Leaching of Valuable Elements from the Waste Chromite Ore Processing Residue: A Kinetic Analysis

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ABSTRACT: The efficacious treatment and resource utilization of the chromite ore processing residue (COPR) is important for chromate salt production. In this study, the leaching of valuable elements from the waste COPR was investigated. X-ray diffraction (XRD) analysis showed that the COPR mainly contained periclase (MgCr₂O₄), magnesiochromite ((Fe, Mg)(Cr, Fe)₂O₄), Fe(Cr, Al)₂O₄, and MgFeAlO₄. The optimum parameters for COPR leaching were as follows: mechanical ball-milling time of 120 min, sulfuric acid concentration (w/w % H₂SO₄) of 60%, reaction temperature (T) of 403 K, liquid–solid ratio (L/S) of 8 mL/g, and reaction time (t) of 6 h. Under these conditions, the valuable components such as Fe, Al, and Cr were extracted with an ideal leaching efficiency of 94.8, 75.1, and 76%, respectively. The results of the leaching kinetics analysis indicated that the leaching of Fe and Cr from the COPR was controlled by a surface chemical reaction, and the leaching of Al was controlled by diffusion through a product layer. The apparent activation energy of the leaching of Fe, Cr, and Al was calculated to be 23.03, 44.15, and 17.54 kJ/mol, respectively. It is believed that this approach has potential applications for the chromate salt industry because of its advantage of ideal leaching efficiency.

1. INTRODUCTION

Chromate salts, particularly sodium chromate, are an important inorganic chemical products that have broad application prospects in areas such as high-performance alloys,⁵,⁶ leather,⁵,⁶ electroplating,⁵,⁶ and ceramics.⁸,¹⁰ The chromite ore processing residue (COPR) is an inevitable solid emission in chromate salt production. It is an industrial waste produced during the extraction of Cr(VI) from a chromite ore using the high-temperature roasting process.¹¹ In general, the COPR is alkaline (pH > 12),⁵,⁷ and because of the presence of partially water-soluble, transportable, and carcinogenic hexavalent chromium, it is classified as a hazardous solid waste.¹²⁻¹⁴ The main components of the COPR vary depending on the roasting process. The COPR from the calcium roasting process is the residue of water leaching after mixing chromite, sodium carbonate (Na₂CO₃), and dolomite and calcining at high temperatures.¹⁵ This residue contains a large amount of calcium and a small amount of iron, aluminum, chromium, etc. However, the COPR from the non-calcium-roasting process always contains a higher amount of iron, aluminum, and chromium, a small amount of unreacted chromite, and a small quantity of Cr(VI) absorbed on the surface or encapsulated into the residue. As a hazardous solid waste, Cr(IV) contained in the residue can easily penetrate into the underground with rainwater and lead to a serious threat to the surroundings and human health. Therefore, the COPR must be treated carefully. At present, the treatment of COPR focuses on environmentally friendly treatment by chemical reduction,¹⁶ hydrolysis,¹⁷,¹⁸ electro-repair,¹⁹ stabilization/immobilization,²⁰,²¹ micro-organisms,²²,²³ biomass repair methods,²⁴ etc. Most of these methods aim to reduce the hexavalent chromium (Cr(VI)) to trivalent chromium (Cr(III)) and to keep it in the mineral phase through ensuing treatments.²⁵ However, there have been some problems and limitations for these methods, including the large amount of the reducing agent used, high cost,¹⁷,²⁶ and the increased volume of residue after detoxification.²⁷,²⁸ Besides, the components of the detoxified slag become more complicated because of the introduction of additional substances that make the subsequent resource utilization of the valuable elements difficult. Moreover, the hexavalent chromium may not be reduced completely, and the mineral phase in the COPR may be unstable and hence hazardous to the environment. Furthermore, all of these methods failed to utilize the valuable metal elements in the COPR, which resulted in the waste of resources. To realize the utilization of
various elements in the COPR, it is necessary to leach it by a wet method.

Here, in this work, the leaching of COPR from non-calcium-roasting process was investigated. The effects of the experimental parameters, such as w/w % H2SO4, L/S, leaching temperature, and leaching time, on the leaching of Fe, Cr, and Al were discussed. Furthermore, the kinetics of the leaching process was also discussed.

2. RESULTS AND DISCUSSION

2.1. Effect of Mechanical Ball Milling. The effect of mechanical ball milling was studied. In the experiments, the w/w % H2SO4 was 50%, the liquid–solid ratio (L/S) was 8 mL/g, the reaction temperature (T) was 373 K, and the reaction time (t) was 6 h. Figure 1 shows that a longer ball-milling time can result in a better leaching effect for the elements. When the mechanical ball-milling time reached 120 min, the leaching efficiency of T-Fe increased from 51.5 to 68.9%. Furthermore, the efficiency of Al leaching increased from 40.1 to 55.3%. The extraction of T-Cr increased from 40.4 to 60.5%. This was attributed to the fact that mechanical ball milling helps reduce the particle size of the residue (see Figure 1 black line), which can increase the reaction activity of the particle surface. Moreover, the longer the mechanical ball-milling time, the more thorough was the destruction of the slag inclusion. Therefore, the leaching efficiency can be enhanced with a longer ball-milling time. In the following experiments, the mechanical ball grinding time was controlled for 120 min.

2.2. Effect of H2SO4 Concentration. To study the effect of H2SO4 concentration on the leaching process, the w/w % H2SO4 was varied from 40 to 80%. In the experiments, the temperature was 373 K, L/S was 8 mL/g, and the leaching time was 6 h. Figure 2 shows that when the w/w % H2SO4 was increased from 40 to 80%, the leaching efficiency of T-Cr, Al, and T-Fe first increased to the maximum values and then decreased. When the w/w % H2SO4 was increased from 40 to 60%, the leaching efficiency of T-Fe increased from 64.4 to 83.5% and Al increased from 47.0 to 67.3%. Furthermore, the leaching efficiency of T-Cr increased from 40.4 to 60.5%. However, when the w/w % H2SO4 continued to increase to 80%, the leaching efficiency of those elements reduced and the leaching efficiency of T-Fe, Al, and T-Cr decreased to 19.3, 59.3, and 43.0%, respectively. As has been reported in the literature, both the leaching reaction rate and the viscosity of the solution increased with increasing acidity; these are not conducive to the leaching reaction, so the leaching efficiency reduced. Furthermore, due to the high acid concentration, the COPR surface may be passivated, which also affects the leaching efficiency.

2.3. Effect of Liquid–Solid Ratio. The L/S is a very crucial factor in the acid-leaching process of an ore or residue. To figure out the influence of L/S, a series of experiments with varying L/S from 4 to 10 mL/g at 60% of w/w % H2SO4, 373 K, and a leaching time of 6 h were conducted, and the results are shown in Figure 3. A conclusion drawn from Figure 3 is that the leaching efficiency increased with the increase of L/S. The leaching efficiency of T-Fe, Al, and T-Cr increased to 77.4, 65.25, and 67.31%, respectively, when the L/S increased to 8 mL/g. However, when L/S was greater than 8 mL/g, there was no significant increase in the leaching efficiency. Therefore, the L/S was kept constantly at 8 mL/g for the subsequent experiments.

2.4. Effect of Temperature. For the purpose of investigating the effect of temperature, a series of experiments with varying T from 363 to 403 K were carried out. The results are shown in Figure 4a–c. From Figure 4a, it can be concluded that the leaching efficiency of T-Fe increased with the rise of temperature. The maximum leaching efficiency of T-Fe was 93.28% at 393 K and 94.8% at 403 K within 6 h. Figure 4b,c shows that the leaching of T-Cr and Al from COPR increased with the rise of temperature in the case of T-Fe. The maximum leaching efficiency of T-Cr and Al was 76 and 75.1% at 403 K, respectively, after leaching for 6 h.

2.5. Kinetic Analysis. The solid–fluid leaching reaction is always expressed as

\[ a A_{\text{fluid}} + b B_{\text{solid}} \rightarrow \text{product} \]  

(1)

where \( a, b, A, \) and \( B \) represent the stoichiometric coefficients, fluid reactant, and solid undergoing dissolution, respectively.

The shrinking core model (SCM) is often used to describe the kinetics of leaching reactions. If the surface chemical
reaction is the rate-controlling step of leaching of Fe, Cr, and Al from the COPR, the leaching process is expressed as

\[ 1 - (1-X)^{1/3} = k_t t \]  

If the diffusion through a product layer is the rate-controlling step of the leaching of these elements, the process is expressed as

\[ 1 - 2/3X - (1-X)^{2/3} = k_d t \]  

where \( X, k_t (k_r \text{ or } k_d), \) and \( t \) represent the leaching efficiency of each valuable element, the apparent rate constant for each rate-controlling step, and the leaching time, respectively.

The results of the kinetics analysis are provided in Table 1 according to eqs 2 and 3. It indicated that the leaching of Fe and Cr follows the surface chemical reaction model. Furthermore, from the X-ray diffraction (XRD) analysis (Figure 12), it can be seen that Fe and Cr mainly exist in the chromite spinel structure (magnesiochromite) and the surface chemical reaction of the spinel may control the leaching process. However, aluminum mainly exists in MgFeAlO\(_4\), and its leaching is much easier, and at temperatures of 373, 383, 393, and 403 K, the \( R^2 \) value of model 1 - 2/3X - (1-X)\(^{2/3}\) is greater than that of the model 1 - (1-X)\(^{1/3}\), hence, the leaching of Al follows eq 3, i.e., the diffusion through the product layer model.

The reaction rates of Fe, Cr, and Al at different temperatures are shown in Figures 5–7. The activation energy \( E_a \) of Fe, Cr, and Al of the acid-leaching process of the COPR was

Table 1. Kinetics Analysis Results: \( k_r, k_d, \) and Correlation Coefficients (\( R^2 \))

| elements | T (K) | \( k_r \) (min\(^{-1}\)) | \( R^2 \) | \( k_d \) (min\(^{-1}\)) | \( R^2 \) |
|----------|-------|-----------------|--------|-----------------|--------|
| Fe       | 363   | 0.0536          | 0.9854 | 0.0139          | 0.9223 |
|          | 373   | 0.0699          | 0.9792 | 0.0218          | 0.942  |
|          | 383   | 0.0851          | 0.9795 | 0.0301          | 0.930  |
|          | 393   | 0.1016          | 0.9811 | 0.0398          | 0.9186 |
|          | 403   | 0.1130          | 0.9923 | 0.0446          | 0.9377 |
| Cr       | 363   | 0.0504          | 0.9697 | 0.0111          | 0.8408 |
|          | 373   | 0.0554          | 0.9740 | 0.013           | 0.9165 |
|          | 383   | 0.0591          | 0.9812 | 0.0153          | 0.9392 |
|          | 393   | 0.0643          | 0.9875 | 0.0186          | 0.9562 |
|          | 403   | 0.0660          | 0.9800 | 0.0199          | 0.9742 |
| Al       | 363   | 0.0439          | 0.9841 | 0.0102          | 0.9722 |
|          | 373   | 0.0472          | 0.9643 | 0.0119          | 0.9796 |
|          | 383   | 0.0536          | 0.9764 | 0.0146          | 0.9786 |
|          | 393   | 0.0576          | 0.9822 | 0.0168          | 0.9829 |
|          | 403   | 0.0577          | 0.9583 | 0.0176          | 0.9885 |

The activation energy \( E_a \) of Fe, Cr, and Al of the acid-leaching process of the COPR was.

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c02194)  

**Figure 4.** Effect of leaching temperature (w/w % H\(_2\)SO\(_4\) = 60%, L/S = 8 mL/g, \( t = 6 \) h).

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c02194)  

**Figure 5.** Plot of \( 1 - (1-X)^{1/3} \) vs \( t \) at various temperatures for Fe leaching.

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c02194)  

**Figure 6.** Plot of \( 1 - (1-X)^{1/3} \) vs \( t \) at various temperatures for Cr leaching.

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c02194)  

**Figure 7.** Plot of \( 1 - 2/3X - (1-X)^{2/3} \) vs \( t \) at various temperatures for Al leaching.
calculated according to the Arrhenius equation (eq 4). The Arrhenius plot of the leaching of Fe, Cr, and Al from the COPR is shown in Figures 8−10. The apparent activation energy of the leaching of Fe, Cr, and Al was calculated to be 23.03, 44.15, and 17.54 kJ/mol, respectively.

\[
\ln K = \ln A - \frac{E_a}{RT}
\]

(4)

where \( K \) is the reaction rate constant, \( A \) is the frequency or pre-exponential factor, \( E_a \) is the apparent activation energy, \( R \) is the universal gas constant, and \( T \) is the absolute temperature.

2.6. XRD and Morphology Analysis. After leaching, the residue is dried to a constant weight at 353 K for XRD and SEM tests. The scanning electron microscopy (SEM) analysis of the COPR before and after leaching is shown in Figure 11. It is clearly indicated that due to the effect of sulfuric acid and the extraction of the elements from the COPR, it changes from larger agglomerated particles to more dispersed fine particles. Figure 12 shows the XRD analysis of the COPR before and after leaching. It could be observed that the COPR mainly contained magnesiochromite ((Fe, Mg) (Cr, Fe) _2O _4), MgFeAlO _4, Fe (Cr, Al) _2O _4, and periclase (MgCr _2O _4). However, the main composition of the COPR is not changed after leaching, but the intensity of each peak is reduced, which is due to the leaching of a large number of elements.

3. CONCLUSIONS

In this work, the leaching of valuable elements like Fe, Al, and Cr from the COPR was investigated. The leaching efficiency of T-Fe, Al, and T-Cr reached 94.8, 75.1, and 76%, respectively, under the optimum conditions: mechanical ball-milling time of 120 min, 60% of w/w % H _2SO _4, L/S of 8 mL/g, 403 K, and 6 h. The leaching kinetics of the COPR showed that the leaching process of Fe and Cr was controlled by a surface chemical reaction with the \( E_a \) of 23.03 and 44.15 kJ/mol, respectively. The \( E_a \) of the leaching of Al was 17.54 kJ/mol and the rate-controlling step was the diffusion through a product layer.

4. EXPERIMENTAL SECTION

4.1. Reagents and Materials. In this study, all of the reagents were purchased from Chongqing Chuandong Chemical (Group) Co. Ltd. Unless otherwise specified, all
Table 2. XRF Analysis of the COPR

| component | Cr₂O₃ | Fe₂O₃ | Al₂O₃ | MgO | Na₂O | SiO₂ | TiO₂ | CaO | Other |
|-----------|-------|-------|-------|-----|------|------|------|-----|-------|
| content (%) | 11.34 | 39.49 | 31.35 | 10  | 3.4  | 2.69 | 1.35 | 0.22| 0.16  |

reagents used in the experiments were analytical grade. A filter membrane with a filter accuracy of 0.45 μm was also used in this study, which was purchased from Shanghai Xinya Purification Device Factory.

The COPR used in this work was obtained from a domestic chromate salt factory. Its particle size ranged from 100 to 150 μm, and its pH was about 8. The results of X-ray fluorescence (XRF) analysis of the COPR are shown in Table 2. It is shown that the main elements in the COPR were Fe, Al, Mg, and Cr, of which Fe (calculated by Fe₂O₃) was up to 39.49%, followed by Al (31.35% calculated by Al₂O₃), and Cr (11.34% calculated by Cr₂O₃).

4.2. Experimental Procedure. The COPR was first baked at 378 K for 4 h and then sieved. Subsequently, a certain amount of residue with particle size ranging from 101 to 150 μm was mechanically ball-milled in a ball crusher (QM-3SP4, Nanjing University Instrument Factory). The mass ratio of the residue to the steel ball was 4:3, and the stirring rate was 450 rpm. The residue enduring different ball-milling times was collected, and then served as the material for the following acid-leaching process.

The residue (7.5 g) obtained after ball milling and a certain volume of sulfuric acid solution with different mass concentrations were placed into an autoclave. Then, the autoclave was sealed and placed into a homogeneous reactor (KLJX-12A, Yantai Keli Chemical Equipment Co., Ltd.). When the predesigned temperature was reached, the homogeneous reactor was started at a set rotation rate. After completion of the reaction, the mixture was filtered using a filter membrane. The filter residue was washed three times using distilled water. For each run, 30 mL of deionized water was used. The filtrate was collected and used to determine the total Cr (T-Cr), total Fe (T-Fe), and Al concentrations. The leaching efficiency was calculated by referring the amount of leached Cr/Al/Fe in the liquor to its original input quantity.

4.3. Analysis Method. The T-Fe concentrations in the leach liquor were determined using the O-phenanthroline spectrophotometry method as per the Chinese National Standard GB/T 3049-2006. The Al concentration in the leach liquor was measured using the chrome azurol-S spectrophotometric method as per the Chinese National Standard GB/T5750.6-2006. The T-Cr concentration in the leached liquor was determined by an atomic absorption spectrophotograph (AA 800, Platinum Elmer, Germany) in the COPR before and after leaching was analyzed by XRD (Shimadzu XRD-7000). The wavelength used was Cu Kα radiation generated at 40 kV and 40 mA and selected via an energy-dispersive detector. The 2θ ranged from 10 to 90° with a step size of 0.02° and a counting time of 4 s per step. The particle size was analyzed by a Betterson 2000 laser particle size distributor.

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Notes

The authors declare no competing financial interest.

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