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Ultrasound and mechanical activation cleaner promote lattice manganese extraction: A combined experimental and modeling study

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A B S T R A C T

The potential of ultrasound and mechanical activation (MA) in cutting down the acid amount required for low-grade MnO (manganese ore as received) extraction was extensively investigated in this study. Results showed that MA and heating-up combination could obviously promote Mn dissolution kinetics and thereby achieve higher extraction efficiency under identical H_2SO_4 dosage. The positive role of ultrasound was found to be evident in the extraction of MnO_A (manganese ore after MA), but negligible for MnO. Such a difference was correlated with the much different physicochemical properties of the liquid/solid systems that ultrasound involved in, as MA was confirmed to induce the dissociation of Mn-containing flocs and SiO_2 particles. High potential of ultrasound in weakening the agglomeration of ultra-fine MnO_A was also recommended. Semi-empirical Averami equation was found to well model the Mn extraction kinetics, which was much more diffusion controlled after MA based on the modeling. The modeling disclosed high capability of MA in decreasing the activation energy of Mn extraction (from 11.33 to 5.43 kJ/mol), whereas, ultrasound was effective in enhancing mass transfer or promoting pre-exponential factor A. Considering the potential in assisting efficient extraction via a cleaner way, ultrasound and MA combination provides a feasible alternative in mediating the hydrometallurgy of low-grade minerals.

1. Introduction

As a very effective and non-polluting method of activation, ultrasound has played an important role in chemical and physical activities of the process industry in the recent decades (Song et al., 2008; Sicaire et al., 2016; Cesaro et al., 2014). It was confirmed that ultrasonic energy could produce an alternating adiabatic compression and rarefaction of the liquid media being irradiated, which would further lead to the generation of microbubbles (Papadopoulos et al., 2016). The implosion of these microbubbles, which was induced by the continuous input of ultrasonic energy, would result in high local pressure (up to 1000 atm) and high transitory temperature (up to 5000 K), thereby promote the chemical reaction (Flint and Suslicks, 1991). Meanwhile, it was also found that ultrasound could also reduce the liquid film thickness, enhance mass transfer and reduce bubble coalescence, which would be beneficial for the interfacial reaction (Weavers and Hoffmann, 1998; Zhang et al., 2007). As a potential promoter, ultrasound mediated technologies exerted significant additional effect on the rate of various processes involving extraction. For example, ultrasound could accelerate the enzymatic hydrolysis of the untanned solid leather waste by promoting the breakdown of helical regions of collagen which are difficult to be attacked by proteases (Song et al., 2008). The myrobalan extraction efficiency was found to be 90% with ultrasound without external heating as compared to 77% for control process at 70 °C, indicating the application of ultrasound in tannin extract manufacture is a viable option with added advantages (Sivakumar et al., 2006). Therefore, the potential of ultrasound in promoting the mineral extraction was interesting and needed to be investigated.

After rapid development for more than 60 years, China now has a dominant role in global electrolytic manganese metal (EMM) production and its annual EMM output exceeded 1.0 million tons for the first time in 2007 (Duan et al., 2010). However, while the

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development of EMM industry contributes greatly to the economic growth, it also brings about the concerns of environmental pollution, as the EMM industry as a whole is defined as an industry with high levels of resources consumption and large quantities of wastes discharge (Duan et al., 2010; Lemy, 2004; Reilly, 2006). As a promising environmental management tool, cleaner production emerged to be the first-rate choice to maintain sustainable development (Gale, 2006; Rathi, 2003; Jegannathan and Nielsen, 2013). For electrolytic manganese metal industry, a new model was put forward by Duan for cleaner production promotion (Duan et al., 2011). However, using rhodochrosite ($MnCO_3$) as the raw material to extract lattice Mn, China's EMM industry still adopted the hydrometallurgical technology developed by the Bureau of Mines U.S. (Brantley and Rampacek, 1968). Large amounts of H_2SO_4 were consumed, which would finally result in the generation of acidic wastewater containing various kinds of pollutants including Mn^{2+}, Cr^{6+}, and SO_4^{2-}, in high concentrations (Duan et al., 2011). The situation was getting worse as the grade of available manganese ore getting lower due to rapid depletion of Mn-containing mineral resources, which means increasingly more H_2SO_4 amount would be consumed and correspondingly more acidic wastewater was generated (Duan et al., 2010). In this case, more efforts and energy were dedicated to curb the gradually severe pollution situation, taking the much stricter sewage discharge standard into consideration (Li et al., 2014).

A typical electrolytic manganese metal production process mainly consisted of milling, leaching, oxidation combined neutralization, filtering, purifying and electrolysis. Attempts were made in our investigation to decrease the amount of H_2SO_4 that needed to be consumed in the leaching process. Ultrasound was adopted as the eco-friendly promoter to mediate the dissolution of manganese ore (MnO). Ultrasound was reported to promote the dissolution kinetics of phosphate rocks by enhancing primarily the collision of H^+ with crystal lattice (Tekin et al., 2001). Similarly, activation energy of colemanite dissolution showed negligible change in the absence and presence of ultrasound, though the dissolution kinetics was promoted (Okur et al., 2002). Meanwhile, mechanical activation (MA) was also employed, considering its high potential in generating new surface and trigging physicochemical changes from particle comminution (Tan and Li, 2015; Alex et al., 2016). The impact of MA on the mineralogical feature of MnO has been extensively investigated by us, and it was found that residual Mn (cannot be extracted effectively by acid) content decreased dramatically, which was beneficial for the full use of MnO (He et al., 2016). In fact, discussions of thermodynamic parameters among these processes were included but not limited to. Our investigation focus on (i) evaluating the potential of heating-up, MA and their combination in MnO dissolution promotion by comparing the related dissolution kinetics under identical condition, (ii) modeling and discussing the kinetics of various MnO dissolution processes involving MA, ultrasound and heating-up, (iii) bringing insight into the phenomenon that positive role of ultrasound was significant for the dissolution of mechanical activated manganese ore (MnO_A), but negligible for MnO.

2. Materials and methods

2.1. Chemicals and materials

All reagents (Sinopharm Chemical Reagent), such as H_2SO_4, NaOH were analytical grade and used without further purification. Ultrapure water (18 $M\Omega cm^{-1}$, Millipore) was used for all experiments. The 0.45 μm PTFE syringe filters were obtained from ANPEL Scientific Instrument. The obtained MnO was characterized extensively, and the related information was provided in Table S1 and Fig. S1. Generally, manganese mainly existed in the form of carbonate, as kunohorite ($CaMn(CO_3)_2$) and the gangue minerals are quartz (SiO_2), gypsum ($CaSO_4 \cdot 2H_2O$), dolomite ($CaMg(CO_3)_2$) and magnesian ($CaMg(CO_3)_2$). Obviously, Mn dissolution kinetics would be affected by these gangue minerals.

The obtained MnO 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 MnO 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 rmp for all the bath experiments. Finally, the samples after mechanical activation (MnO_A) were dried overnight at 75 °C and ready for investigation. The particle size distributions of both MnO and MnO_A were shown in Fig. S2 and Table S2. Results showed that d_{50} and d_{90} of were 2.36 μm, 7.3 μm for MnO_A, and 17.6 μm, 86.2 μm for MnO, indicating that MA was quite effective in decreasing the particle size, and the surface area exposed was increased evidently. Such a conclusion could also be inferred from Fig. 1, in which the particle sizes of MnO were observed to be larger in distinctly non-uniform size, however, the particle sizes of MnO_A were much smaller in relatively uniform size.

2.2. Batch experiments

A schematic illustration of the experimental set-up was shown in Fig. 2. It consisted of an ultrasonic generator (Kun Shan Ultrasonic Instruments, KBS-250) together with a temperature constant batch reactor. The operating frequency of the ultrasonic generator

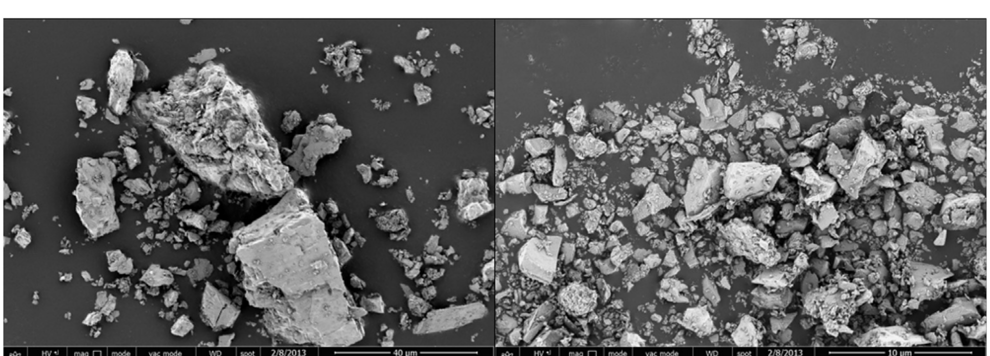

Fig. 1. SEM images of manganese ore before (left, 3000x) and after (after, 12000x) mechanical activation.

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