a stronger oxidizing property, the formed gold complex will be more stable, and the leaching of gold will be easier. Similar to other amphoteric hydroxides, gold hydroxide also has amphoteric properties; however, the compound is more acidic. Au(OH)₃ (also known as H₃AuO₃) is dissolved in a strong alkaline solution to form H₂AuO₃⁻, which can also be further dissolved to form H₄AuO₅²⁻. Under
alkaline conditions, the following reactions occur in the Au-H2O system:

\[
\text{Au(OH)}_3(aq) + 3H^+ (aq) + 3e = \text{Au}(s) + 3H_2O(l)
\]  

Table 3. Horizontal coding of response surface test factors.

| Factor                              | Variable | Level |
|-------------------------------------|----------|-------|
| Potassium chlorate concentration(mol/L) | X1       | -1    |
| Bleaching powder addition amount(g) | X2       | 0.15  |
| pH                                  | X3       | 20    |
|                                    | X4       | 12    |

Table 4. Response surface design scheme and experimental results.

| Numbering | X1(mol/l) | X2(g) | X3(°C) | X4 | Gold leaching rate(Y)(%) |
|-----------|-----------|-------|--------|----|--------------------------|
| 1         | 0.1       | 30    | 30     | 13 | 54.16                    |
| 2         | 0.15      | 30    | 30     | 14 | 57.15                    |
| 3         | 0.15      | 22.5  | 25     | 14 | 43.25                    |
| 4         | 0.15      | 30    | 30     | 12 | 55.24                    |
| 5         | 0.15      | 22.5  | 30     | 13 | 48.89                    |
| 6         | 0.15      | 30    | 25     | 13 | 68.03                    |
| 7         | 0.1      | 22.5  | 25     | 13 | 42.81                    |
| 8         | 0.15     | 37.5  | 20     | 13 | 67.71                    |
| 9         | 0.15      | 22.5  | 25     | 12 | 42.31                    |
| 10        | 0.15      | 30    | 25     | 13 | 68.03                    |
| 11        | 0.15      | 30    | 25     | 13 | 68.03                    |
| 12        | 0.1      | 30    | 25     | 12 | 44.26                    |
| 13        | 0.15      | 30    | 25     | 13 | 68.03                    |
| 14        | 0.2      | 30    | 20     | 13 | 51.48                    |
| 15        | 0.15      | 30    | 20     | 12 | 48.33                    |

Table 5. Variance analysis of regression model of gold leaching rate (Y).

| Source of variance | Quadratic sum | Degree of freedom | Mean square deviation | F     | P     |
|--------------------|---------------|-------------------|-----------------------|-------|-------|
| models             | 2744.17       | 14                | 196.01                | 68.64 | <0.0001|
| X1                 | 68.78         | 1                 | 68.78                 | 24.09 | 0.0002|
| X2                 | 1504.61       | 1                 | 1504.61               | 526.91| <0.0001|
| X3                 | 95.03         | 1                 | 95.03                 | 33.28 | <0.0001|
| X4                 | 8.93          | 1                 | 8.93                  | 3.13  | 0.0988|
| X1X2               | 0.63          | 1                 | 0.63                  | 0.22  | 0.6453|
| X1X3               | 10.82         | 1                 | 10.82                 | 3.79  | 0.0719|
| X1X4               | 1.44          | 1                 | 1.44                  | 0.5   | 0.4893|
| X2X3               | 32.21         | 1                 | 32.21                 | 11.28 | 0.0047|
| X2X4               | 0.18          | 1                 | 0.18                  | 0.063 | 0.8051|
| X3X4               | 0.13          | 1                 | 0.13                  | 0.045 | 0.8344|
| X12                | 542.87        | 1                 | 542.87                | 190.11| <0.0001|
| X22                | 134.04        | 1                 | 134.04                | 46.94 | <0.0001|
| X32                | 368.12        | 1                 | 368.12                | 128.91| <0.0001|
| X42                | 479.55        | 1                 | 479.55                | 167.94| <0.0001|
| residual error     | 39.98         | 14                | 2.86                  |       |       |
| Misfit term        | 39.98         | 10                | 4                     |       |       |
| pure error         | 0             | 4                 | 0                     |       |       |
| summation          | 2784.15       | 28                |                       |       |       |

\( R^2 = 0.9856 \),  
\( \text{AdjR}^2 = 0.9713 \).
The calculated $\Delta rG^\theta$ of the above chemical reactions are $-428.06$ kJ mol$^{-1}$, $-65.52$ kJ mol$^{-1}$, $-75.89$ kJ mol$^{-1}$, $-290.12$ kJ mol$^{-1}$, $-493.59$ kJ mol$^{-1}$, $-569.57$ kJ mol$^{-1}$; and $-659.69$ kJ mol$^{-1}$. The E-pH diagram of Au-H$_2$O system (298 K) was plotted by the above chemical formula, and figure 5 was obtained.

It can be seen from figure 5 that Au(OH)$_3$, as an amphoteric hydroxide, can dissolve Au by thermodynamic analysis to ensure sufficient oxidation potential and an alkaline environment. Under the condition of sufficient alkalinity and potential, Au(OH)$_3$ will exist in the solution as H$_2$AuO$_3$ and HAuO$_3$$^-$ to achieve gold leaching.

$$H_2AuO_3(aq) + H^+(aq) = Au(OH)_3(aq)$$

(5)

$$HAuO_3^- (aq) + H^+(aq) = H_2AuO_3(aq)$$

(6)

$$AuO_3^{2-} (aq) + H^+(aq) = HAuO_3^{-} (aq)$$

(7)

$$H_2AuO_3 (aq) + 4H^+(aq) + 3e^- = Au(s) + 3H_2O(l)$$

(8)

$$HAuO_3^{2+} (aq) + 5H^+(aq) + 3e^- = Au(s) + 3H_2O(l)$$

(9)

$$AuO_3^{2-} (aq) + 6H^+(aq) + 3e^- = Au(s) + 3H_2O(l)$$

(10)
3.2. Thermodynamic analysis of Cl-H2O system

According to actual measurements, there may be many ions and compounds in the Cl-H2O system. Among them, Cl\(^{-}\), HClO, ClO\(^{-}\), HClO\(_2\), ClO\(^2-\), ClO\(^3-\), and ClO\(^4-\) are in the dissolved state, and HCl, Cl\(_2\), Cl\(_2\)O, and ClO\(_2\) are in the gas state. This study only analyzes the relationship between Cl\(^{-}\), Cl\(_2\), HClO, and ClO\(^-\). Figure 6 shows a simple E-pH diagram of the Cl-H2O system. As shown in the figure, under acidic conditions, the dissolved chlorine gas may undergo a disproportionation reaction to form HClO, which is unstable and decomposes into O\(_2\). When Cl\(_2\) is introduced into the solution in a strong alkali medium, the following reaction occurs:

\[ \text{Cl}_2 + 2\text{NaOH} \rightarrow \text{NaClO} + \text{NaCl} + \text{H}_2\text{O} \]  (11)

As shown in figure 6, the solution is mainly in the form of ClO\(^-\), and the ClO\(^-\) potential is higher than O\(_2\). Therefore, hypochlorite oxidation is greater than that of oxygen, and ClO\(^-\) can oxidize many substances that O\(_2\) cannot. Hence, ClO\(^-\) is more easily oxidized than O\(_2\) to decompose the gold-bearing mineral.

3.3. Thermodynamic analysis of Au-Cl-H2O system

Chlorination of aqueous solutions is carried out under acidic conditions, and gold is stable in the form of AuCl\(_4^-\). However, AuCl\(_4^-\) is reduced by water owing to the increase in solution pH and the decrease in oxidation potential, forming Au(OH)\(_3\) and AuO\(_2\) precipitates; as the pH increases, the dissolved chlorine is converted into hypochlorous acid. If the pH continues to increase, hypochlorous acid continues to be converted into hypochlorous acid ions, and hypochlorous acid has a strong oxidizing property. If the pH continues to increase further, Au(OH)\(_3\) dissolves in the solution to form H\(_2\)AuO\(_3\), H\(_2\)AuO\(_3\) \(_2\) unstable is converted to HAuO\(_3\)\(_2^-\). According to the alkalinity, the following reactions occur:

\[
\text{Au(s)} + 3/2\text{ClO}^- (aq) + 3/2\text{H}_2\text{O(l)} = \text{Au(OH)}_3(aq) + 3/2\text{Cl}^- (aq) \]  (12)

\[
\text{Au(OH)}_3(aq) + \text{OH}^- (aq) = \text{H}_2\text{AuO}_3^- (aq) + \text{H}_2\text{O(l)} \]  (13)
According to the calculation, $\Delta G^0$ of the above reactions are $-30.23 \text{ kJ mol}^{-1}$, $-12.96 \text{ kJ mol}^{-1}$, $-3.72 \text{ kJ mol}^{-1}$, and $11.38 \text{ kJ mol}^{-1}$, respectively. It shows that in the standard state, the reaction trend of these reactions is getting smaller and smaller. When pH > 13, Au can be dissolved in the Cl-H$_2$O system and mainly exists in the form of H$_2$AuO$_3$ and HAuO$_3^{2-}$. The E-pH diagram of Au-Cl-H$_2$O is shown in figure 7.

3.4. Thermodynamic analysis of potassium chlorate dissolving gold

The following calculation is performed using the Nernst equation to obtain the theoretical dosage for the effective leaching of gold in the gold ore.

The reaction equation of potassium chlorate dissolving gold is

\[
2\text{Au} + \text{ClO}_3^- + \text{H}_2\text{O} + 2\text{OH}^- = 2\text{H}_2\text{AuO}_3^- + \text{Cl}^-
\]  

The Nernst equation is:

\[
E = (E_{\text{ClO}_3^-/\text{Cl}^-}^0 - E_{\text{Au}^{3+}/\text{Au}}^0) - \frac{2.303RT}{2F} \ln \left( \frac{a_{\text{ClO}_3^-}^2 \cdot a_{\text{Cl}^-} \cdot a_{\text{H}_2\text{O}}}{a_{\text{Au}^{3+}} a_{\text{Au}}^3} \right)
\]

\[
E_{\text{ClO}_3^-/\text{Cl}^-}^0 = 0.62V \quad E_{\text{Au}^{3+}/\text{Au}}^0 = 1.498V
\]

The gold grade of the gold ore used in this experiment was 15.03 g/T. It is assumed that 50 g of gold ore is leached in a 400 ml aqueous solution system, and the gold content in the solution system is $9.5 \times 10^{-6} \text{ mol l}^{-1}$. It is also assumed that all Au in the system is converted to H$_2$AuO$_3^-$, that is, [H$_2$AuO$_3^-] = $9.5 \times 10^{-6} \text{ mol l}^{-1}$. The ion activity coefficient is 1, and the ion concentration is used instead of the ion activity. When the pH of the gold leaching system is 8 and the concentration of potassium chlorate is 0.01 mol L$^{-1}$, E > 0, which proves that the gold leaching reaction of potassium chlorate can proceed in the positive direction.
3.5. Thermodynamic analysis of bleaching powder dissolving gold

To obtain the theoretical dosage for the effective leaching of gold in the gold ore, the following calculation is performed using the Nernst equation:

The reaction equation of bleaching powder dissolving gold is

$$2\text{Au} + 3\text{ClO}^- + \text{H}_2\text{O} + 2\text{OH}^- = 2\text{H}_2\text{AuO}_3^- + 3\text{Cl}^-$$  \hspace{1cm} (19)

By the Nernst equation:

$$E = (E_{\text{ClO}}^-/\text{Cl}^- - E_{\text{Au}^{3+}/\text{Au}}^0) = \frac{2.303RT}{2F} \ln \frac{a_{\text{H}_2\text{AuO}_3^-}^2 \cdot a_{\text{Cl}^-}^3}{a_{\text{ClO}}^-^2 \cdot a_{\text{OH}}^-^2}$$  \hspace{1cm} (20)

$$E_{\text{ClO}}^-/\text{Cl}^- = 0.89V \cdot E_{\text{Au}^{3+}/\text{Au}}^0 = 1.498V$$  \hspace{1cm} (21)

The gold grade of the gold ore used in this experiment is 15.03 g t$^{-1}$. It is assumed that 50 g of gold ore is leached in a 400 ml aqueous solution system, and the gold content in the solution system is $9.5 \times 10^{-6}$ mol l$^{-1}$. Assuming that all Au in the system is converted to H$_2$AuO$_3^-$, that is, [H$_2$AuO$_3^-$] = $9.5 \times 10^{-6}$ mol l$^{-1}$, the ion activity coefficient is taken as 1, and the ion concentration is used to replace the ion activity. When pH = 12 and the amount of bleaching powder is 1 g, the standard electrode potential $E^0 > 0$, it is proved that the gold leaching reaction of bleaching powder can proceed positively.

4. Results and discussion

4.1. Response surface methodology experiment on combined leaching of refractory gold ore from Guizhou by potassium chlorate and bleaching powder

4.1.1. Response surface test design

According to previous single-factor test results, the zero level was selected as the maximum value of the single-factor test. The change interval selects the part with a noticeable change that is symmetrically distributed on both sides of the single factor maximum. The effects of potassium chlorate concentration, bleaching powder addition, leaching temperature, leaching pH, and the significance of each factor on the gold leaching rate were studied. The RSM was used to design the interaction experiment, and the BBD design module was used to conduct the central composite design experiment with four factors and three levels. According to the BBD composite test design principle, the zero level should be the maximum value of a single-factor test. The center point and level of the response surface test factors were reasonably selected. In the variation interval of each factor in the experiment, the authors selected the part with a noticeable change, and the maximum value of a single factor was symmetrically distributed on both sides. The base change steps in the single-factor test are listed in table 3.

4.1.2. Response surface test results

The experimental factors and level values in table 3 were input into Design Expert v8.0.6.1, and the experiment was carried out according to the experimental scheme generated by the software. There were 29 groups of points in the experimental scheme. The experimental scheme and results are listed in table 4.

The test data in table 4 were fitted using a multivariate quadratic equation. The fitted regression equation is given by equation (22).

$$Y = -1905.15083 + 1443.3833 \cdot X_1 + 8.44289 \cdot X_2 + 18.41850 \cdot X_3 + 226.16917 \cdot X_4 + 1.06000 \cdot X_1^2 + 6.58000 \cdot X_1 \cdot X_2 + 12.00000 \cdot X_1 \cdot X_3 - 0.075667 \cdot X_1 \cdot X_4 - 0.028333 \cdot X_2^2 + 0.036000 \cdot X_3 \cdot X_4 - 3659.33333 \cdot X_4^2 + 0.08081 \cdot X_2^2 - 0.30133 \cdot X_3^2 + 8.59833 \cdot X_4^2 \hspace{1cm} (22)$$

The variance analysis data of the regression model of the gold leaching rate (Y) in table 5 can be obtained using Design Expert v8.0.6.1 software for variance analysis.

The $P$-value is usually used to represent the significance of the model in the variance analysis; when $P < 0.05$, the model is significant, and when $P < 0.001$, the model is highly significant. As can be seen from table 5, the regression model $P < 0.0001$ indicates that the regression model reached a highly significant level. Variance $R^2 = 0.9856$, indicating that the model can explain 98.56% of the change in the response value. The model has a good degree of fitting [31].

Figure 8 exhibits the comparison result between the actual value and the predicted value. The closer the distance between the point in the graph and the slash, the closer is the actual value and the predicted value. The higher the fitting degree of the equation because the points in figure 8 are concentrated near the slash, it shows that the model fits well and has little difference from the actual conditions.
Figure 9 shows the relationship between the residual and the number of experiments. It can be seen from the figure that the experimental points are randomly distributed at both ends of the residual zero-point line, indicating that the residual distribution is uniform and the residual is small. In addition, it can be seen from figure 9 that the range of residuals is $-3$–$3$ under the condition of 1–29 experiments, indicating that the experimental fitting degree is good and can well represent the gold leaching model.

Three-dimensional response surface plots can better demonstrate the influence of the interaction between different factors (potassium chlorate concentration, bleaching powder addition, reaction temperature, and reaction pH) on the gold leaching rate, as shown in figures 10–14. If the curvature of the response surface is high, the interaction between the two factors significantly affects the gold leaching rate. In contrast, the low curvature of the response surface indicates that the interaction between the two factors has little effect on the gold leaching rate [32, 33].

The interaction between potassium chlorate concentration ($X_1$) and bleaching powder addition ($X_2$) is shown in figure 10. As the concentration of potassium chlorate gradually increased from 0.1 mol $l^{-1}$ to 0.2 mol $l^{-1}$, the gold leaching rate increased rapidly with the increase of bleaching powder addition. The effect of bleaching powder addition on the gold leaching rate is greater than that of potassium chlorate concentration. In the contour map, the contour density along the direction of the bleaching powder addition ($X_2$) is substantially higher than that along the direction of the potassium chlorate concentration ($X_1$), indicating that the influence of bleaching powder addition on the gold leaching rate is more significant than that of the potassium chlorate concentration.

Figure 11 shows that when the reaction temperature increases from 20 °C to 30 °C, the gold leaching rate increases significantly with the addition of bleaching powder. The effect of bleaching powder addition on the gold leaching rate is greater than that of the reaction temperature. The contour density along the direction of the bleaching powder addition ($X_2$) is larger than that along the direction of the reaction temperature ($X_3$) in the contour map, showing that the influence of bleaching powder addition on the gold leaching rate is more substantial than that of the reaction temperature.

As shown in figure 12, the interaction between the quantity of bleaching powder added ($X_2$) and the reaction pH ($X_4$) increases the gold leaching rate as the reaction pH rises from 12 to 14 as the amount of bleaching

![Figure 12. Response surface and contour plots of the effects of two interactive factors of bleaching powder addition and reaction pH on gold leaching rate.](image-url)
powder supplied rises. The effect of bleaching powder addition on the gold leaching rate is more significant than that of the reaction pH. The contour density along the route of bleaching powder addition (X2) is larger than that along the direction of reaction pH (X4) in the contour map, showing that the influence of bleaching powder addition on the gold leaching rate is more substantial than that of the reaction pH.

The relationship between potassium chlorate concentration (X1) and reaction temperature (X3) can be seen in figure 13. As the concentration of potassium chlorate gradually increases from 0.1 mol l\(^{-1}\) to 0.2 mol l\(^{-1}\), the gold leaching rate increases significantly with the increase in reaction temperature. Therefore, the influence of the reaction temperature on the gold leaching rate is larger than that of the potassium chlorate concentration. In addition, the contour density along the direction of the reaction temperature (X3) is greater than that along the direction of the potassium chlorate concentration (X1) in the contour map, indicating that the influence of the reaction temperature on the gold leaching rate is more important than that of the potassium chlorate concentration.

The relationship between potassium chlorate concentration (X1) and reaction pH (X4) can be seen in figure 14. As the reaction pH gradually climbs from 12 to 14, the gold leaching rate increases significantly with the rise in potassium chlorate concentration. The influence of potassium chlorate concentration on the gold leaching rate is larger than that of the reaction pH. The contour density on the contour map is significantly larger along the direction of potassium chlorate concentration (X1) than along the direction of the reaction pH (X4), showing that the influence of potassium chlorate concentration on the gold leaching rate is substantially more significant than that of the reaction pH.

In summary, the significant factors affecting the gold leaching rate are X2, X3, X1, and X4, in descending order, and the interactions between factors X2 and X3 are more significant compared to other interactions.

The experiment was optimized using a numerical module. For the combined leaching of potassium chlorate and bleaching powder, the following conditions are optimal: potassium chlorate concentration of 0.16 mol l\(^{-1}\), bleaching powder addition of 37.5 g, reaction temperature of 25 °C, and reaction pH of 13. It is predicted that, under these conditions, the primary leaching rate of gold can reach 74.91%.

**Figure 13.** Response surface and contour plots of the effects of two interactive factors of potassium chlorate concentration and reaction temperature on gold leaching rate.
4.2. **Confirmatory experiment**

The mixture was leached for 4 h at 50 g ore powder, an 8:1 liquid-solid ratio, a stirring rate of 400 rpm, a reaction temperature of 25 °C, a potassium chlorate concentration of 0.16 mol l$^{-1}$, a bleach amount of 37.5 g, and a pH of 13. The slag was then subjected to secondary leaching under identical conditions. Three parallel experiments were performed under the above conditions to verify the stability and repeatability of the optimal conditions. The results are listed in table 6.

![Figure 14. Response surface and contour map of interaction between potassium chlorate concentration and pH on gold leaching rate.](image)

![Figure 15. XRD map of raw ore and leaching slag.](image)
It can be seen from table 6 that the average leaching rate of gold in the three parallel samples under the optimal conditions is 74.39%. The highest secondary leaching rate of slag after washing is 84.20%, and the average total leaching rate is 90.84%. The average difference between the predicted value of the primary leaching rate and the experimental value is 0.52%, which verifies the model’s reliability.

4.3. XRD analysis of ore samples before and after leaching
XRD spectroscopy experiments were carried out on raw ore and leaching residue under better process conditions. The experimental results are shown in figure 11. XRD patterns of ore and leaching residue, where figure 11(a) is ore and figure 11(b) is leaching residue. Figure 11(b) is the optimal leaching condition of 4.2 leaching.

The diffraction peaks in the slag-scanning pattern after leaching primarily included SiO₂, Ca(CO₃)₂, CaMg(CO₃)₂, and Fe(OH)₃ phases, as shown in figure 15. Compared to the XRD pattern of the raw ore powder, the diffraction peak of FeAsS in the raw ore disappears. Instead a new Fe(OH)₃ diffraction peak is formed. After oxidation, arsenopyrite in the raw ore has a good dissociation action and interacts with potassium chlorate to generate Fe(OH)₃ under alkaline conditions. Because silica and dolomite are insoluble in water and stable in nature, they are not engaged in the gold-leaching process and have diffraction peaks before and after. Under optimal leaching conditions, the combination of potassium chlorate and bleaching powder has better leaching ability for Guizhou Carlin-type gold mine, and the encapsulation of gold by arsenopyrite is opened. The ideal gold leaching rate is obtained through XRD analysis of ore samples before and after leaching.

5. Conclusion
(1) The result of the thermodynamic study of gold-bearing minerals and gold dissolution demonstrates that a higher oxidation potential can effectively open the gold package in an alkaline environment. FeS₂ and FeAsS are oxidized to HAsO₄²⁻, AsO₄³⁻, and SO₄²⁻, and gold is dissolved in the form of H₂AuO₃⁻ and HAuO₃₂⁻ in the solution.

(2) Through thermodynamic analysis of leaching of gold by potassium chlorate and bleaching powder, and calculating the results by using Nerst equation, the standard electrode potential E⁰ in the reaction equation of gold dissolution is greater than zero, which proves the feasibility of gold leaching with potassium chlorate and bleaching powder.

(3) The response surface model is significant and fits well. The addition of bleaching powder, reaction temperature, potassium chlorate concentration, and pH influence the leaching rate in descending order. The relationship between the amount of bleaching powder and the reaction temperature significantly influences the response value. The optimal conditions for model optimization are obtained as 0.16 mol l⁻¹ potassium chlorate concentration, 37.5 g bleaching powder addition, 25 °C reaction temperature, and pH of 13. Under these conditions, the primary leaching rate of gold is 74.54%, the secondary leaching rate of slag after washing is 84.20%, and the average total leaching rate is 90.84%.

(4) The advantages of potassium chlorate and bleaching powder combined with the leaching of Carlin-type gold ore in Guizhou are a high leaching rate, no need for pre-oxidation of gold ore, low cost, low optimum reaction temperature, and simple process, making this a feasible method in industrial applications and providing a new way for gold leaching.

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Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

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