Development of a Redox Microtitration Method for the Determination of Metallic Iron Content in Reduced Micron-Sized Iron Ore Concentrate Particles

YUXIANG CHENG, ZHONGJIE SHEN, YIRU YANG, QINFENG LIANG, and HAIFENG LIU

The determination of the metallic iron content in the reduced iron ore concentrates is essential to evaluate the reduction efficiency in the process metallurgy field. In this study, a redox microtitration method was developed to determine the metallic iron content in the reduced micron-sized iron ore concentrate particles. The effects of the dissolving time, dissolving temperature, and the concentration of the $FeCl_3$ solution as a reagent were investigated to achieve an optimized titration condition. The results showed that the temperature for the maximum solubility of the metallic iron content needed to be controlled below 25 °C. A stable metallic iron content highly close to the standard value was measured when the dissolution time exceeded 40 minutes. The $FeCl_3$ concentration of more than 100 g/L was suitable for dissolving the total metallic iron. Highly purified commercial standard iron powders were used to validate the developed method with good agreements between the measured data and standard value. Finally, this method was used to determine the metallic iron content in the reduced iron ore concentrate particle compared to the conventional titration method (standard test method). The relative error was lower than 3.0 pct, which proved that this method was accurate and reliable.

I. INTRODUCTION

MASSIVE greenhouse gas emissions from the iron-making and steelmaking industries have been attracted worldwide attention for decades, which account for about 33.8 pct annual emission and 5.0 pct world amount.[1,2] In order to solve this issue, several new ironmaking technologies, such as HYL process,[3] MIDREX process,[4] FINMET,[5] and Circored,[6] using iron ore pellet or iron ore concentrate as solid materials and operate at low temperature,[7] have been developed to shorten the process and reduce the emission of CO_2. A new flash ironmaking technology was developed by Sohn et al.[8] at the University of Utah to produce iron at high temperatures, potentially reducing energy consumption and emissions. The flash ironmaking technology uses iron ore concentrate to react with gaseous reducing agents, and its operating temperature is higher than the melting temperatures of products such as FeO and slag.[9] Therefore, using iron ore concentrate in the direct reduction ironmaking technology can remove the sintering and coking procedures and further reduce CO_2 emission,[10] providing a great potential for carbon neutrality in the future.

However, the reduction degree and metallization rate of the iron ore concentrate were significantly affected by the gas atmosphere, particle size, material type (e.g., hematite and magnetite), and reduction temperature.[11–13] Elzohiery et al.[12] studied the reduction characteristics of magnetite concentrates in the H_2 atmosphere. The results showed that the reduction degree was inversely proportional to the particle size from 1623 K to 1873 K and increased from 50 to 80 pct when the particle size was reduced from 53 to 20 μm. Fan et al.[13] investigated the reduction kinetics of magnetite concentrate particles in H_2/CO mixtures. It was found that the magnetite particles tended to fuse and melt at temperatures above 1350 °C changing the reduction mechanism. An enhanced synergistic effect was found in H_2/CO mixtures via computational fluid dynamics simulation and experimental method. Xing

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et al.[14] found that the metallic iron could be easily enwrapped in the liquid product as wüstite, and this process was highly dependent of the reaction temperature. The interfacial chemical reaction on the liquid surface became the rate-controlling step, which affected the reduction degree and metallic iron content in the product. This phenomenon was frequently found during the reduction process of iron ore concentrates at high temperature,[11–14] resulting in difficulties to the measurement of the reduction degree and metallization rate. Thus, a highly accurate determination of the reduction degree and metallization rate is critical to evaluate the reduction efficiency.

The metallization rate is the ratio of the metallic iron content to the total iron content in the reduced sample. Generally, redox titration method,[15,16] atomic absorption spectroscopy (AAS),[17] and inductive coupled plasma emission spectrometer (ICP)[18] were used to determine the content of iron or other iron valence states in tested samples. Table I lists the information for different standard test methods to determine the total iron or metallic iron contents. ISO-5416[19] used a bromine-methanol solution with a concentration of 50 mL/L as a dissolution reagent for dissolving the iron. The mass of the experimental material was 0.5 g. After dissolution, the solution was titrated with potassium dichromate solution (0.01667 mol/L). However, the removal of bromine and methanol in this method was complicated and requires extra use of a mercury-containing reagent (Mercury(II) chloride solution, 50 g/L). The range for determining the metallic iron content was from 15 to 95 pct. The latest international standard for the determination of the metallic iron content is ISO-16878-2016.[20] Based on the standard test method ISO-16878,[20] a 35 mL ferric chloride solution with a concentration of 250 g/L was used to dissolve a 0.2 g sample. Then, Fe^{2+} is titrated by potassium dichromate solution (0.01667 mol/L) using a sodium diphenylamine sulfonate indicator. The determination range of the metallic iron content is 57.5 to 90.5 pct. Both ASTM and JIS have relevant standards for determining the total iron content in the iron ore.[21,22] Total iron refers to all valence forms (Fe^0, Fe^{2+}, and Fe^{3+}) of iron in iron ore. No ASTM and JIS standard test methods for determining the metallic iron content for iron ores have been defined. The conventional method used in the manuscript was GB/T 38812.2-2020 from China.[23] In this standard test method, 40 mL of ferric chloride solution with a concentration of 100 g/L was used to dissolve 0.1 g of the sample. After that, the Fe^{2+} in the

solution was titrated by potassium dichromate (0.01667 mol/L). The determination range of the metallic iron content was above 50 pct. From Table I, a 0.1g solid reduced iron sample or more is typically required by the standard test methods. The kinetics of single-particle iron concentrates are extremely important for studying the reduction properties of iron concentrates. However, it is challenging to quantify the metallic iron content or reduction degree of the reduction products of single-particle iron concentrates by the conventional redox method due to the sample mass and experimental apparatus limitations. In order to determine the metallic iron content of a small amount or even a single iron ore concentrate particle, the current redox titration method is not suitable, and a new microtitration method is needed.

Generally, $FeCl_3$ solution was usually used to dissolve the metallic iron, and the valence state of iron (III) was reduced to Fe^{2+} as shown in Reaction [1].

$$2Fe^{3+}(l) + Fe^0(s) = 3Fe^{2+}(l) \qquad [1]$$
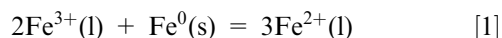
Compared with other reagents used as dissolution reagents for metallic iron such as $HgCl_2$, $CuSO_4$, and $PbCl_2$, $FeCl_3$ solution reacts with metallic iron more accurately.[24] One advantage is that using $FeCl_3$ dissolution does not require adding acid and mercury-containing solutions, which is environmental-friendly and convenient for the subsequent experimental waste disposal. After dissolution, the Fe^{2+} content can be determined by three methods that were abovementioned.[15–18] However, Fe^{3+} as an interfering ion will affect the measurement of metallic iron content for the AAS method.[25] ICP can only measure the total iron content in solution,[26] and the addition of high concentration $FeCl_3$ solution makes it impossible to quantify the Fe^{2+} content dissolved from the sample. Therefore, the redox method is an efficient and accurate way to determine Fe^{2+} in the solution and further calculate the metallic iron content in the reduced samples.

This study developed a redox microtitration method to determine the metallic iron content in the reduced micro-scale iron ore concentrate particles. The effects of the dissolving time, dissolving temperature, and reagent concentration on the solubility of the metallic iron and the titration result were investigated. Highly purified commercial standard iron powders (Fe, Fe_2O_3, and Fe_3O_4) were used to simulate the partially reduced iron ore particles with different reduction degrees and metallization rate were titrated to validate the developed method. Errors of all redox microtitration experiments

Table I. Information for Different Standard Test Methods

Standard	Measurement Items	Sample Mass (g)	Dissolution Reagent	Titration Reagent
ISO-5416[19]	metallic iron	0.5	Br_2-CH_3OH	$K_2Cr_2O_7$
ISO-16878[20]	metallic iron	0.2	$FeCl_3$	$K_2Cr_2O_7$
ASTM E246-2001[21]	total iron	0.5	HCl, H_2SO_4	$K_2Cr_2O_7$
JIS M8212-2005[22]	total iron	0.4	Na_2CO_3, Na_2O_2	$K_2Cr_2O_7$
GB/T 38812.2-2020[23]	metallic iron	0.1	$FeCl_3$	$K_2Cr_2O_7$

Table II. Chemical Compositions of the Materials Used in This Study (Wt. Pct)

Samples	Total Fe	Fe$_2$O$_3$	Fe$_3$O$_4$	Si	Mg	Ca	Al	Heavy Metals
Sample A	99.9	—	—	—	—	—	—	0.01
Sample B	99	—	—	—	—	—	—	≤ 0.005
Sample C	98	—	—	—	—	—	—	≤ 0.15
Sample D	65.01	—	—	1.91	0.50	0.59	0.272	—
Fe$_2$O$_3$	69.73	99	—	—	—	—	—	≤ 0.01
Fe$_3$O$_4$	71.69	—	99	—	—	—	—	≤ 0.01

were analyzed. The reduction degrees of different reduced iron ore concentrate particles were measured by the developed redox microtitration method. The results were compared with the measured value of the conventional titration method.

II. EXPERIMENT

A. Materials

Six materials, including three commercial iron powders (denoted as Sample A, Sample B, and Sample C), Fe$_2$O$_3$ powder, Fe$_3$O$_4$ powder, and iron ore concentrate (Sample D), were used in this study. The chemical compositions of all samples used in this study are given in Table II. The particle sizes for samples A, B, and C are 150 μm, 48 μm, and 38 μm, respectively, manufactured by Shanghai Macklin Biochemical Co., Ltd., China. According to the information from the vendor, the purities of three commercial iron powders were 99.9, 99, and 98 pct, respectively. Moreover, Sample A is an analytical reagent. Fe$_2$O$_3$ and Fe$_3$O$_4$ powders (purity 99 pct, Shanghai Macklin Biochemical Co., Ltd., China) were used to mix with sample A to simulate the partially reduced iron ore concentrates with different reduction degrees. Sample D was hematite powder (provided by Baoshan Iron & Steel Co., Ltd, China) with a particle size range of 43 to 50 μm.

The real reduced or partially reduced iron ore concentrate samples were prepared in the high-temperature tube furnace. The experimental apparatus is shown in Figure 1, including gas cylinders, controlling system, heating furnace, gas transportation system, and sample basket (φ25mm × 40mm). The heating furnace consists of a reaction tube (φ48 mm × 1100 mm), heating elements, and insulation layer inside the metal shell. The reduction reaction is carried out at atmospheric pressure. Sample D was placed in the basket with one particle thickness inside the tube furnace. The tube furnace was heated up to 850 °C at a heating rate of 10 °C/min. The flow rate of N$_2$ was set to 600 mL/min before the reduction experiment to remove air. Then, the sample basket was put down to the center of the tube furnace. Meantime, H$_2$ with a 600 mL/min flowrate was introduced into the furnace after the temperature stabilized. To get the reduced or partially reduced samples, H$_2$ was introduced within different time periods (e.g., 12, 15, 20, and 30 minutes). Four reduced or partially reduced samples with different reduction
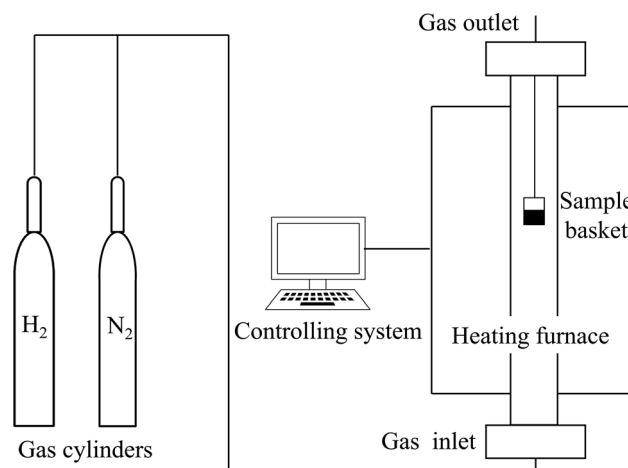

Fig. 1—The schematic diagram of the experimental apparatus for reduced iron sample preparation.

degrees were denoted as Sample D1 to D4, respectively. After reduction, H$_2$ was shifted to N$_2$ to cool down the sample and prevent re-oxidization. The reduced sample was collected after the furnace was cooled down.

The developed redox microtitration method used different reagents in this study. H$_2$SO$_4$ (> 96.0 vol pct Shanghai Hushi Chemical Co., Ltd) was mixed with H$_3$PO$_4$ (> 85.0 vol pct, Shanghai Macklin Biochemical Co., Ltd) to prepare the H$_2$SO$_4$–H$_3$PO$_4$ mixed acid. The volume mixing ratios of H$_2$SO$_4$, H$_3$PO$_4$, and water were 15:15:70. FeCl$_3$ solution reagent (100 g/L) was prepared with dissolving 10 g FeCl$_3$ powder (≥ 99.9 wt pct purity, Meryer (Shanghai) Chemical Technology Co., Ltd., China) in the deionized water (100 mL). Fe(NH$_4$)$_2$·(SO$_4$)$_2$·6H$_2$O solution reagent (40 g/L) was prepared with dissolving 40 g Fe(NH$_4$)$_2$·(SO$_4$)$_2$·6H$_2$O (99.5 wt pct purity, Shanghai Aladdin Biochemical Technology Co., Ltd, China.) into sulfuric acid and diluted to 1000 mL with deionized water. K$_2$Cr$_2$O$_7$ standard solution (concentration $c(1/6K_2Cr_2O_7)$ = 0.1000 mol/L) was prepared with dissolving 4.9036 g K$_2$Cr$_2$O$_7$ (≥ 99.8 wt pct, Sinopharm Chemical Reagent Co., Ltd., China) in the deionized water (1000 mL). Sodium diphenylamine-4-sulfonate (C$_{12}$H$_{10}$NNaO$_3$S) indicator solution (4 g/L) was prepared with dissolving 0.4 g C$_{12}$H$_{10}$NNaO$_3$S (≥ 97.0 pct, Shanghai Macklin Biochemical Co., Ltd) in 100 mL of Na$_2$CO$_3$ solution (2 g/L) into deionized water.

B. Experimental Method

The experimental procedure of the redox microtitration method developed in this study is shown in Figure 2(a). About 1.00 mg solid sample was fully dissolved in the $FeCl_3$ solution in a test tube and vibrated on a vortex mixer (HT-200 Shanghai HUXI Industrial Co., Ltd., China) with a vibration frequency of 200 rpm. To prevent the oxidation of divalent iron ions by oxygen in the solution or in the air, the deoxygenated water was used to prepare the $FeCl_3$ solution, and N_2 was continuously blown into the test tube during the dissolution process. Then, a 20 μL liquid from the dissolved solution was pipetted into a Durham tube via a high precision micropipette (0.5 to 10 μL, Eppendorf (Shanghai) International Trade Co. Ltd., China). 1 mL sodium diphenylamine-4-sulfonate ($C_{12}H_{10}NNaO_3S$) indicator solution was diluted to 100 mL, and then 10 μL of the diluted indicator solution was added to the titration solution. Meantime, 10 μL H_2SO_4–H_3PO_4 mixed acid was added. The aim of adding H_3PO_4 in the titration process was to reduce the potential of the Fe^{3+}/Fe^{2+} pair before the stoichiometric point.[27] Thus, the titration jump range was enlarged and included inside the color-changing range for reducing the error. The color did not change when the dosage of the adding mixed acid was below 10 μL. Finally, $K_2Cr_2O_7$ standard solution was titrated until the solution was stable as purple for the endpoint. The addition volume (V) of the $K_2Cr_2O_7$ standard solution was achieved. Each redox titration experiment with effects of the dissolving time, dissolving temperature, and reagent concentration was repeated five times.

In addition, the blank test experiment was carried out, and the procedure is shown in Figure 2(b). The blank test experiment was to reduce the error from the external effects of the operator, water, purity of reagent, and cleanliness of instruments. 20 μL $FeCl_3$ solution was pipetted in the Durham tube without adding any solid sample, as the blank sample. Then, 10 μL Ammonium iron (II) sulfate ($Fe(NH_4)_2·(SO_4)_2·6H_2O$) solution was added to the 20 μL $FeCl_3$ solution, followed by 10 μL H_2SO_4–H_3PO_4 mixed acid. 1 mL sodium diphenylamine-4-sulfonate ($C_{12}H_{10}NNaO_3S$) indicator solution was diluted to 100 mL, and then 10 μL of the diluted indicator solution was added to the blank test solution. After that, the $K_2Cr_2O_7$ standard solution was titrated until the color of the solution shifted to purple and stabilized. The first titrated dosage of $K_2Cr_2O_7$ was recorded as titration volume (V_1). Then, 10 μl $Fe(NH_4)_2·(SO_4)_2·6H_2O$ solution was added to this solution until the purple missed. The solution was titrated with $K_2Cr_2O_7$ standard solution until it changed to a stabilized purple liquid. The secondary titrated volume of $K_2Cr_2O_7$ was noted as V_2. The blank value (V_0) was calculated via the difference of V_1 and V_2.

(a) Redox microtitration method
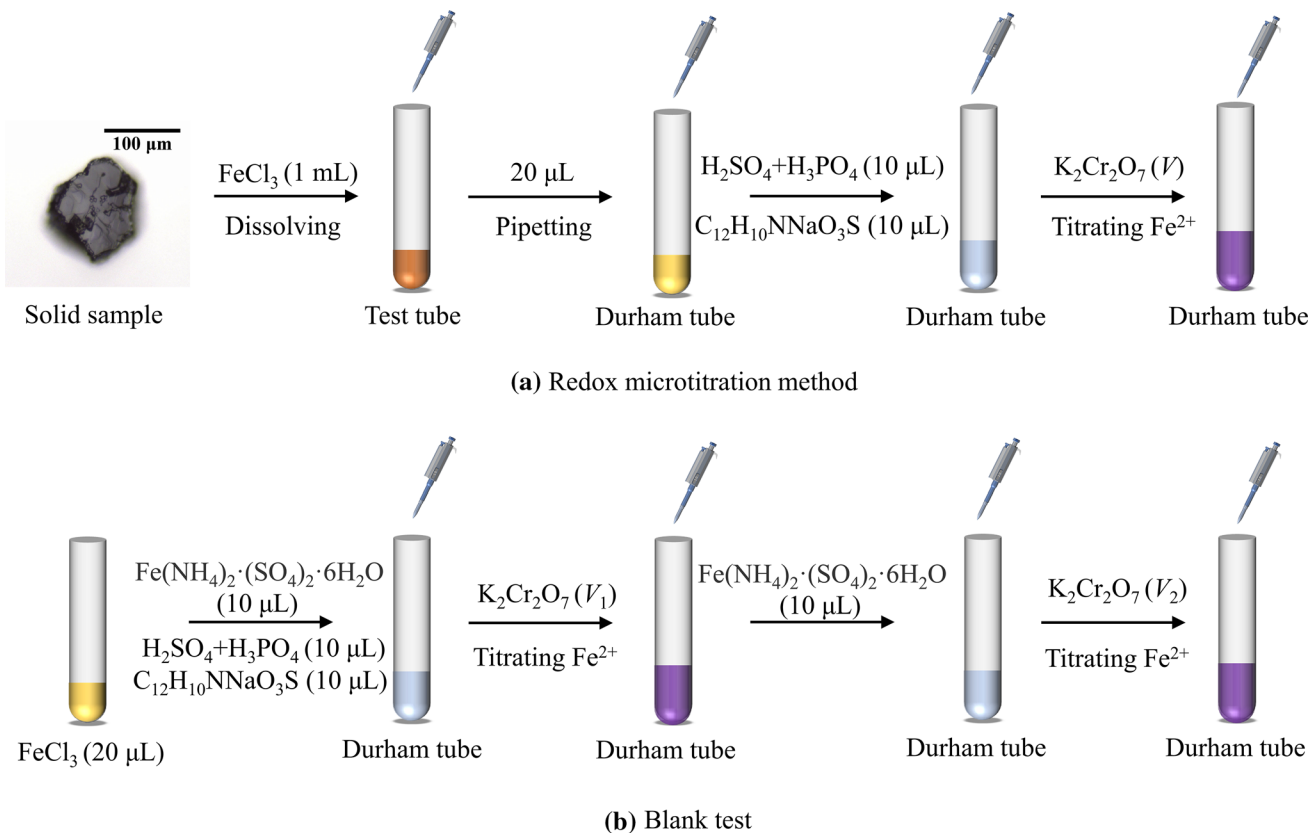

(b) Blank test

Fig. 2—The diagram of the procedure of the developed redox microtitration method in this study. (a) Redox microtitration method; (b) Blank test.

The reaction of $K_2Cr_2O_7$ with Fe^{2+} is shown in Eq. [2]. The amount of Fe^{2+} can be deduced from the amount of $K_2Cr_2O_7$, while the amount of Fe^0 was equal to $1/3$ Fe^{2+} concentrate, based on Eq. [1]. The metallic iron content of the raw material is derived from the ratio of the mass of Fe^0 to the mass of the raw material, and the calculation formula is shown in Eq. [3].

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad [2]$$
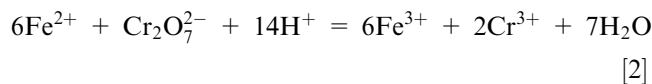
$$W_{Fe} = \frac{c \times (V - V_0) \times M \times f}{3 \times m} \times 100 \quad [3]$$

where W_{Fe} is the metallic iron content, f is the volume ratio of the dissolved solution to the volume of the titrating solution. In this study, the volume ratio (f) is set to 50. c is $1/6$ of the concentration of the $K_2Cr_2O_7$ standard solution (mol/L), $c = 0.1000$ mol/L. V is the volume of the $K_2Cr_2O_7$ standard solution consumed by the titration with Fe^{2+} (L), and V_0 is the volume of $K_2Cr_2O_7$ standard solution calculated from the blank test experiment, namely $V_0 = V_1 - V_2$. M is the atomic mass of Fe ($M = 55.85$ g/mol), "3" is the factor that the molar ratio of Fe^{2+} to Fe^0, and m is the mass of the raw sample (g).

III. RESULTS AND DISCUSSION

A. *Effect of Dissolving Temperature*

In order to investigate the effect of dissolution temperature, experiments were conducted at different temperatures (*e.g.*, 4 °C, 25 °C, 40 °C, and 60 °C). The dissolution time was set to 3 hours. The experimental results the used the microtitration method to determine the iron concentration in the solution is shown in Figure 3. The metallic iron contents denoted as W_{Fe} and measured by the redox microtitration method at 4 °C and 25 °C were both 98 pct. This indicated that the
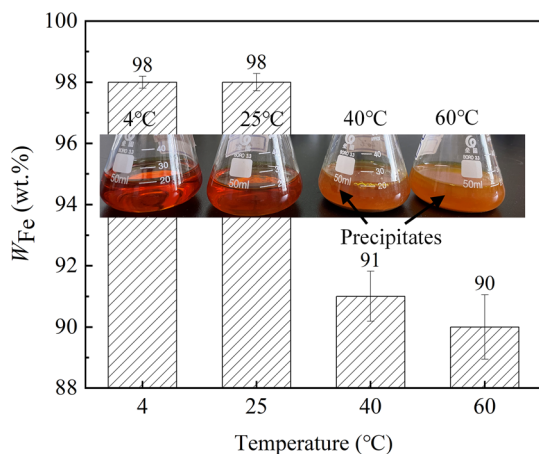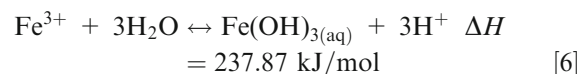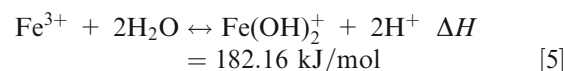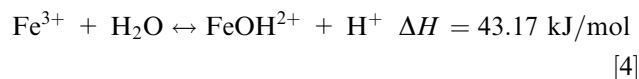
metallic iron content in the sample was fully dissolved into $FeCl_3$ solution. When the temperature was higher than the room temperature (25 °C), the dissolution degree of the iron in the $FeCl_3$ solution, which was assumed to the reduction degree, was reduced to 91 and 90 pct at 40 °C and 60 °C, respectively. Therefore, increasing the temperature has a negative effect on the dissolution of the metallic iron in $FeCl_3$ solution. At 40 °C and 60 °C, the amount of Fe^{3+} was reduced, resulting in less iron dissolved in the $FeCl_3$ solution. In addition, with combined analyses of bar graph and images in Figure 3, solutions at 4 °C and 25 °C were clean without any precipitates. In comparison, turbid liquid solutions were displayed at 40 °C and 60 °C, indicating that the iron (III) hydroxide formed in the liquid. $FeCl_3$ is a strong electrolyte that undergoes a complex series of reactions in water. Related reactions are shown from Eqs. [4] through [6]. The ΔH was calculated by FactSage 7.2 software.[28]

$$Fe^{3+} + H_2O \leftrightarrow FeOH^{2+} + H^+ \quad \Delta H = 43.17 \text{ kJ/mol} \quad [4]$$

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2^+ + 2H^+ \quad \Delta H = 182.16 \text{ kJ/mol} \quad [5]$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3(aq)} + 3H^+ \quad \Delta H = 237.87 \text{ kJ/mol} \quad [6]$$

All three reactions were endothermic, and the increasing temperature of the solution would cause the reaction move towards the right side. In the $FeCl_3$ solution, the hydrolyzed iron ion (III) polymerized to iron (III) hydroxide when the temperature increased,[29] the concentrate of Fe^{3+} in the solution decreased and hence it was difficult to completely dissolve Fe^0 from the sample to the solution, based on Eq. [1]. Therefore, all iron powder and reduced samples were dissolved at the set temperature of 4 °C to study other effects on the redox microtitration method.

B. *Effect of Dissolving Time*

The dissolution degree of the iron ore sample in the $FeCl_3$ solution that affected by the dissolution time will finally change the determination of the metallic iron content of the iron ore concentrate. The metallic iron contents of Samples A and D3 were measured at the different dissolving time periods from 10 to 100 minutes in this study. The operating temperature was set to 4 °C, based on the results in Figure 3. The effect of the dissolving time on the determination of the metallic iron content is shown in Figure 4. Results showed that the metallic iron content of both tested samples increased with the increasing dissolving time when the time was less than 40 minutes. The measured metallic iron content reached the maximum value when the dissolving time was 40 minutes. When the dissolving time was more
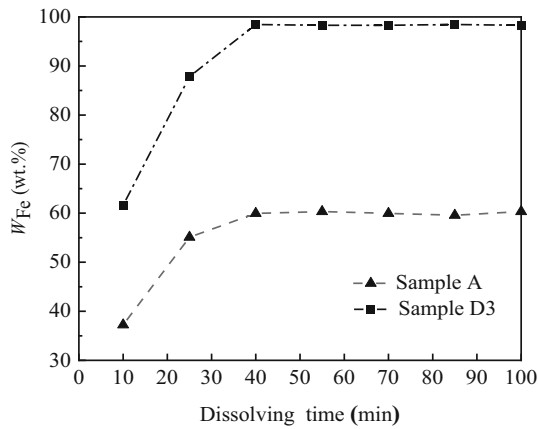

Fig. 3—Effect of the dissolution temperature on the determination of iron content.

Fig. 4—Effect of dissolving time on the determination of metallic iron content *via* redox microtitration method.
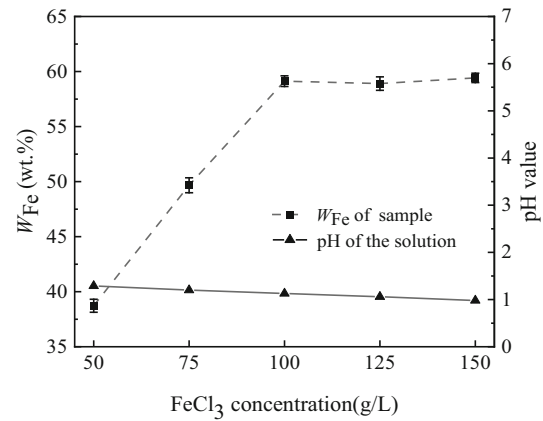

Fig. 5—Effect of FeCl$_3$ concentration and pH value on the metallic iron content tested from the redox microtitration method.
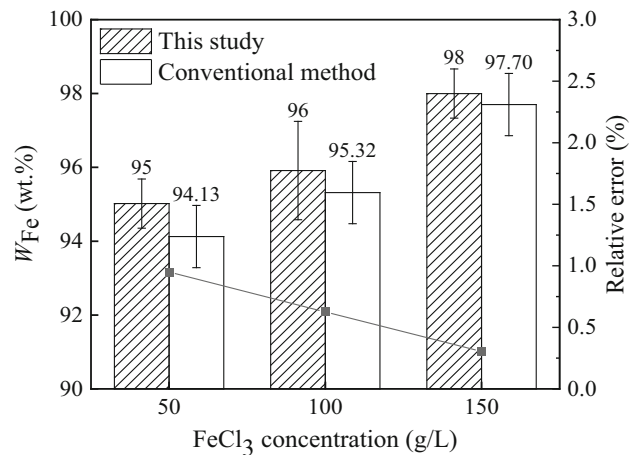

Fig. 6—Comparison of the measured metallic iron content under different FeCl$_3$ concentrations between the conventional titration method and redox microtitration method in this study.

than 40 minutes, the determined metallic iron content was stable. Therefore, the minimum dissolving time for the dissolution of all iron in a 1.00 mg solid sample was suggested to be more than 40 minutes. In this study, to completely dissolve the iron, all subsequent experiments adopted the dissolution time to 60 minutes.

C. *Effect of FeCl$_3$ Concentration*

In this study, FeCl$_3$ solution is the reagent used to dissolve metallic iron in the solid samples. The effect of FeCl$_3$ concentration (*e.g.*, 50, 75, 100, 125, and 150 g/L) on the determination of metallic iron content was studied using Sample D3, and the results are given in Figure 5. With the increasing concentration of FeCl$_3$ solution but below 100 g/L, the measured metallic iron content increased. When the FeCl$_3$ concentration was higher than 100 g/L, the determined metallic iron content was stable at a high value. For the Reactions (4) through (6), Fe^{3+} hydrolysis reaction makes the solution acidic, and the pH value of the FeCl$_3$ solution decreases with increasing the FeCl$_3$ concentration. The pH values of different concentrations of FeCl$_3$ solutions are shown in Figure 5. Theoretically, H$^+$ in the solution may react with the iron in the sample and bias the measurement. However, the pH value of the solution should not be adjusted because pH adjusters, such as NaOH and acid, can react with Fe^{3+} or metallic iron and make the measurement inaccurate.[30] From Figure 5, the pH value of the solution was close to 1.0 regardless of the experimental concentration range, indicating the influence of the pH value on the results can be ignored. A low concentration of FeCl$_3$ in the solution will cause an incomplete dissolution of the metallic iron and affect the determination and results with errors. When FeCl$_3$ was dissolved in water, various iron complexes (*e.g.*, FeOH^{2+}, Fe(OH)$_2^+$, and Fe(OH)$_{3(aq)}$) formed, thus it needed a particular concentration that higher than the critical value to dissolve total Fe^0 in the sample completely. Therefore, to ensure the complete dissolution of metallic iron and minimize the

influence of the acidity on the dissolution process, the concentration of FeCl$_3$ solution should be more than 100 g/L.

The experimental results under different FeCl$_3$ concentrations (50, 100, 150 g/L) were compared between the conventional titration method[15,16] and the redox microtitration method developed in this study, which are given in Figure 6. The conventional titration method was carried out according to the standard test method GB/T 38812.2-2020,[23] as shown in Table I. The experimental procedure was to dissolve 0.1 g of sample in 40 ml of FeCl$_3$ solution (100 g/L) and then titrate using K$_2$Cr$_2$O$_7$ solution (c = 0.1000 mol/L) with a burette. Five repeated experiments were performed for each data point to assess the error. The relative error is shown on the right y-axis. The relative error in Figure 6 refers to the ratio of the difference between the conventional titration method and microtitration method to the measured data of the conventional titration method. Results showed that the mean determined metallic iron content from the developed redox microtitration method at three concentrations were 95, 96, and 98

pct, respectively. The experimental results measured by the conventional titration method were 94.12, 95.31, and 97.70 pct, respectively. The relative error decreased when the $FeCl_3$ concentration increased from 50 to 150 g/L, and the minimum error value was about 0.3 pct. This result also proved that a high $FeCl_3$ concentration benefitted the dissolution of the metallic iron. The results of the microtitration method developed in this study are in good agreement with the conventional method.

D. *Method Validation*

Experiments for the determination of the metallic iron content in the standard samples (Samples A, B, and C) were carried out to validate the accuracy of the redox microtitration method. The determined metallic iron contents measured by the redox microtitration method were 99, 98, and 99 pct, respectively, with error bars shown in Figure 7. Compared to the iron contents in three standard samples (99.9, 99, and 98 pct), the relative errors were 1.4, 0.86, and 0.61 pct. In this section, the error was defined as the ratio of the absolute value of the difference between the measured value and the theoretical value to the theoretical value. The maximum error was less than 3.0 pct for the five repeated experiments using the microtitration method in this study. The relative standard deviations (RSD) were 0.86, 0.83, and 0.68 pct, respectively, indicating that the results from the developed redox microtitration method were close to the standard value.

During the reduction process of iron ore concentration, the evolution of the reduction degree is a crucial parameter to study the kinetic characteristics. In this study, samples of mixing iron powder (Fe) with Fe_2O_3 or Fe_3O_4 were prepared to simulate the reduced or partially reduced iron ore concentrates with different reduction degrees. The mixed samples were prepared by adding different weight percentages of Fe_2O_3 or Fe_3O_4 into t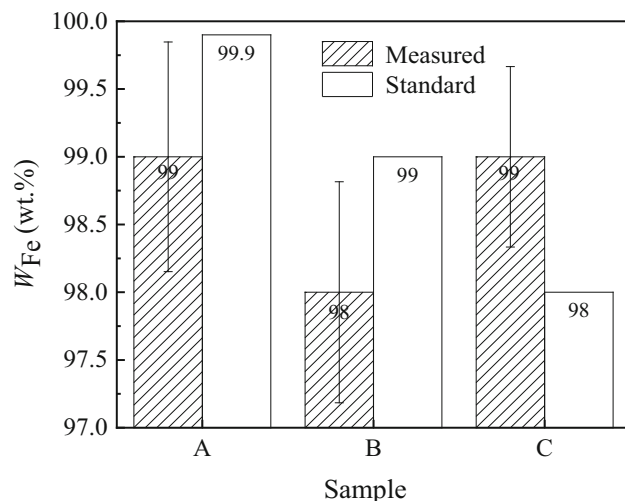he high purity commercial reduced iron powder (Sample A). The simulation sample was then titrated to determine the metallic iron content and compared with the actual value of the metallic iron content, and the measured results are shown in Figure 8. The results showed that the measured values matched well with the actual values in the simulation samples. Similarly, the relative error was calculated for each experiment condition. For the method developed in this study, errors may arise from the titration process, including losses during the pipetting of the solution and the judgment of the titration endpoint. The errors were all within 5 pct, and it was found that with the increasing metallic iron content the error reduced obviously, proving that this method is suitable for the determination of the metallic iron content to calculate the reduction degrees of iron ore concentrates.

E. *Measurement of Reduced Iron Ore Concentrates*

The metallic iron contents of reduced real iron ore concentrate samples at different reduced time periods (Samples D1 to D4) were measured by the redox microtitration method. The blank test data (V_1, V_2, V_0) and the $K_2Cr_2O_7$ standard solution dosage (V) for both methods are presented in Tables III and IV. The standard deviations (SD) of the titration volumes of the $K_2Cr_2O_7$ standard solution for the both methods are shown in Table IV. Each experiment was repeated five times. The dosage of $K_2Cr_2O_7$ standard solution in the conventional method was much higher than that of the microtitration method of this study, due to the different solution volume. However, the standard deviation of the microtitration method was lower than the results of the conventional method. This indicated that the stability of the measurement results of the developed method was better than the conventional method.

The results of the determination of the metallic iron content in the real reduced iron ore concentrate samples are given in Figure 9. Results showed that the mean metallic iron contents of Samples D1 to D4 were 22, 43, 60, and 83 pct, respectively. The experimental results measured from the conventional titration method were
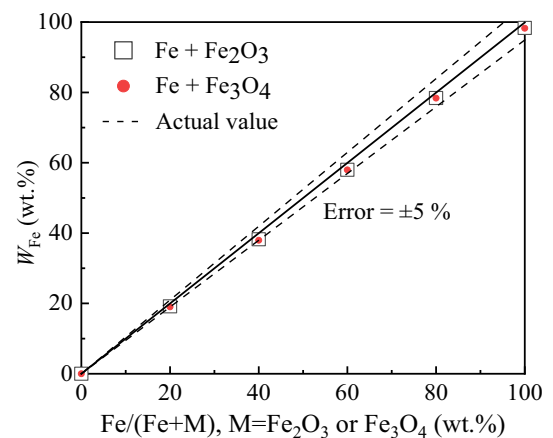
Fig. 7—Comparison of the result of the microtitration method with the standard sample.

Fig. 8—Comparison of the metallic iron content measured by the microtitration method with actual iron content.

Table III. Blank Test Data for Both Microtitration Method and Conventional Titration Method

Method	Number	V_1 (mL)	V_2 (mL)	V_0 (mL)	Average of V_0 (mL)
This Study	1	10.3×10^{-3}	10.2×10^{-3}	0.1×10^{-3}	0.1×10^{-3}
	2	10.2×10^{-3}	10.1×10^{-3}	0.1×10^{-3}	
	3	10.3×10^{-3}	10.2×10^{-3}	0.1×10^{-3}	
	4	9.9×10^{-3}	9.8×10^{-3}	0.1×10^{-3}	
	5	10.0×10^{-3}	9.9×10^{-3}	0.1×10^{-3}	
Conventional Method	1	10.53	10.16	0.37	0.37
	2	11.23	10.78	0.45	
	3	10.38	10.13	0.25	
	4	10.79	10.41	0.38	
	5	11.14	10.72	0.42	

Table IV. Dosages (V) of the $K_2Cr_2O_7$ Standard Solution for Both Microtitration Method and Conventional Titration Method

| Method	Sample	Weight(g)	V (mL) 1	2	3	4	5	SD	Average of V (mL)
This Study	D1	0.00100	2.5×10^{-3}	2.5×10^{-3}	2.4×10^{-3},	2.6×10^{-3}	2.5×10^{-3}	0.070	2.5×10^{-3}
	D2	0.00100	4.7×10^{-3}	4.8×10^{-3}	4.7×10^{-3}	4.7×10^{-3}	4.7×10^{-3}	0.045	4.7×10^{-3}
	D3	0.00100	6.6×10^{-3}	6.5×10^{-3}	6.5×10^{-3}	6.5×10^{-3}	6.5×10^{-3}	0.045	6.5×10^{-3}
	D4	0.00100	9.0×10^{-3}	8.9×10^{-3}	9.0×10^{-3}	9.0×10^{-3}	9.0×10^{-3}	0.045	9.0×10^{-3}
Conventional Method	D1	0.1000	11.89	12.48	12.27	12.58	11.84	0.3364	12.21
	D2	0.1000	23.41	24.11	23.68	23.04	24.43	0.5512	23.74
	D3	0.1000	32.91	33.55	33.66	33.16	32.85	0.3671	33.23
	D4	0.1000	43.96	44.22	44.04	43.84	42.90	0.5174	43.79
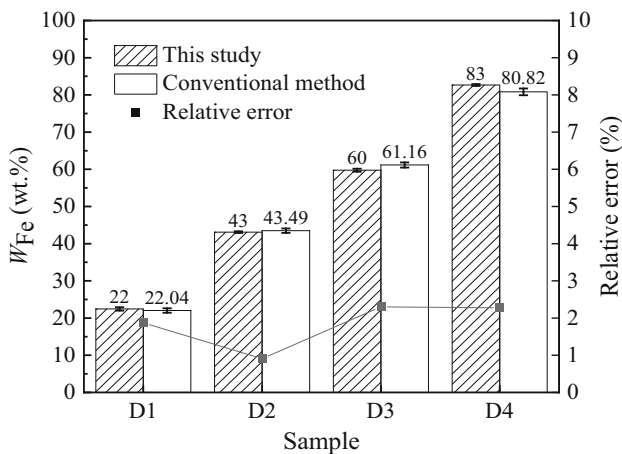
Fig. 9—The measured metallic iron content in the reduced iron ore concentrates with different reduction degrees by microtitration method and conventional titration method.

22.04, 43.49, 61.16, and 80.82 pct, respectively. According to the relative error shown on the right y-axis, it can be seen that the relative error between the conventional method and developed method of this study were less than 3 pct. The error below 3 pct is the post-experimental statistics but not a critical error. This value was obtained by comparing the average experimental data obtained from five repeated experiments with the conventional method. Therefore, the developed redox microtitration method can be used to determine the metallic iron content in the micron-sized iron concentrates with various reduction degrees.

IV. CONCLUSION

In this study, a redox microtitration method was developed to determine the metallic iron content in the micron-sized iron ore concentrate particles. Factors that affect the accuracy of the determination of the metallic iron content were considered and studied, including the dissolving time, dissolving temperature, and $FeCl_3$ solution concentration. The dissolving temperature below the room temperature (25 °C) was found to be suitable for the determination of the metallic iron content. When the dissolving time exceeds 40 min, a stable content of the metallic iron close to the standard value was measured. For the $FeCl_3$ solution concentration, more than 100 g/L was proved to be suitable for the complete dissolution of the metallic iron. In addition, the comparative experiment *via* testing commercial standard iron powders of high purity validated the developed method of this study, and the error was below 3.0 pct. The measured data of the reduced or partially reduced iron ore concentrates showed good agreement with the conventional titration method results. The relative error was lower than 5.0 pct, indicating that this method is reliable. This redox microtitration method

provides to measure minute amount of the metallic iron content in the micron-sized iron concentrate particle, and the dosages of reagents are significantly reduced compared to conventional titration methods.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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