Energy saving Chemical Beneficiation Method of Improving Low Grade Nigeria Chromite Ore for Use in Steel Industries

*Kuranga I. Ayinla, 1Alafara A. Baba, 2Rukayat T. Oyewumi-Musa,
3Bankim C. Tripathy, 4Gold A. Anafi and 3Ranjank K. Dwari

1Department of Industrial Chemistry, University of Ilorin, Ilorin, Nigeria.
2Department of Chemical and Geological Sciences, Al-Hikmah University, Ilorin, Nigeria.
3CSIR - Institute of Minerals and Materials Technology, Bhubaneswar, India.
4Department of Science Laboratory Technology, Kwara State Polytechnic, Ilorin, Nigeria

ibkuranga@gmail.com | baalafara@yahoo.com | (titilayomusa | bankimtripathy | angold | ranjandwari)@gmail.com

Received: 25-AUG-2023; Reviewed: 12-DEC-2023; Accepted: 26-DEC-2023

http://doi.org/10.46792/fuoyejet.v8i4.1094

ORIGINAL RESEARCH

Abstract- This study detailed how direct acid leaching can be used to extract high grade chromite from low grade chromite ore for utilization in the steel industry. The suggested method, which makes use of nitric acid, avoids using traditional pyrometallurgical processes because they use a lot of energy. The leaching procedure is adjusted in accordance with the circumstances that will maximize chromium recovery. In this context, the independent variables are the nitric acid concentration (0.5–4 M), temperature (28–80°C), liquid to solid ratio (L/S) (3–10 mL g⁻¹), and leaching period (10–120 min). The three parameters that affect the leaching process most effectively are, in order, acid concentrations, temperature, and particle sizes. By doing this, 86.7% of the chromite in the lean chromite ore was recovered. Shaking core model examination of the kinetics of leaching reveals that internal diffusion reaction controls the rate of leaching, and the apparent activation energy calculated is 24.8 kJ/mol. This approach is successful and relatively inexpensive for chromite beneficiation. The gap is thus filled by the use of all-known inefficient acid dissolution procedures, which are less expensive and could serve as an alternate way of chromite beneficiation for use in iron and steel.

Keywords- Acid leaching, Activation energy, Beneficiation, Characterization, Kinetic, Lean ore

1 INTRODUCTION

The market for chromite ore was estimated to be worth USD 8859.99 million in 2022 and is projected to grow at a compound annual growth rate (CAGR) of 6.61% to reach USD 13009.94 million by 2028 (IRB, 2023). Due to the global decline in high-quality ore deposits, lower grade and more complex ores are receiving more attention. Complex sulphide ores are frequently challenging to treat using traditional mineral processing techniques, and the concentrates produced are frequently insufficiently pure, making these ores challenging to market (Ji, 2012; Sandstrom and Petersson, 1997).

Less energy intensive metal extraction processes are gaining popularity as conventional ore grades decline and the cost of energy increases both economically and environmentally (Liu and Shi, 2002). Due to its intrinsic complexity, chromite recoveries are a significant challenge, especially when treating finely scattered ores. The primary beneficiation method used to recover chromite material is gravity separation. However, handling tiny and ultrafine size particles (less than 75 μm) makes these traditional chromite processing methods difficult and ineffective, which results in losses market values (Padilla et al., 2008; Sylwestrak, 2010).

Additionally, because of the complicated ore structure and the presence of close density minerals, it can be very challenging to separate chromite from other related minerals. Specific gravity and size-based separations are the most practical and economical techniques for beneficiating chrome ore. (Liu et al. 2011).

The majority of chromite ore beneficiation businesses are looking for an affordable method of enriching ultrafine chromite while eliminating wasteful gangue minerals, increasing recovery, and reducing operational costs. The average annual production of chromite in South Africa has increased over the past five years to 1500 000 t, with the exception of 2016, when there was a little decline of about 900 000 t (Michael, 2016). A bulk yield of between 37 and 45% is produced by conventional chromite methods with an average recovery of between 50 and 65%. The reason for the low recoveries is that ultrafine material, which is carried into the tailings section by the force of process water, especially when operating at a dilute slurry, is the cause of the low recoveries. If a method exists that can efficiently recover fine and ultrafine chromite, this usual recovery suggests that South African chromite production can be enhanced by an additional 15 to 20% (Cicek, and Cocen, 2002; Abubakre et al., 2007).

One of the most popular methods in extractive metallurgy for recovering valuable minerals using aqueous solutions is the leaching process. Its use in hydrometallurgical routes is encouraged by its attractive properties, which include low energy consumption, reduced environmental contamination, and the capacity to process low-grade ores (Das et al., 1995). This procedure, which is frequently employed in the processing of nickel ore, copper ore,
uranium ore, and iron ore, appears to be an established technique for the extraction of metal components from ores and secondary resources (Chen et al., 2003; Yarkadas and Yilkiz, 2009; Hussein et al., 1972). In order to protect human health and reduce environmental contamination, the chromium salt manufacturing sector has focused a lot of emphasis on the acid leaching process because no chromium (VI)-bearing compounds are generated (Zhang et al., 2004). Sulfuric acid is the preferred choice for this cleaning method due to its chemical activity (Chen et al., 2013; Qi et al., 2011).

The impacts of various variables on the chromite leaching behaviour were reviewed which showed that increasing leaching temperature, pressure, and acid dose within reasonable ranges greatly increased the chromium extraction yield. (Sampath et al., 1990; Li et al., 2011). The main restriction on use of sulfuric acid leaching in chrome salt business is that chromite has a solid and dense spinel structure that makes them difficult to dissolve in sulfuric acid solution under air circumstance (Jagupilla et al., 2015). Even when exposed to hot, strong acid solutions, chromite is incredibly stable (Dey and Paul, 2016; Zhao et al., 2017). To increase the rate at which chromite dissolves during the leaching procedure, an oxidant is always employed. During the leaching procedure, all of the Cr\textsuperscript{3+} in the oxidant was converted to Cr\textsuperscript{6+} without producing any additional Cr\textsuperscript{6+}-containing materials (Wilbur et al., 2018; Liu et al., 2009). Despite a rise in studies on the chromite sulfuric acid leaching process in recent years, efforts to understand the decomposition mechanism are still inadequate (Senol, 2004). By adding an oxidant to a solution of sulfuric acid, it is possible to achieve the leaching of chromites under atmospheric pressure. Perchloric acid was utilized as an oxidant by Geveci et al. (2003) and Vardar et al. (1994), who also researched the leaching behaviour of chromite and calculated the apparent activation energy of the sulfuric acid leaching process. Both of them demonstrated the viability of the sulfuric acid leaching procedure when used in conjunction with the proper oxidants, however the rate of chromium oxidation under their experimental setup was quite low. The key factor contributing to the reduced leaching rate was the inappropriate additive choice. Zhao et al. (2020) discovered that 176 °C, 0.12 dichromic acid/chromite mass ratios, and 81% sulfuric acid concentration were the best process variables for leaching treatment of chromite ore. Additionally, experiments were conducted to find out how chromite breaks down during the leaching process and what impact dichromic acid has on it. It was found that the breakdown efficiency was strongly influenced by the Fe(II) concentration of the chromite and that dichromic acid acted as an oxidant and a catalyst in the leaching process. According to another study by Shi et al. (2017), the sulfuric acid leaching procedure has a lot of potential for practical application because it is a quick and safe way to recover chromate from chromite. The microwave technique has a better leaching efficiency when compared to the process using an oxidizing agent. The efficiency could go over 85% when the mass fraction of sulfuric acid was 80% and the leaching period was 20 min. These two technologies’ systems also function very differently from one another. The silicate was initially leached and then expanded during the leaching process while an oxidizing agent was present. Also, Biermann and Heinrichs (1960) reported that the decomposition of the chromite lattice is induced by a protonic attack.

To avoid the need for additives and prevent induction owing to the protonic effect, it is necessary to discover energy-saving and environmentally friendly alternatives in order to get around these established constraints. Since nitric acid is one of the most often employed main oxidants for the breakdown of minerals and organic compounds, it was chosen for this investigation. Strongly oxidizing HNO\textsubscript{3} that is hot and concentrated will liberate trace elements as incredibly soluble nitrate salts from a range of materials. However, nitric acid must be maintained at a high concentration because it loses its ability to oxidize materials when diluted below 2 M. The current study thoroughly evaluated the Fe leaching procedure to upgrade the chromite ore using Nigerian chromite as the starting material. Furthermore, the study focuses on optimizing various leaching parameters such as HNO\textsubscript{3} concentration, system temperature, particle diameters, and the effect of leaching duration, as well as the kinetics of processing Nigeria chromite ore. The results have important ramifications for chrome production that is clean for use in the chemical, metallurgical, and refractory industries.

2 MATERIAL AND METHODS
2.1 SAMPLES COLLECTION AND ANALYSIS
The National Steel Raw Material Agency, Malali, and Kaduna, Nigeria, provided the chromite ore sample that was used in this study. The sample originated from TungaKaduka origin in Anka Local Government of Nassarawa State. All the chemical constituents of the chromite ore were identified by X-ray Fluorescence (XRF) techniques. The ore morphology and mineralogy were determined using scanning electron microscopy (SEM) image and an X-ray diffraction (XRD) pattern respectively.

2.2 EXPERIMENTAL PROCEDURES
The ore was crushed and screened to create chrome powder with an average particle size of -110+78 µm. In an Erlenmeyer flask, 100 mL of nitric acid was mixed with a temperature-controlled electric heater. A temperature-controlled electric heater was used to mix 100 mL of nitric acid in an Erlenmeyer flask. When the temperature reached the specified level, 10 g of chrome powder was added and the entire leaching process was agitated. Deionized water was added to the container to keep the volume of the solution constant in case evaporation caused an excessive increase in the acid’s concentration (Senol, 2004; Zhao et al., 2015). After a predetermined timespan, the leachate was diluted with deionized water for subsequent filtration, and the pregnant filtrate was analysed for chromium by inductively coupled plasma (ICP) and chemical analysis according to the People Republic of China national standard. The extraction yield of chromium was estimated as the mass ratio of chromium in the residues to chromium in the raw

© 2023 The Author(s). Published by Faculty of Engineering, Federal University Oye-Ekiti.
material. After drying for 24 hours at 80 °C, the leaching residues were weighed and analysed using ICP, XRD, SEM, and EDAX.

3 RESULTS AND DISCUSSIONS

3.1 CHROMITE ORE COMPOSITION AND MINERAL PHASES
The Nigeria origin chromite was used in the experimental investigation, and the chemical composition, X-ray diffraction (XRD) pattern, photograph and scanning electron microscopy (SEM) images were reported in part 1 of the study (Ayinla et al., 2019). The major phases of the ore were determined by energy-dispersive X-ray spectroscopy (EDAX) to compliment the result of liberation structure by SEM.

3.2 INFLUENCE OF LEACHING CONDITIONS ON CHROMITE ORE UPGRADING
The current study presents a larger-scale experiment that was conducted for a longer duration (0-120 min). In the current investigation, a batch of leaching experiments were performed for 120 minutes at varied temperatures (28, 30, 40, 60, 80°C) and sulfuric acid concentrations (0.5-3.0 M).

3.2.1 Effect of Nitric Acid (HNO₃) Concentration
The concentration of HNO₃ used during reaction is an important factor, influencing mass transportation and chromite amount in the entire process. In Figure 1, the effect of HNO₃ concentration on chromite extraction from the ore was depicted.

Experimental condition: HNO₃ concentration = 0.5 – 4.0 M; Temperature = 55°C; Particle size fraction = -110+78µm; Moderate stirring speed, 200 rpm.

The extraction ratio jumps from 15.26 % at HNO₃ concentration 0.5M for 180 minutes to 48.97 % at HNO₃ concentration 3.0 M for 180 minutes. For different HNO₃ concentration, very slight increase of chromite yield was observed at the first stage (0 – 30 min) and apparently increases at latter stages of the reaction. However, the investigation was maintained at 4 M concentration due to poor yield experienced. The reaction between a simple chromite spinel and nitric acid can be represented as:

\[2\text{FeCr}_2\text{O}_4(s) + 6\text{HNO}_3(aq) \rightarrow 2\text{Cr}_2\text{O}_3(S) + 2\text{Fe(NO}_3)_3(aq) + 3\text{H}_2\text{O}(l)\]  

(1)

3.2.2 Effect of Temperature
The temperature elevation also has favourable influence on the leaching rate of chromite ore. The reaction temperature at this point is known to be the most important factor affecting the speeds of chemical reaction. Therefore, the effect of reaction temperature was carried out in the range of 28 – 90 °C under condition of -110-78 µm particle size, HNO₃ concentration 3.0 M over a period of 3 hours. The effect of temperature on leaching ratio is given in Figure 2.

3.2.3 Effect of Particle Sizes
A cogent consideration is given to decrease of particle size to be an important aspect of mechanical activation (Zhang et al., 2010). The fixed conditions were considered as the particle size of -110+78µm and - 520 +300 µm. As presented in Figure 3, the leaching rate of chromite ore increase as the particle diameter is decreasing.

3.2.4 Effect of Leaching Duration
The duration at which a reaction is been accomplished for the leaching process is also very important. To ascertain the effect of leaching time on the chromite ore dissolution, the ore was ground to a particle size -110+78µm, HNO₃ concentration of 3.0 M and the temperature was fixed at 80 °C. This enhancement can be seen in Figure 4.
It can be seen from the result that at early stage of the leaching, the iron interference slowdown in the rate at which chromite was extracted but further increased when the leaching extended beyond 1 hour while other conditions are kept constant. When the experiment extended for duration of 2, 3 and 4 hours, the highest recovery was observed after 3 hours leaching duration i.e. 97.3 %. As the leaching duration extends beyond 3 hours, little or no different in the chromium yield was observed. In the subsequent experiments, 3 hours was chosen as the leaching duration. Thus, it was concluded that the experiment can be easily finalised in a short time.

3.3 MACROKINETIC ANALYSIS

The concentration and temperature dependence of chromite ore leaching can be used to estimate the reaction order, enthalpy changes and the apparent activation energy, which are useful parameters for reactor scale up and project exercise (Sun et al., 2009). Considering fluid-solid heterogeneous reaction system, the reaction rate can be generally controlled by (1) diffusion through the liquid film (2) diffusion through the ash layer and (3) chemical reaction at the surface of the core of un-reacted materials (Chen et al., 2014; Levenspiel, 1972). To determine the rate-controlling step in this leaching process, the experimental data were fitted to the shrinking core models (Equation 3 and 4).

\[ 1 - \frac{2}{3} \alpha - \left(1 - \alpha\right)^{\frac{2}{3}} = k_d \]  
\[ 1 - \left(1 - \alpha\right)^{\frac{1}{3}} = k_r \]  

The left-hand sides of these expressions were plotted with respect to leaching time, and the dependency of these models on the kinetic data was evaluated using correlation coefficient \( R^2 \) values. The slope of these plots gave the apparent rate constant \( k_d \) and \( k_r \) for the given equations. The rate control model equation 2 yield better straight line in comparing to equation 3 versus time. The result profile was presented in Figure 5.

The natural logarithm of estimated apparent rate constant \( k_d \) from Figure 5 was later plotted against natural logarithm of concentration of HNO\(_3\) (Figure 6).

From the result in Figure 6, the slope of the straight-line graph was estimated to be 0.427 with \( R^2 \geq 0.968 \). This indicates that the reaction order with respect to H\(^+\) ion for HNO\(_3\) leaching is 0.427 with HNO\(_3\) concentration \( \leq 3.0 \) M. However, from the result in Figure 6, the linearization of the data gave a straight-line graph as presented in Figure 7.

The slope of these data in Figure 7 was evaluated which gave the apparent rate constant \( k_r \). The Arrhenius plot (Figure 8) was obtained by using apparent rate constants fitted from Figure 7.
3.4 Assessment of Product Residues by XRD, FESEM and EDAX

Figure 9 shows the discovered primary components as determined by XRD spectra, which were then analysed using X’Pert HighScore Plus analytical software to confirm the mineral phase.

The software provided the following results: aluminium chromate (Al₂O₃·CrO₃) [31-1171]; chromium Oxide (Cr₂O₃) [38-4015] as the major mineral phase, with hydrotalates [(MgO)₆(Al₂O₃)CO₃·5H₂O] [60-2007] and hydrogarnet [Al₂O₃·(H₂O)₆] [16-2342] as trace mineral phase. The phases chemical symbols and JCPDS file number were displayed appropriately. A cross-section of the leached residues is made and studied using FESEM to determine the internal structure of partially reacted chromite ore. Figure (10a-b) shows backscattered electron images at various magnifications. The existence of rectangular spinel chromite with flakes of silica oxide spreading over the rectangular chrome phase is clearly visible in leach residues formed using 3.0 M nitric acid solution, as shown in Figure 10a. The microscopic study (Figure 10b) indicated that no ash layer was produced during the leaching process, and there was a significant reduction in the starting particles as the reaction progressed.

According to Figure 10b, the grain chemical composition revealed a visibly eroded rough surface of the mineral, consisting of diverse irregular sizes of various mineral grain phases. The identity of the aforementioned grains was determined using EDAX analysis (Fig 10D). The result reveals metal peaks representing, Cr, Al, Mg, and Fe with their appropriate elemental weight percentages.

4 Discussion

The amount of water molecules and valence level of aqueous nitrates cannot be known with sufficient accuracy to calculate stoichiometric amount of nitric acid and other extracting reagent concentration because structural identity of chromite spinel was much more complex than what was given in equation (1). These were duly considered to resemble previous studies (Xia and Pickles, 1999; Kayiritchyanukul et al., 2004). The aforementioned low yield in chromium extraction with increasing HNO₃ concentration can be attributed to a spontaneous increase in chromium partial dissolution when the oxidising power of nitric acid increased (Fig. 1). As shown in Figure 2, increasing the temperature can accelerate leaching rate and shorten response time of the chromite breakdown process. The chromium extraction was rather low after 2 hours of reaction at 28 °C, but rose with leaching temperature, and a high extraction was reached at 80 °C. The results of other similar studies (Xia and Pickle, 1999; Liu et al., 2014; Jiang et al., 2014) showed that chromite mineral is very active at high temperature but this study was particularly limited to 80°C because of significant loss of acid solution via evaporation.

The observed increase could be attributed to the increase in the particle number per amount of solid when the particle size decreases and a corresponding increase in the surface area, which causes better exposure of chromite ore in the surface to the solution (Liu, et al., 2014). The optimum parameter for chromite ore leaching were proposed as: nitric acid concentration 3 M; reaction temperature of 80°C; liquid-solid ratio (L/S) of 10g/L and reaction time (t) of 2 hours. Under these conditions, important components like Fe, Al, and Cr were removed into the leaching solution with optimal leaching efficiencies of 91.8, 96.3, and 3.4%, respectively. While a higher percentage of chromite phase was collected, as evidenced by the residue analysis. The results of the leaching kinetics analysis indicated that the leaching of Fe from the chromite was controlled by diffusion through a product layer. The apparent activation energy of the leaching process was calculated to be 24.8 KJmol⁻¹. Because of the reported lower activation energy, this approach is expected to have potential applications in upgrading lean chromite ore to meet metallurgical grade requirements.

5 Conclusion

The leaching of iron gangue from Nigerian lean chromite ore was examined in this study. The chemical beneficiation parameters at nitric acid concentration of 3 M; reaction temperature of 80°C; liquid-solid ratio (L/S) of 10g/L; and reaction time (t) of 2 hours upgrade the ore to a concentrate with highest grade of 51.27% Cr₂O₃ and optimum recovery of 92.52%. The chromite leaching
kinetics revealed that the Fe leaching process was regulated by diffusion through a product layer, with an Ea of 24.03 kJ/mol. This chemical beneficiation strategy will not only assure the best possible chromite recovery in current technology, but will also benefit the exploitation of chromite waste dumps and other sub-grade ores.

ACKNOWLEDGMENT
We will like to thank CSIR-IMMT Bhubaneswar, Odhisa, India for financial support on this work

REFERENCES