



Analytical and mineralogical study of a Ghana manganese ore: Quantification of Mn speciation and effect of mechanical activation



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HIGHLIGHTS

- Extensive characterization was conducted to understand the manganese ore.
- TG-DSC curve was quite consistent with that of TG-FTIR and thermodynamics analysis.
- It was found that mechanical activation could change the distribution of Mn speciation.
- Mn speciation distribution variation was correlated with the dissociation of Mn-containing flocs and SiO₂ particles.

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ABSTRACT

In-depth understanding of the manganese ore would be beneficial to make the best use more environmental-friendly. A Ghana manganese ore before/after mechanical activation (MA) was therefore extensively characterized in our investigation. Surface Mn⁴⁺(35.5%), Mn³⁺(35.9%), Mn²⁺(28.6%) were detected by XPS, though XRD only revealed the presence of Mn²⁺-containing minerals. Thermal decomposition curve of manganese ore obtained by TG-DSC was divided into four stages from 373.15 K to 1273.15 K, which were quite consistent with the pattern of generated gases obtained by TG-FTIR and the theoretical thermodynamics analysis of the incorporated components involving ΔG_f^θ and K_p^θ . Mn species distribution showed no difference for manganese ores before/after MA, but quantitative analysis showed the decrease of residual Mn content (cannot be extracted effectively by acid, from about 12% to 1%), and thereby the increased contents of other four Mn species (exchangeables, carbonates, oxides, organics), which was suggested to be correlated with the dissociation of Mn-containing flocs and SiO₂ particles witnessed by SEM-EDS. It was also found that MA could obviously promote the Mn dissolution kinetics in acid condition, though the dissolution of manganese ore before/after MA were both diffusion controlled. This investigation gives benignant inspiration for the resource utilization of manganese ore, taking the increasingly severer situation of Mn resource supply into consideration.

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1. Introduction

With the rapid development of Chinese economy in the recent decades, the production capacity of electrolytic manganese metal (EMM) in 2011 expanded 16.1-fold compared with that in 2000 (Xu et al., 2014). In this case, China played a dominant role in global EMM production, and the capacity in 2008 has already accounted

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for as high as 98.58% of the world's overall capacity of EMM production (Duan et al., 2010). As a matter of fact, China's dominant role was directly combined with the closure of EMM production in France, Japan and USA, due to the increasing environment and resource costs of EMM industry (Manganese Metal Company (MMC), 2009). The average annual wastewater effluent was estimated to be 1.55 million ton in the past 13 years, and high concentrations of Mn²⁺ (2000 mg/L), Cr(VI) (300 mg/L) and NH₃-N (2800 mg/L) (before treatment) were contained (Duan et al., 2011a). What's worse, besides discharging 6–9 tons solid waste and 1–3 tons wastewater, additional 0.9–1.9 kg selenium is consumed to produce 1 ton EMM (Lemly, 2004). The situation is getting worse as

the grade of manganese ore gets lower due to the rapid depletion of mineral resources, which means more and more waste will be discharged due to EMM production (Duan et al., 2010).

In this case, various attempts were performed to promote cleaner Mn production. Xin investigated and correspondingly confirmed the reductive dissolution of manganese from manganese dioxide ore by autotrophic mixed culture under aerobic conditions in the presence of cheap sulfur and pyrite (Xin et al., 2015). Selective sulfation roasting-water leaching is also creatively proposed by You for recovering manganese from iron rich low-grade manganese oxide ores using SO_2 as reductant (You et al., 2015a). Meanwhile, as the electrolytic manganese slag discharged per year increased to more than 2×10^6 tons due to massive EMM production (Duan et al., 2010), Mn recovery from electrolytic manganese slag draws increasing attention taking the growing scarcity of natural resources into consideration. Bioleaching was employed in the extraction of manganese from electrolytic manganese residues and it was found that acid dissolution of Mn^{2+} and Fe^{2+} catalyzed reduction of Mn^{4+} were the bioleaching mechanisms involved for Mn extraction (Xin et al., 2011). Another Mn bioleaching from manganese residues by Duan (Duan et al., 2011b) concluded that sulfur-oxidizing bacteria and iron-oxidizing bacteria assured the maximum Mn extraction. Besides, a water balance investigation was also performed for a representative EMM enterprise to study the details of water consumption and generation in the production process, and it was found that complete wastewater recycling could be achieved after water balance regulation and optimization (Xu et al., 2014). Based on the experience of electrolytic manganese metal industry, China's new model for cleaner production promotion was put forward by Duan (Duan et al., 2011a), and the best way to curtail environmental pollution from the industry is to apply new and modern technology to cut off the pollution before it is generated (Duan et al., 2010).

While meaningful results were obtained by previous investigations in Mn extraction, which would obviously promote the cleaner production of EMM, little was known about the details of manganese ore itself. Therefore, besides main components determination by XRD and acidic digestion, XPS was applied in our investigation to reveal the surface distribution of Mn species (Manning et al., 2007), which would impact the Mn dissolution occurring on the solid/water interface. Besides, thermal decomposition of manganese ore was also investigated using TG/DSC (Elbaz et al., 2015) and TG/FTIR (Rishwana et al., 2015) from 373.15 K to 1273.15 K under air atmosphere, and the theoretical thermodynamics analysis of incorporated components within this temperature range was simultaneously conducted. Particularly, quantitative analysis of Mn speciations including exchangeables, carbonates, oxides, organics and residuals before and after mechanical activation (MA) were creatively conducted by adopting the sequential extraction procedure by Tessler et al. (Tessler et al., 1979). SEM-EDS were employed to reveal the morphology and constitution of manganese ore before and after MA, which was favorable to interpret the Mn speciation variation induced by MA. Finally, the Mn dissolution kinetics of manganese ore before and after MA under acetic acid solution in an initial pH of 2.0 were compared and discussed.

2. Experimental section

2.1. Chemicals and materials

All reagents (Sinopharm Chemical Reagent), such as H_2O_2 , NaOAc, HOAc, HNO_3 , HF, HClO_4 were analytical grade and used without further purification. Ultrapure water ($18 \text{ M}\Omega \text{ cm}^{-1}$, Millipore) was used for all experiments. The $0.45 \mu\text{m}$ PTFE syringe filters

were obtained from ANPEL Scientific Instrument. Part of the manganese ore was subjected to MA, which was achieved with a customized stirring mill driven by a commercial available drill press equipped with a speed-tuned motor. For each grinding experiment, the manganese ore samples (50 g in each batch) were added into a stainless steel chamber (1000 mL) with 600 mL Zirconia milling balls (in different diameters), then the samples were subjected to wet milling (water) in ambient atmosphere without any other additives during the milling. The samples were activated in the stirring ball for 1 h at 600 rpm for all the bath experiments. Finally, the samples after MA were obtained and ready for characterization.

2.2. Characterization

XRD pattern of the samples was collected using a D8 Advance Powder X-ray Diffractometer (Bruker, Germany) using a $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation source (40 kV, 40 mA), the diffraction angle (2θ) was recorded from 10° to 80° , with a scanning speed of $1^\circ/\text{min}$ and a step size of 0.02° . Morphologies of manganese ore before and after MA were obtained using a field emission Scanning Electron Microscope (SEM) (Hitachi S-4800, Japan), and further energy dispersion X-ray spectrometer (EDS) at 200 kV was applied to reveal the elements distribution of the samples in various diameters. Particularly, Mn species on the surface of manganese ore before and after MA were analyzed by X-ray Photoelectron Spectroscopy (XPS) using a PHI-5000 Versaprobe spectrometer equipped with a rotating Al anode generating $\text{Al K}\alpha$ X-ray radiation at 1486.6 eV. Particle size distributions of manganese ore before and after MA were measured by Mastersizer 3000 Laser Diffraction Particle Size Analyzer with the refractivity index and density of manganese ore fixed to be 1.6 and 4.7 g/cm^{-3} . TG-DSC analysis of manganese ore was performed on a SDT Q600 thermogravimetric analyzer (TA, USA). Constant mass of the sample was used in order to avoid the effect of variation on sample weight on peak shape and temperature. The temperature was raised from 373.15 K to 1273.15 K with a linear heating rate of 10 K min^{-1} under air atmosphere. What's more, the TG-FTIR simultaneous measurement for the on-line analysis of volatile compounds formed during TG runs under air atmosphere consists of the above thermogravimetric analyzer coupled to a FTIR (PerkinElmer Spectrum™ 100 Infrared Spectrometer) by a TL 8000 transfer line with a 10 cm gas cell. The transfer line and gas cell were heated to 553.15 K to avoid any risk of condensation of heavier organic compounds. The FTIR spectra over the range of $4000\text{--}800 \text{ cm}^{-1}$ were collected every 6.8 s at 4 cm^{-1} resolution.

2.3. Quantification of Mn speciation

Total Mn content presented was determined by converting all Mn, irrespective of the oxidation state, to water-soluble Mn using a $\text{H}_2\text{SO}_4\text{--H}_3\text{PO}_4$ method (Zhang et al., 2013). The following chemical extraction method was retained for Mn Speciation of manganese ore before and after MA, including exchangeables (Mn_{ex}), carbonates (Mn_{ca}), oxides (Mn_{ox}), organics (Mn_{or}) and residuals (Mn_{re}) (Tessler et al., 1979). For exchangeable manganese, 5.0 g dry sample was extracted at room temperature for 1 h with 40 mL sodium acetate solution (1 M NaOAc, pH 8.2) with continuous agitation and the Mn content in supernatant was denoted to be Mn_{ex} . Then the residue was leached at room temperature with 40 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). After 2 h continuous agitation, the Mn content in supernatant was denoted to be Mn_{ca} . Again, the residual obtained was extracted at $96 \pm 3^\circ \text{C}$ for 2 h with 100 mL 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HOAc with occasional agitation, and the Mn content in supernatant was denoted to be Mn_{ox} . Once more, the residual particles was extracted at $85 \pm 2^\circ \text{C}$

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