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## Kinetics and mechanism of one-step reductive leaching of manganese oxide ores by EDTA/EDTA-2Na

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**Abstract:** In this research, the kinetics and mechanism of one-step reductive leaching of manganese oxide ores by ethylenediaminetetraacetic acid (EDTA) or its disodium salt (EDTA-2Na) in an aqueous medium have been investigated. The kinetic data of this reductive leaching process may be described by the Avrami model, and the apparent activation energy was determined to be 15.8 kJ·mol<sup>-1</sup>/7.9 kJ·mol<sup>-1</sup> for leaching by EDTA/EDTA-2Na with a reaction order of -1.7/2.0. The EDTA/EDTA-2Na leach liquor characterized and analyzed by X-ray photoelectron spectra (XPS), Fourier transform infrared spectra (FTIR), and total organic carbon (TOC) determination denoted that the oxidation-reduction reaction happened between manganese(IV) and EDTA/EDTA-2Na, and a coordination complex, EDTA-manganese(II/III) formed. This new process can be easily used to leach manganese from manganese oxide ores in a moderate environment with the pH range of 5–8.

**Keywords:** Manganese oxide ores, EDTA, EDTA-2Na, reductive leaching, kinetics

### 1. Introduction

Manganese, as a strategically important metal, is mainly used in steel production, non-ferrous alloys, battery materials and chemical reagents (Sahoo et al., 2001). With the increase of consumption of manganese products and the decrease of high-grade manganese carbonate ores, the use of more abundant but low-grade and refractory manganese oxide ores is catching the attentions of manganese researchers and manganese industries.

Usually, manganese occurs predominately as higher oxides with a valence of +4 in manganese oxide ores. Because manganese(IV) is stable under acid or alkaline oxidizing conditions, a reduction process must be conducted pyrometallurgically or hydrometallurgically to convert the insoluble manganese(IV) to soluble manganese(II) before leaching it from ores. The conventional treatments to recover manganese from the manganese oxide ores include reductive roasting followed by acid leaching, and directly, reductive leaching in an aqueous medium using various reductants and acids (Pagnanelli et al., 2004). For example, manganese can be extracted from manganese oxide ores by sulfur-based reductive roasting-acid leaching (Zhang et al., 2013). Metal sulfides or ferrous iron (Kai et al., 2000), sulfur dioxide (Senanayake et al., 2015), oxalic acid (Sahoo et al., 2001), hydrogen peroxide (Jiang et al., 2004), and corncob (Tian et al., 2010) or guar meal (Kursunoglu and Kaya, 2013) can be used as the reductants to recover manganese from manganese oxide ores or secondary sources in a dilute H<sub>2</sub>SO<sub>4</sub> solution. Leaching manganese nodules in a dilute HCl solution by using pyrite as the reductant and leaching low-grade manganese oxide ores by a HNO<sub>3</sub> solution in the presence of glucose were reported by Kanungo (1999) and Pagnanelli et al. (2004), respectively. Pyrometallurgical reduction processes are of high energy consumption, low efficiency, and environmental pollution. The applications of hydrometallurgical processes are on the other hand restricted by the purification of manganese from the leach liquors and high production cost (Zhang et al., 2013). Besides, the

conventional acid leaching of manganese by  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , or  $\text{HNO}_3$  after reduction will lead to a low pH of the leach liquor, which may be unfavorable for subsequent steps (e.g. the purification of the leach liquor, or the treatment of manganese-silver ores which requires a neutral or alkaline environment for cyanidation or thiosulfate leaching of silver after acid leaching of manganese).

In many different industrial applications, EDTA/EDTA-2Na, a kind of aminocarboxyl chelating agent, is used for sequestering metal ions due to its excellent metal binding and solubilizing properties (Ghiselli et al., 2004). In this research, EDTA/EDTA-2Na was firstly employed as both reductant and lixiviant in one-step reductive leaching of manganese oxide ores in an aqueous medium. The leaching efficiency is high, and the leaching environment is relatively moderate with the pH range from 5 to 8, which will be beneficial to the purification of the leach liquor, or the treatment of some complicated manganese oxide ores (e.g. the treatment of manganese-silver (gold) ores which requires a neutral or alkaline environment for cyanidation or thiosulfate leaching of silver or gold after the leaching of manganese). Most of EDTA can be recovered by acidification in the form of precipitate. And then, the pregnant liquor containing manganese ions can be transferred to manganese electrolysis process. The residual EDTA in the electrolyte can prevent the generation of anode mud. Moreover, trimanganese tetroxide ( $\text{Mn}_3\text{O}_4$ ), as another product, can be obtained by the roasting of the EDTA-Mn crystallized product.

Kinetics studies of leaching manganese oxide ores or pyrolusite were reported previously. For instance, Lasheen et al. (2009) proved that manganese can be extracted from manganese oxide ores in the presence of molasses in a  $\text{HNO}_3$  solution, and the kinetics model  $1-(2X/3)-(1-X)^{2/3}=kt$  was found to fit the leaching data the best. The apparent activation energy was determined to be  $25.7 \text{ kJ mol}^{-1}$ , and the leaching process can be regarded as being controlled by film diffusion through the insoluble layer of the relevant minerals. Similarly, Jiang et al. (2004) investigated the kinetics of reductive leaching of pyrolusite with  $\text{H}_2\text{O}_2$  in a  $\text{H}_2\text{SO}_4$  solution at room temperature, and found that the kinetics data can be better described by  $1-(2X/3)-(1-X)^{2/3}=kt$  for the film diffusion-controlled case with an apparent activation energy of  $4.45 \pm 0.3 \text{ kJ mol}^{-1}$ . The reductive leaching of pyrolusite in a  $\text{H}_2\text{SO}_4$  solution with potassium oxalate as the reductant was conducted by Alaoui et al. (2016) and the kinetics analysis showed that this leaching process with an apparent activation energy of  $63.7 \text{ kJ mol}^{-1}$  was controlled by chemical reaction. In addition, a variable activation energy term introduced in the kinetic model of a manganese ore leaching process by Vegliò et al. (2001) could effectively reduce the deviation between estimated and experimental data (viz. better describe the leaching process by kinetic model). However, there has been no report on kinetics study of leaching manganese oxide ores by EDTA/EDTA-2Na before. Hence the kinetics model, the apparent activation energy, and the reaction order of this one-step reductive leaching process were considered and determined in this research.

Moreover, reaction process and mechanism analysis for leaching manganese from pure  $\text{MnO}_2$  by EDTA/EDTA-2Na were also explored tentatively.

## 2. Material and methods

### 2.1 Materials

The sample of manganese oxide ore used in this study was obtained from a manganese mine located in Hebei province with a particle size of 80% passing 200 mesh ( $-75 \mu\text{m}$ ). All chemical reagents used in this study were of analytical grade and deionized water was used throughout the whole experiment.

### 2.2 Leaching procedures

The kinetics tests were conducted by adding various amounts of EDTA/EDTA-2Na to a fixed amount of 20 g ore sample and 200  $\text{cm}^3$  deionized water in a 500  $\text{cm}^3$  flask. And then, the slurry was stirred at different temperatures by a PTFE impeller stirrer for a fixed reaction time of 60 min. The concentration of manganese ion in leach liquor was tested in a specified time interval.  $\text{MnO}_2$  with analytical grade was used to investigate the reaction process and mechanism for leaching manganese from  $\text{MnO}_2$  by EDTA/EDTA-2Na.

## 2.3 Analytical methods

The manganese content in leach liquor along with washing was analyzed volumetrically by ammonium ferrous sulfate (0.4 mol/dm<sup>3</sup>) titration using N-phenylanthranilic acid (0.2 wt.%) as the indicator. The leaching efficiencies of manganese can be calculated as follows:

$$LE = M \times C \times (V_1 - V_2) \times V / (m_0 \times V') \quad (1)$$

where *LE* is the leaching efficiency of manganese; *M* and *m*<sub>0</sub> represent the molecular mass and weight of manganese; *C* is the mole concentration of ammonium ferrous sulfate; *V*<sub>1</sub> and *V*<sub>2</sub> represent the volume reading of before and after titrating; *V'* is the volume for testing and *V* represent the total volume of leach liquor and washing water.

Solid coordination compound products generated from the reaction between MnO<sub>2</sub> and EDTA/EDTA-2Na were obtained by adding filtrated leach liquors to equal cold ethanol. The precipitated crystals were then filtrated and washed with ethanol, finally dried in the vacuum drying oven. The dried solid products were characterized by XPS and FTIR to analyze the valence of manganese and the organic structure of coordination compound. The XPS of the products were recorded on the Thermo Scientific ESCALAB 250Xi by operating Al K $\alpha$  X-ray source at 200 W with 20 eV pass energy. And the vacuum pressure was ranged from 10<sup>-7</sup> to 10<sup>-6</sup> Pa and the takeoff angle was 90°. The spectrometer was calibrated by setting the C1s binding energy at 284.6 eV. The FTIR spectra were recorded at a 4 cm<sup>-1</sup> resolution in the region of 4000–400 cm<sup>-1</sup> through KBr disks on a G510PFTIR infrared spectrometer from Nicolet, USA. TOC concentration of the leach liquor was measured by using Shimadzu TOC-V CPH with TNM-1 apparatus to analyze the oxidized products of EDTA/EDTA-2Na.

## 3. Results and discussion

### 3.1 Chemical and mineralogical analyses

The chemical compositions (wt.%) of ore sample is given in Table 1. The sample characterized by x-ray diffraction (XRD) cannot present the accurate mineral phases of manganese in this ore; therefore, the chemical phase analysis, based principally on a selective solvent, a chelate, resin or other isolating agent (Choudhury, 1994; Zhang, 1992), was adopted, and the result is listed in Table 2.

Table 1. Chemical compositions of the manganese oxide ore

| Elements       | Mg    | Al   | Si    | P    | S    | K    | Ca   | Ti   | Mn    |
|----------------|-------|------|-------|------|------|------|------|------|-------|
| Content (wt.%) | 0.55  | 5.08 | 14.89 | 0.14 | 0.25 | 2.75 | 0.84 | 0.19 | 26.99 |
| Elements       | Fe    | Ni   | Cu    | Zn   | As   | Sr   | Ag   | Pb   | O     |
| Content (wt.%) | 10.43 | 0.02 | 0.08  | 0.84 | 0.13 | 0.08 | 0.05 | 0.77 | 35.92 |

Table 2. Phase distributions of manganese minerals in the manganese oxide ore

| Phase            | In sulfide minerals | Manganese carbonate | Manganese oxides | Manganese -iron oxide | Manganese silicate |
|------------------|---------------------|---------------------|------------------|-----------------------|--------------------|
| Distribution (%) | 1.16                | 1.22                | 90.53            | 5.71                  | 1.38               |

### 3.2 Kinetics analysis

#### 3.2.1 Effect of temperature

The effect of the temperature on the leaching efficiency of manganese was investigated in the range of 303–368 K under the conditions of 0.37 mol/dm<sup>3</sup> EDTA/0.52 mol/dm<sup>3</sup> EDTA-2Na, stirring rate of 400 rpm, and L/S ratio of 10:1 over a period of 60 min, and the results are shown in Figure 1.

For the purpose of obtaining the kinetics equation and the apparent activation energy of manganese dissolving in EDTA/EDTA-2Na solution, the experimental data in Figure 1 were substituted to the frequently-used kinetics models as expressed by the following equations for solid-liquid reactions (Habashi, 1970; Levenspiel, 1999; Ray, 1993); however, the fitting is not so well.

$$X = kt \tag{2}$$

$$1 - (2X/3) - (1 - X)^{2/3} = kt \tag{3}$$

$$1 - (1 - X)^{1/3} = kt \tag{4}$$

$$-\ln(1 - X) = kt \tag{5}$$

$$X/(1 - X) = kt. \tag{6}$$

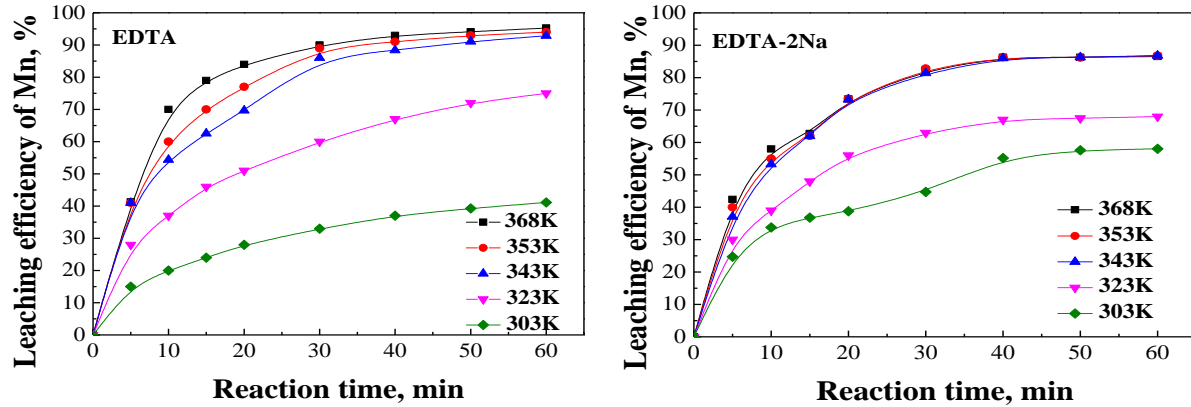


Fig. 1. Effect of temperature on the leaching efficiency of manganese

Whereas the semi-empirical Avrami model as presented in Eq. (7), which was firstly reported by Avrami (1939) for kinetics modeling of a new phase nucleation during solid-state phase changes, could satisfactorily represent the data of reductive leaching of manganese oxide ores by EDTA/EDTA-2Na. This model was also applied by Kabai (1973) to study on the dissolution of more than 50 metals and metal oxides in acidic solutions.

$$-\ln(1 - X) = kt^n \tag{7}$$

where  $k$  is the rate constant,  $t$  is the leaching time,  $n$  is a model parameter which can be used to indicate the nature of the control step as pointed out by Christian (2002) or served as a function of properties and geometry of the nucleated phase as reported by Kabai (1973) and  $X$  is the fraction leached.

The Avrami model can be expressed as the following form after differentiation (Guo et al., 2011).

$$\ln(-\ln(1 - X)) = \ln k + n \ln t. \tag{8}$$

The plots of  $\ln(-\ln(1-X))$  against  $\ln t$  and the linear relationships are presented in Fig.e 2. The slopes of lines represent the  $n$  values, which were classified by Kabai (1973):  $n < 1$ , the reaction rate is infinite at the very start but decreases with the prolonging time;  $n = 1$ , the initial reaction rate is finite;  $n > 1$ , the initial reaction rate is close to zero. The values of  $n$  for temperatures of 303, 323, 343, 353 and 368 K are calculated to be 0.49, 0.59, 0.68, 0.69 and 0.66 for leaching by EDTA, and 0.46, 0.62, 0.49, 0.59 and 0.55 for leaching by EDTA-2Na. This indicates that the initial leaching rate is infinite but the rate continually decreases with the prolonging time for this process. The intercepts of the lines are values of  $\ln k$ , which are used in the Arrhenius equation  $k = A \exp(-E_a/(R \cdot T))$  to determine the apparent activation energies of the reactions.

The plots of  $\ln k$  versus  $1/T$  are straight lines where the slopes are  $(-E_a/R)$  (Fig. 3). The  $E_a/R$  value is found to be 1899.8/944.6 for leaching by EDTA/EDTA-2Na, respectively. Therefore, the activation energy value was determined to be 15.8 kJ mol<sup>-1</sup>/7.9 kJ mol<sup>-1</sup>. Usually, the leaching process is controlled by diffusion when its activation energy value is in the range of 5-15 kJ mol<sup>-1</sup>. If the reaction is controlled by electrochemical reaction, its activation energy value is higher than 42 kJ mol<sup>-1</sup>. Activation energy value in the range of 15-42 kJ mol<sup>-1</sup> indicates that the reaction is controlled by both diffusion and electrochemical reaction (Fang, 2007). Thus, this EDTA/EDTA-2Na leaching process can be regarded as being controlled by diffusion (Kursunoglu and Kaya, 2014; Li et al., 2017; Zhang et al., 2017). The activation energy for leaching by EDTA is higher than that for leaching by EDTA-2Na, probably because the solubility of EDTA is lower than that of EDTA-2Na, particularly during the diffusion-controlled process.

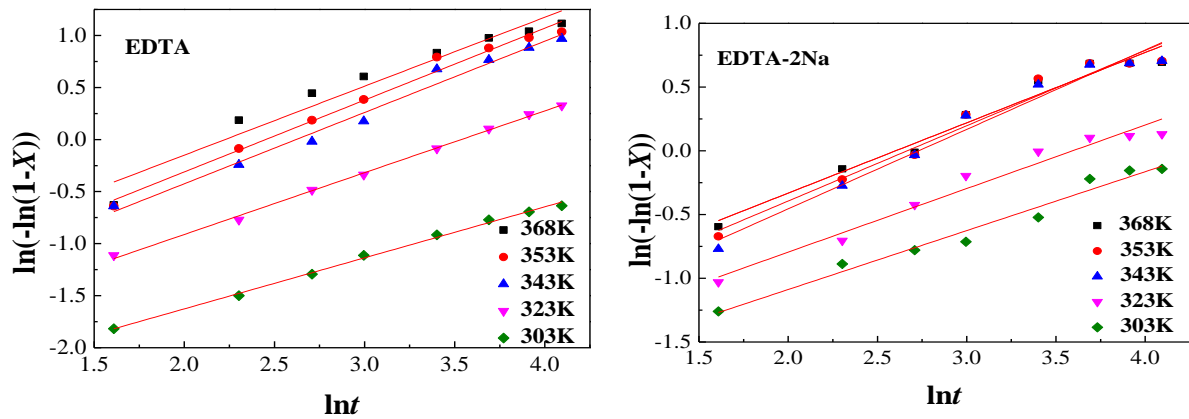


Fig. 2. Relationship between  $\ln(-\ln(1-X))$  and  $\ln t$  for leaching manganese by EDTA/EDTA-2Na at different temperatures (on basis of the data in Fig. 1)

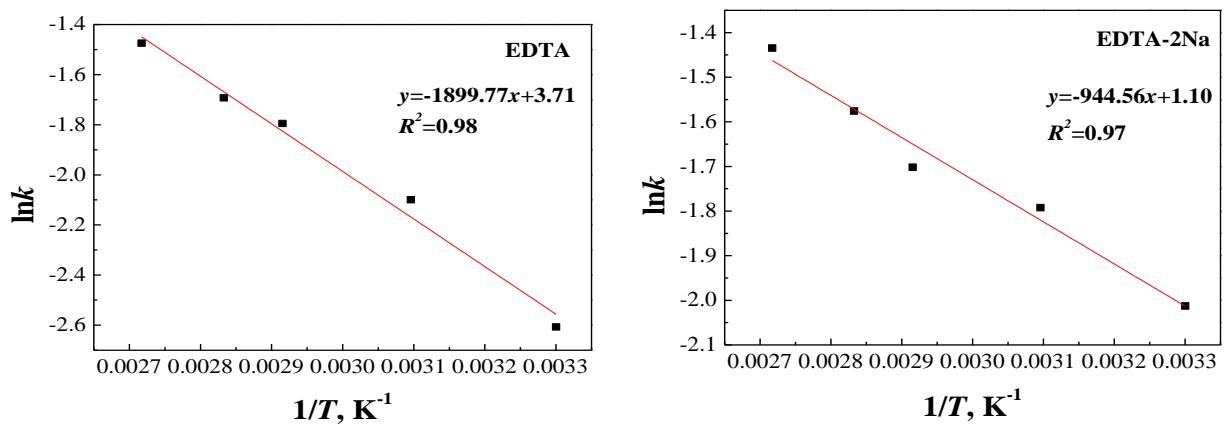


Fig. 3. Arrhenius plot for leaching manganese by EDTA/EDTA-2Na (on basis of the data in Fig. 2)

### 3.2.2 Effect of EDTA/EDTA-2Na additive amount

The effect of the EDTA/EDTA-2Na additive amount on the leaching efficiency of manganese was investigated in the range of 0.22–0.37 mol/dm<sup>3</sup> for EDTA and 0.19–0.52 mol/dm<sup>3</sup> for EDTA-2Na under the leaching conditions of 368 K, stirring rate of 400 rpm, and L/S ratio of 10:1 over a period of 60 min (Figure 4). Leaching environment is relatively moderate with the pH range from 5 to 6 for leaching by EDTA, and 7 to 8 for leaching by EDTA-2Na.

Fig. 5 shows the linear correlations of  $(-\ln(1-X))$  against  $\ln t$ . The values of  $\ln k$  can be obtained from the intercepts of lines, which will be used in the next step to determine the reaction orders.

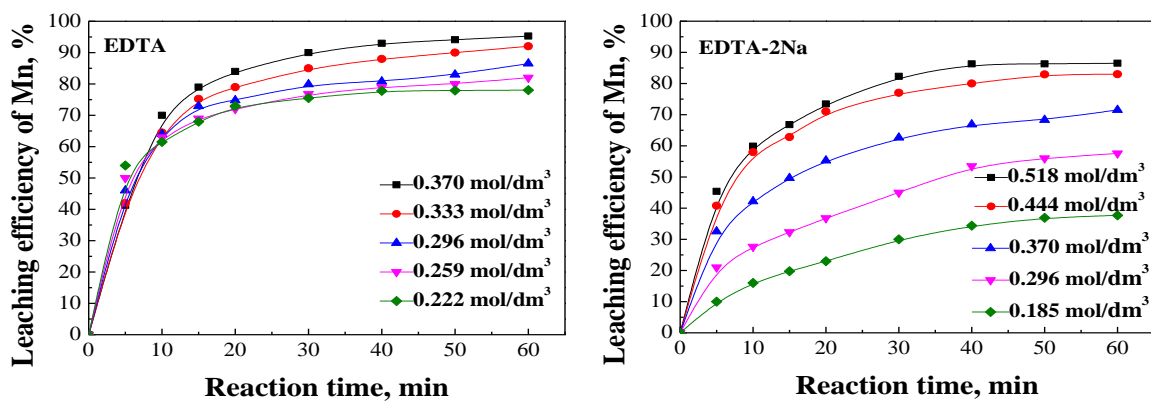


Fig. 4. Effect of EDTA/EDTA-2Na additive amount on the leaching efficiency of manganese

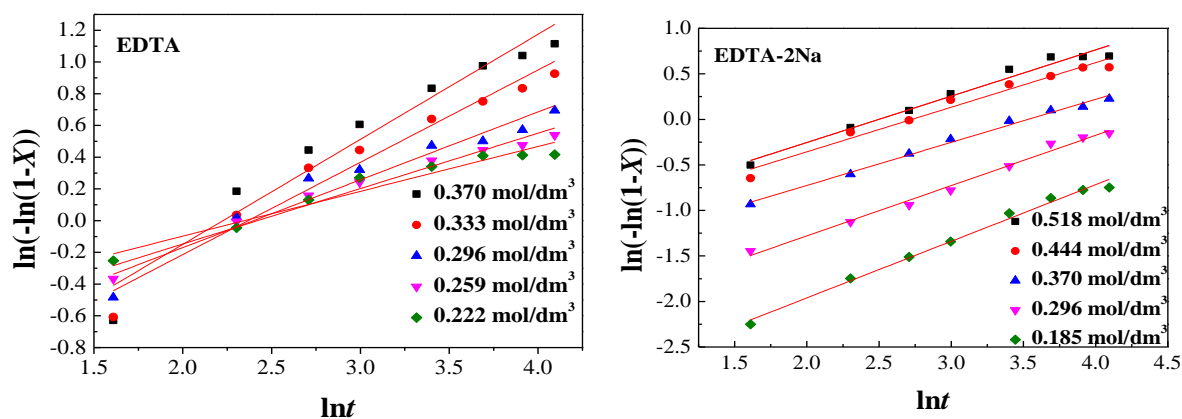


Fig. 5. Relationships between  $\ln(-\ln(1-X))$  and  $\ln t$  for manganese leaching at different EDTA/EDTA-2Na additive amounts (on basis of the data in Fig. 4)

The reaction orders of leaching manganese by EDTA and EDTA-2Na can be obtained by  $\ln-\ln$  plots of the rate constants versus the additive amounts of EDTA and EDTA-2Na, and the slopes or the reaction orders were found to be -1.7 and 2.0, respectively (Fig. 6). Therefore, the leaching efficiency of manganese strongly depends on the additive amount of EDTA-2Na, but not the additive amount of EDTA because of its low solubility.

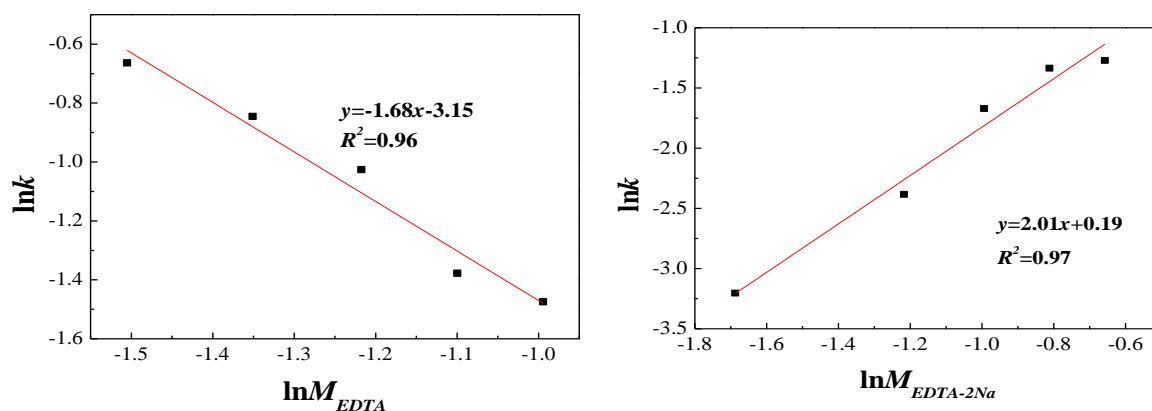


Fig. 6. Relationship between rate constants and EDTA/EDTA-2Na additive amounts (based on the data in Fig. 5)

### 3.3 Reaction mechanism

The coordination complex formed by the reaction between  $MnO_2$  and EDTA/EDTA-2Na was investigated and analyzed by XPS, FTIR and TOC.

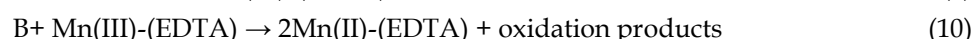
#### 3.3.1 XPS analysis

Fig. 7 shows the XPS of the product crystallized from EDTA leach liquor. The  $Mn2p$  spectrum of the product exhibits two main peaks with two satellite peaks. The main peak of  $Mn2p_{3/2}$  spectrum may be divided into two components, i.e. manganese(II) (640.35 eV) and manganese(III) (641.85 eV) (Castro and Polzonetti, 1989; Foord et al., 1984; Murray et al., 1985; Oku et al., 1975). Combined with the satellite peaks as the characteristic of manganese(II) (Fujiwara et al., 1995), the valences of the central manganese ions of the product can be preliminarily judged as +2 and +3, specifically +2.

The  $Mn3s$  spectrum exhibits two peaks in 88.24 eV and 82.54 eV. The splitting of binding energy of these two peaks is 5.70 eV, conforming to the description between manganese(II) and manganese(III) (Castro and Polzonetti, 1989; Foord et al., 1984; Murray et al., 1985; Oku et al., 1975). In consequence, the valences of the manganese ions of the product can be determined as both +2 and +3 by XPS. In addition, for manganese(II) complexes, the higher energy peaks are weaker than the lower energy peaks in intensity and for manganese(III) and manganese(IV) complexes, the intensity of the higher energy peaks are stronger (Fujiwara et al., 1995); however, the intensity of each peak can also be

affected by both manganese(II) and manganese(III).

The coexistence of both manganese(II) and manganese(III) can also be verified from the experimental phenomenon that the color of leach liquor exhibited deep red initially, which was the characteristic color of manganese(III) with ligand in an aqueous medium, and then turned to light red, even yellow, demonstrating that the process from manganese(III) to manganese(II) has happened. The mechanism study of the reaction between  $\text{MnO}_2$  and EDTA had been conducted by Yoshino et al. (1962) years ago and proved that manganese(III)-EDTA complex had formed. However, the manganese(III)-EDTA complex was not stable, especially in the daylight or at high temperature, and decomposed rapidly, leaving behind a colorless mass (probably manganese(II)-EDTA). Subsequently, Schroeder and Hamm (1964) concluded that the decomposition of manganese(III)-EDTA was in agreement with the following equation:



where B is a reactive intermediate with negligible concentration;  $\text{EDTA}_f$  is free EDTA.

Fig. 7 shows two peaks in C1s spectrum with the binding energy of 284.8 eV and 287.39 eV, corresponding to the binding energy values of C1s in methylene and carboxyl of EDTA.

Two main peaks can be dissociated from N1s spectrum with the binding energy of 400.54 eV and 398.66 eV (Fig. 7). As reported in literature (Yoshida and Sawada, 1974), two main peaks with the binding energies of 401 eV and 399 eV were found in the N1s spectrum of EDTA and its related compounds. In uncoordinated EDTA-4H, the heights of these two main peaks were almost equal, but in its Na salts, the height of the peak with the higher binding energy would decrease when the number of carboxylate groups increased. In ionized EDTA-4Na, only a single peak with the lower binding energy could be observed. In another literature (Atzei et al., 1993), a negative shift of about -1.3 eV was observed in N1s spectrum of EDTA complexes with transition metals, such as nickel(II), cobalt(II), and copper(II).

One main peak can be observed in O1s spectrum of the product, and it can be determined as the O1s from the carboxyl of EDTA with the value of 530.37 eV.

The XPS data of the product crystallized from EDTA-2Na leach liquor are similar to the product crystallized from EDTA leach liquor, only with a small decrease of binding energy due to the increase of the ionization degree. Especially, in N1s spectrum, only a single peak with a lower binding energy of 398.68 eV can be observed.

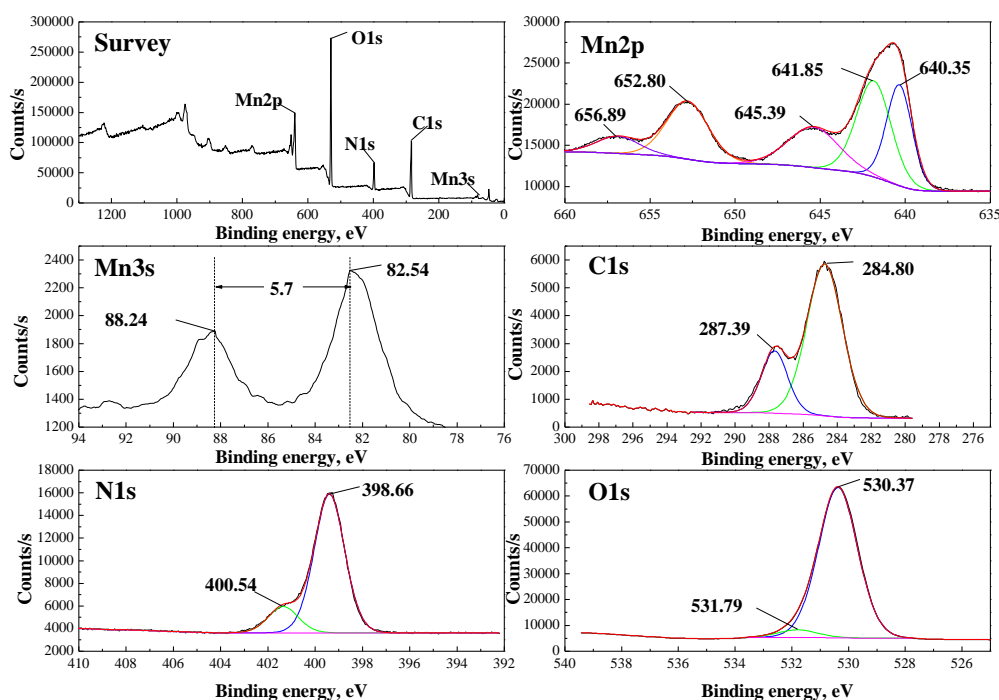


Fig. 7. XPS spectra of the product crystallized from EDTA leach liquor

### 3.3.2 FTIR analysis

According to the analytical results of FTIR spectra of EDTA, EDTA-manganese, EDTA-2Na, and EDTA-2Na-manganese (Fig. 8), the stretching vibration can be detected in characteristic regions of EDTA and its coordination complexes. The characteristic peaks of EDTA, EDTA-2Na, and the complexes formed by the reactions of EDTA-2Na with  $\text{MnO}_2$  and EDTA with  $\text{MnO}_2$  are located in 1700.97, 1627.24, 1597.41 and 1593.11  $\text{cm}^{-1}$ , respectively.

According to reference (Socrates, 2001), un-ionized free EDTA-4H, absorbed strongly in the region of 1750–1700  $\text{cm}^{-1}$  due to the stretching vibration of the  $\text{CO}_2$  group, whereas for ionized EDTA-2Na/4Na in the region of 1630–1575  $\text{cm}^{-1}$ , and coordinated EDTA complexes with bivalent metals, like zinc(II), copper(II), or trivalent metals, like chromium(III), cobalt(III), absorptions usually occurred in the region of 1650–1620 or 1610–1590  $\text{cm}^{-1}$ .

The FTIR results of the raw materials and the crystalized products from leach liquors presented in Fig. 8 are all in accordance with reported reference (Socrates, 2001), and the positions of characteristic peaks of the coordinated EDTA/EDTA-2Na with manganese are more similar to the coordinated EDTA with reported trivalent metals. For further verification, the complex formed by the reaction between EDTA and  $\text{MnCO}_3$  as the source of manganese(II) was chosen to contrast. As a result, the characteristic peak occurs in 1605.11  $\text{cm}^{-1}$  which is also in the region of EDTA with reported trivalent metals but exhibits a small difference to the characteristic peak of EDTA with  $\text{MnO}_2$ . This phenomenon may be caused by the different natures between manganese(II) and zinc(II) or copper(II), incomplete statistics of FTIR results of EDTA coordinating with metals, or the existence of both manganese(II) and manganese(III) in EDTA complex.

Combining the FTIR results with XPS results, it can be deduced that both manganese(II) and manganese(III), with different proportions, will be found in coordination complex formed by the reaction between EDTA/EDTA-2Na and  $\text{MnO}_2$ . The reduction equivalent in the dissolution process decreased, compared with that when all manganese(IV) was reduced to manganese(II) by other reagents.

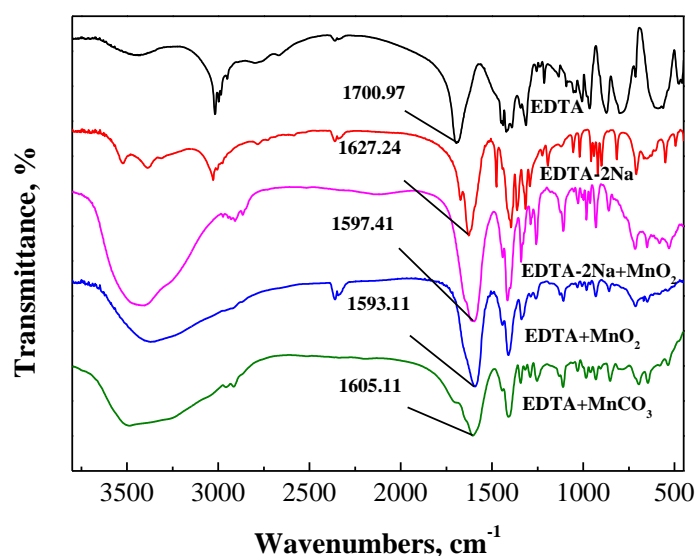


Fig. 8. FTIR results of EDTA/EDTA-2Na and EDTA-manganese/EDTA-2Na-manganese

### 3.3.3 Tentative exploration of the oxidation products

Manganese(IV) in  $\text{MnO}_2$  can be reduced and leached by EDTA/EDTA-2Na in an aqueous medium, forming coordination complexes between EDTA/EDTA-2Na and manganese(II/III). The oxidized intermediates of EDTA, such as ethylenediaminetriacetic acid (ED3A), ethylenediamine diacetic acids (EDDA-N,N' and EDDA-N,N), ethylenediaminemonoacetic acid (EDMA), imidoacetic acid (IMDA), and glycine formed where decarboxylation reaction happened, and the dangling  $\text{CH}_2\text{COO}^-$  group was further oxidized to  $\text{CO}_2$  and  $\text{HCHO}$  as reported (Ghiselli et al., 2004; Kocot et al., 2006; Pakalapati et al., 1996; Schroeder and Hamm, 1964; Yoshino et al., 1962). Average 8.7 or 6.7% of TOC removal and



20.9 or 17.1% of TN (total nitrogen) removal from EDTA or EDTA-2Na leach liquor were observed in our test, respectively. It can be deduced that CO<sub>2</sub> and N<sub>2</sub>, even NO<sub>x</sub> seems to be generated as part of the oxidation products of EDTA or EDTA-2Na.

#### 4. Conclusions

This new process can be used to recover manganese from manganese oxide ores with a high efficiency in a moderate environment. The moderate leaching environment can play a positive role in the purification of the leach liquor, or the treatment of some complicated manganese oxide ores. In addition, most of EDTA can be recovered by acidification, especially when other reduction reagents were used synergically. This process can become economic by means of recovering high-value associated metals or producing high-value manganese products, though EDTA is an expensive chemical reagent.

The kinetics of reductive leaching of manganese oxide ores by EDTA/EDTA-2Na in an aqueous medium did not follow a shrinking core kinetic model which was extensively adopted well, but the Avrami model was used successfully to explain the kinetic data. Apparent activation energy of 15.8 kJ mol<sup>-1</sup>/7.9 kJ mol<sup>-1</sup> for leaching by EDTA /EDTA-2Na is the typical value for diffusion-controlled case. The reaction order of leaching manganese oxide ores by EDTA-2Na was determined to be 2.0, indicating a strong dependency on the additive amount of EDTA-2Na. However, the reaction order of leaching manganese oxide ores by EDTA was determined to be -1.7, representing that the leaching efficiency was not affected pronouncedly by the initial addition of EDTA, probably on account of the low solubility of EDTA.

As characterized and analyzed by XPS and FTIR, manganese(IV) in MnO<sub>2</sub> was reduced to manganese(II) and manganese(III), and a coordination complex, EDTA-manganese(II/III), was obtained. Average 8.7%/6.7% of TOC removal and 20.9%/17.1% of TN from the EDTA/EDTA-2Na leach liquor were observed in our test. It can be deduced that CO<sub>2</sub> and N<sub>2</sub>, even NO<sub>x</sub> were generated as parts of the oxidation products of EDTA/EDTA-2Na.

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#### References

- ALAOUI, A., KACEMI, K.E., ASS, K.E., DARMANE, Y., KITANE, S., 2016. *Kinetic study of the leaching of manganese mine tailings by organic reductant in sulphuric acid solution*. Miner. Process. Extr. M. IMM T., 125(2): 109-116.
- ATZEL, D., FILIPPO, D.D., ROSSI, A., CAMINITI, R., 1993. *X-ray photoelectron spectra of dinitrogen chelating ligands with some transition metals*. Spectrochim. Acta A, 49(12): 1779-1785.
- AVRAMI, M., 1939. *Kinetics of phase change. I General theory*. J. Chem. Phys., 7(12): 1103-1112.
- CASTRO, V.D., POLZONETTI, G., 1989. *XPS study of MnO oxidation*. J. Electron Spectrosc., 48(1): 117-123.
- CHOUDHURY, V.N., 1994. *Chemical Phase Analysis Proceedings of the Workshop on Modern Methods of Analysis for Minerals Metals and Pollutants*, Jamshedpur.
- CHRISTIAN, J.W., 2002. *The Theory of Reaction Rates, The Theory of Transformations in Metals and Alloys*. Pergamon, Oxford, pp. 79-94.
- FANG, Z., 2007. *Leaching*. Metallurgical Industry Press, Beijing, 487 pp.
- FOORD, J.S., JACKMAN, R.B., ALLEN, G.C., 1984. *An X-ray photoelectron spectroscopic investigation of the oxidation of manganese*. Philos. Mag. A, 49(5): 657-663.
- FUJIWARA, M., MATSUSHITA, T., IKEDA, S., 1995. *Evaluation of Mn3s X-ray photoelectron spectroscopy for characterization of manganese complexes*. J. Electron Spectrosc., 74(3): 201-206.
- GHISELLI, G., JARDIM, W.F., LITTER, M.I., MANSILLA, H.D., 2004. *Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation*. J. Photoch. Photobio. A, 167(1): 59-67.
- GUO, X.Y., ZHAN, W.U., DONG, L.I., SHI, W.T., TIAN, Q.H., 2011. *Atmospheric leaching of nickel laterite by*

- hydrochloride acid and its kinetics*. Min. Metall. Eng. (Chinese), 31(4): 69-4.
- HABASHI, F., 1970. General Principles, Principles of Extractive Metallurgy.
- JIANG, T., YANG, Y., HUANG, Z., ZHANG, B., QIU, G., 2004. *Leaching kinetics of pyrolusite from manganese-silver ores in the presence of hydrogen peroxide*. Hydrometallurgy, 72(1-2): 129-138.
- KABAI, J., 1973. *Determination of specific activation energies of metal oxides and metal oxide hydrates by measurement of the rate of dissolution*. Acta Chim. Acad. Sci. Hung., 78: 57-73.
- KAI, T., SUENAGA, Y.I., MIGITA, A., TAKAHASHI, T., 2000. *Kinetic model for simultaneous leaching of zinc sulfide and manganese dioxide in the presence of iron-oxidizing bacteria*. Chem. Eng. Sci., 55(17): 3429-3436.
- KANUNGO, S.B., 1999. *Rate process of the reduction leaching of manganese nodules in dilute HCl in presence of pyrite : Part I. Dissolution behavior of iron and sulphur species during leaching*. Hydrometallurgy, 52(3): 313-330.
- KOCOT, P., KAROCKI, A., STASICKA, Z., 2006. *Photochemistry of the Fe(III)-EDTA complexes : A mechanistic study*. J. Photoch. Photobio. A, 179(1-2): 176-183.
- KURSUNOGLU, S., KAYA, M., 2013. *Recovery of Manganese from Spent Batteries Using Guar Meal as a Reducing Agent in a Sulfuric Acid Medium*. Ind. Eng. Chem. Res., 52(50): 18076-18084.
- KURSUNOGLU, S., KAYA, M., 2014. *Dissolution and precipitation of zinc and manganese obtained from spent zinc-carbon and alkaline battery powder*. Physicochem. Probl. MI, 50(1): 41-55.
- LASHEEN, T.A., HAZEK, M.N.E., HELAL, A.S., 2009. *Kinetics of reductive leaching of manganese oxide ore with molasses in nitric acid solution*. Hydrometallurgy, 98(3-4): 314-317.
- LEVENSPIEL, O., 1999. Chemical Reaction Engineering, third ed. John Wiley & Sons, New York.
- LI, L., FAN, E., GUAN, Y., ZHANG, X., XUE, Q., WEI, L., WU, F., CHEN, R., 2017. *Sustainable Recovery of Cathode Materials from Spent Lithium-Ion Batteries Using Lactic Acid Leaching System*. ACS Sustain. Chem. Eng., 5(6).
- MURRAY, J.W., DILLARD, J.G., GIOVANOLI, R., MOERS, H., STUMM, W., 1985. *Oxidation of Mn(II): Initial mineralogy, oxidation state and ageing*. Geochim. Cosmochim. Ac, 49(2): 463-470.
- OKU, M., HIROKAWA, K., IKEDA, S., 1975. *X-ray photoelectron spectroscopy of manganese - oxygen systems*. J. Electron Spectrosc, 7(5): 465-473.
- PAGNANELLI, F., FURLANI, G., VALENTINI, P., VEGLI, F., TORO, L., 2004. *Leaching of low-grade manganese ores by using nitric acid and glucose: optimization of the operating conditions*. Hydrometallurgy, 75(1): 157-167.
- PAKALAPATI, S.N.R., POPOV, B.N., WHITE, R.E., 1996. *Anodic oxidation of ethylenediaminetetraacetic acid on platinum electrode in alkaline medium*. J. Electrochem. Soc., 143(5): 1636-1643.
- RAY, H.S., 1993. Kinetics of Metallurgical Reactions. Oxford & IBH Publishing Company, India.
- SAHOO, R.N., NAIK, P.K., DAS, S.C., 2001. *Leaching of manganese from low-grade manganese ore using oxalic acid as reductant in sulphuric acid solution*. Hydrometallurgy, 62(3): 157-163.
- SCHROEDER, K.A., HAMM, R.E., 1964. *Decomposition of the ethylenediaminetetraacetate complex of manganese(III)*. Inorg. Chem., 3(3): 391-395.
- SENANAYAKE, G., DAS, G.K., LANGE, A.D., LI, J., ROBINSON, D.J., 2015. *Reductive atmospheric acid leaching of lateritic smectite/nontronite ores in H<sub>2</sub>SO<sub>4</sub>/Cu(II)/SO<sub>2</sub> solutions*. Hydrometallurgy, 152: 44-54.
- SOCRATES, G., 2001. Infrared and Raman Characteristic Group Frequencies: Tables and Charts. 3rd ed. J. Wiley and Sons, Chichester.
- TIAN, X., WEN, X., YANG, C., LIANG, Y., PI, Z., WANG, Y., 2010. *Reductive leaching of manganese from low-grade manganese dioxide ores using corncob as reductant in sulfuric acid solution*. Hydrometallurgy, 100(3): 157-160.
- VEGLI, F., TRIFONI, M., TORO, L., 2001. *Leaching of Manganiferous Ores by Glucose in a Sulfuric Acid Solution: Kinetic Modeling and Related Statistical Analysis*. Ind. Eng. Chem. Res., 40(18): 3895-3901.
- YOSHIDA, T., SAWADA, S., 1974. ChemInform Abstract: X-ray photoelectron Spectroscopy of EDTA, Chemischer Informationsdienst.
- YOSHINO, Y., OUCHI, A., TSUNODA, Y., KOJIMA, M., 1962. *Manganese (III) complexes with ethylenediaminetetraacetic acid*. Can. J. Chem., 40(4): 775-783.
- ZHANG, H.B. (Ed.), 1992. The Chemical Phase Analysis of Ores and Industrial Products. Non-ferrous Metals Industry Analysis Series, 9. Metallurgical Industry Press, Beijing, 376 pp.
- ZHANG, X., LIU, Z., WU, X., DU, J., TAO, C., 2017. *Electric field enhancement in leaching of manganese from low-grade manganese dioxide ore: Kinetics and mechanism study*. J. Electroanal. Chem., 788: 165-174.
- ZHANG, Y., YOU, Z., LI, G., JIANG, T., 2013. *Manganese extraction by sulfur-based reduction roasting-acid leaching from low-grade manganese oxide ores*. Hydrometallurgy, 133(2): 126-132.