A Two-Stage Gravity Separation and Acid Leaching Approach to Produce High-Purity Precursors from Low-Grade Manganese Ore for Nanotechnology Applications

Mona Hajilou[a], Meysam Naseri[b], Akbar Mehdilo[c*], Mehdi Irannajad[d]

a. Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran, mona.hajilou@aut.ac.ir

b. Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran, meysam.naseri@aut.ac.ir

c. Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran, amehdilo@aut.ac.ir

d. Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran, iranajad@aut.ac.ir

ABSTRACT

Manganese is a strategic element playing a vital role in various industries, including steelmaking, batteries, pigments, and pharmaceuticals. Although the majority of produced manganese is consumed in the steel industry, its non-metallurgical applications, particularly in the production of high-purity manganese dioxide nanoparticles, have gained increasing importance. Achieving the quality required for these applications necessitates the use of high-purity manganese solutions with minimal impurities. To this end, the recovery of manganese from low-grade ores remains a significant challenge due to the presence of carbonate and silicate impurities. In this study, a two-stage gravity separation-acid leaching process was developed for the beneficiation of low-grade manganese ore (13.8% MnO). In the first stage, the use of a shaking table significantly reduced gangue minerals, resulting in a concentrate containing 38.9% MnO. In the second stage, acid leaching with hydrochloric and sulfuric acids was performed to remove the remaining carbonate phases. Parameters affecting the leaching process—including acid type and concentration, temperature, and reaction time—were systematically investigated, and the resulting products were evaluated using XRF, XRD, and SEM-EDX analyses. The results demonstrated that under optimal conditions, over 97% of calcium was removed, and a final product with 69.71% MnO (pyrolusite purity exceeding 85%) was obtained. This product, containing quartz and barite as the primary insoluble impurities in reductive manganese leaching, can be utilized as a potential precursor for the synthesis of manganese oxide compounds. Overall, this approach paves the way for the production of high-quality manganese concentrate for advanced industrial and nanotechnology applications.

KEYWORDS

Manganese ore, Pyrolusite, Pre-concentration, Gravity separation, Acid leaching

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1. Introduction

Manganese stands as a critical strategic metal owing to its pivotal role in enhancing the mechanical properties and hardness of steel, making it widely used in the steelmaking industry. In addition, manganese is utilized in the production of non-ferrous alloys, batteries, catalysts, and advanced energy technologies [1, 2]. Furthermore, manganese-based nanoparticles- particularly manganese oxides- have garnered considerable attention in the biomedical and healthcare sectors due to their notable antioxidant and antibacterial activities [3–5]. Given the gradual depletion of high-grade reserves and the increasing industrial demand, the exploitation of low-grade manganese ores and the development of efficient beneficiation methods have become increasingly important [6]. Manganese deposits mainly occur as oxide and carbonate ores, with pyrolusite representing the principal manganese-bearing mineral [7]. For low-grade manganese ores, gravity separation methods are widely deployed, largely driven by the high specific gravity of manganese minerals [18, 20]. Nevertheless, owing to the inherent limitations of physical beneficiation in eliminating fine-grained impurities and attaining high-purity concentrates, hydrometallurgical techniques have gained prominence as complementary treatments [23, 24]. Among these, reductive leaching is critical since the dissolution of manganese from pyrolusite requires a reducing agent such as hydrogen peroxide, iron-bearing species, and various agricultural wastes Hydrogen peroxide, iron-containing compounds, and agricultural wastes [25–27].

Despite the feasibility of achieving high manganese recovery via reductive leaching, the co-dissolution of calcium-bearing gangue minerals often compromises solution purity and induces Consequently, controlling and selectively removing calcium from manganese-rich leach solutions is vital for high-end applications, such as the synthesis of high-purity manganese oxide nanoparticles. To address this challenge, the present study investigates the beneficiation of low-grade ore from the Amir Charaghah deposit (Tabriz, Iran) through an integrated approach combining shaking table gravity separation and selective acid leaching. The primary novelty of this research lies in the targeted elimination of calcite to suppress calcium dissolution, thereby yielding a high-purity precursor tailored for the synthesis of manganese oxide nanoparticles.

2. Materials and Methods

In this study, low-grade manganese ore from the Amir Charaghah deposit was utilized as the feed material. The representative sample comprises 13.8% MnO, 44.4% CaO, and 7% SiO_2, with calcite, pyrolusite, and quartz as the primary mineral phases. The ore was crushed to <2 mm and subsequently ground in a rod mill to achieve a particle size of d80 = 180 µm. A shaking table was then employed to remove a portion of the gangue minerals, producing a manganese concentrate for subsequent acid washing process. To improve concentrate purity, the effects of four key parameters were investigated: acid type (HCl and H_2SO_4), acid concentration (0.1–1 M), temperature (50–70 °C), and contact time (2–5 min). The chemical composition of the samples was determined using X-ray fluorescence (XRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES), while their crystalline phases were identified by X-ray diffraction (XRD). Furthermore, the morphological and microstructural characteristics were examined via scanning electron microscopy (SEM), utilizing secondary electron (SE) and backscattered electron (BSE) detectors, along with a wavelength-dispersive X-ray (WDX) analyzer.

3. Results and Discussion

The results of gravity separation using a shaking table demonstrated that the MnO grade increased from 13.8% in the initial feed to 38.9% in the concentrate. Despite a notable reduction in general impurities, the CaO content remained relatively high. Microscopic studies and XRD analysis confirmed the presence of pyrolusite as the dominant phase, accompanied by calcite, barite, and a minor amount of quartz. Furthermore, the leaching results revealed that hydrochloric acid outperformed sulfuric acid in calcium removal, elevating the MnO grade to 69.71% and decreasing the CaO content to 0.69%. Gypsum precipitation in the sulfuric acid medium was identified as the primary factor limiting calcium removal, as confirmed by XRD analysis (Figure 1). Optimization of the operating parameters established the optimum leaching conditions as 0.5 M HCl, 50 °C, and 5 min. Under these conditions, 97.61% of calcium was removed, whereas manganese dissolution remained below 0.02%. Microscopic studies and WDX analysis further verified the superior efficiency of hydrochloric acid in eliminating calcium-bearing phases, whereas pyrolusite and barite predominantly remained in the solid residue. Additionally, the identification of brandtite ($Ca_2Mn(AsO_4)_2 \cdot 2H_2O$) suggests that this mineral may act as a potential source of arsenic contamination in the solution during subsequent reductive leaching stages. Consequently, its dissolution behavior warrants further investigation in future steps.

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4. Conclusions

The combination of gravity separation using a shaking table and selective acid washing demonstrated high effectiveness in upgrading the manganese grade while eliminating calcite and quartz impurities from the Charaghah manganese ore. Compared to sulfuric acid, hydrochloric acid exhibited superior performance in calcium removal by avoiding the precipitation of insoluble calcium sulfate. Under the optimal leaching conditions (0.5 M HCl, 50 °C, 5 min), over 97% of calcium was removed, yielding a final concentrate containing more than 85% pyrolusite. Furthermore, the trace presence of brandtite underscores the necessity for evaluating arsenic behavior with respect to downstream processing and environmental compliance.

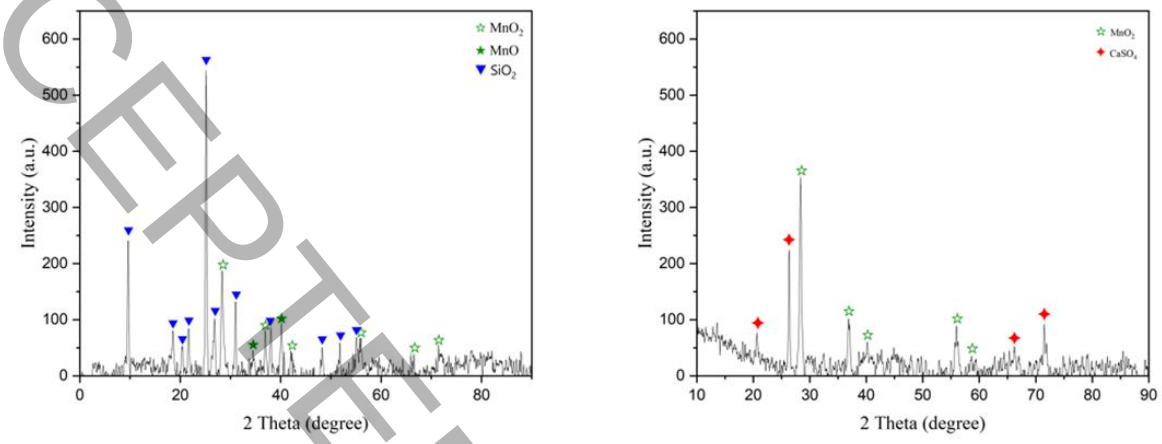


Figure 1: XRD patterns of the solid residue after acid leaching with (a) sulfuric acid and (b) hydrochloric acid

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