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An electrochemical dissolution study of ilmenite fraction of beach sand in sulphuric acid solution

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An Electrochemical Dissolution Study of Ilmenite Fraction of Beach Sand in Sulphuric Acid Solution

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Abstract：Electrochemical techniques have been used to investigate the dissolution behaviors of ilmenite fraction of beach sand of Bangladesh in sulfuric acid solutions at various temperatures. The cyclic voltammetric studies indicated that the dissolution of ilmenite was very difficult without the addition of carbon powder in ilmenite. The effects of ilmenite-carbon ratio, acid concentration and temperature on cyclic voltammograms have been investigated to understand the dissolution process of ilmenite. The investigated results showed that the dissolution rate of ilmenite was slow at low applied reduction potentials and temperatures. However, the dissolution rate was accelerated at more negatively applied reduction potentials and higher temperatures. The dissolution rate was also increased with the increasing acid concentrations up to 1 mol·L^{-1}. At larger acid concentrations and higher reduction potentials, the dissolution rate was decreased due to the starting of H$_2$ gas evolution which eventually reduced the active surface area of pellet by adsorption. The activation energy was evaluated to be 50 ± 10 kJ·mol^{-1} in the higher temperature region, while 15 ± 5 kJ·mol^{-1} in the lower temperature region, suggesting the diffusion controlled process at the lower temperature region and chemically controlled process at the higher temperature region.

Key words: ilmenite; cyclic voltammetry; electrochemical dissolution; activation energy; sulphuric acid

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An estimated 3.5-million-ton of heavy mineral deposit has been discovered in the sand of Chittagong-Cox's Bazar-Teknaf beach and off-shore islands of Moheskhali, Kutubdia, and Nizhum-Dwip of Bangladesh. This deposit includes ilmenite, rutile, magnetite/hematite, zircon, garnet and monazite [1-3]. The Pilot Plant of Bangladesh Atomic Energy Commission (BAEC) at Kalatoli, Cox's Bazar has fractionated the heavy fraction of beach sand into the above cited minerals.

The complete dissolution of ilmenite or leaching out of iron from ilmenite to form synthetic rutile is a very difficult task. Acid leaching (complete or fractional) is not so effective at moderate conditions excepting in hydrofluoric (HF) acid[4]. A thorough study in the dissolution of ilmenite with HF has demonstrated that 5.5 mol·L^{-1} HF at its boiling temperature under an atmospheric pressure can dissolve as much as 81% Ti and 26% Fe presented in ilmenite at solid to liquid (*S/L*) ratio of 0.05 g·mL^{-1} in 300 min. However, this method suffers from inconveniences encountered in HF-handling, considerably long leaching time and too many steps to recover the desired product.

Dilute hydrogen chloride (HCl) is not so effective for ilmenite dissolution[4]. It has been reported that the pressure leaching at 150 ℃ with ~ 12 mol·L^{-1} HCl could leach out iron from ilmenite to get the feed (synthetic rutile) of the chlorination process[5]. Leaching of ilmenite by 6 mol·L^{-1} HCl + 0.5 mol·L^{-1} C$_2$H$_5$OH/ C$_6$H$_5$OH has been thoroughly investigated by Habib et al.[6]. The ethanol mixed reagent could dissolve as much as 88% Ti and 95% Fe; whereas the phenol mixed reagent could dissolve only 81% Ti and 85% Fe in comparison to 74% Ti and 81.5% Fe dissolutions in 6 mol·L^{-1} HCl alone at 110 ℃ and *S/L* = 0.02 kg·L^{-1} in 7 h. The dissolution behaviours of ilmenite from different sources by HCl have been reported by

several workers[7-12]. Moreover, the dissolution of ilmenite on roasting with LPG-pyrolysed products followed by leaching with 6 mol·L^{-1} HCl and 3 mol·L^{-1} H$_2$SO$_4$ has been investigated[13]. At the optimized conditions, 85% Ti and 80.1% Fe dissolutions in 6 mol·L^{-1} HCl; and 52.3% Ti and 60.8% Fe dissolutions in 3 mol·L^{-1} H$_2$SO$_4$ occurred. On the other hand, 93% Ti and 95% Fe dissolutions in 6 mol·L^{-1} HCl could be achieved on roasting ilmenite by reformed product of LPG-H$_2$O mixture in the presence of nickel powder[14].

　　Several reports on mechanical activation of ilmenite followed by acid leaching are available. Baba et al.[15] have reported the mechanical activation of Nigerian ilmenite followed by alkali roasting (60% NaOH at 850 ℃) and H$_2$SO$_4$ leaching (60%, v/v for 4 h at 90 ℃) for 72% Ti-dissolution. Synthetic rutile of 10 ~ 200 nm size with the purity >98% has been prepared from ilmenite following ball milling, carbothermic reduction and HCl-leaching[16]. A new process involving mechanical activation-HCl leaching-conc. H$_2$SO$_4$ decomposition-water leaching-separation of Fe(III) with ethylene diamine tetraacetic acid (EDTA) during hydrolysis has been reported[17] to prepare high purity TiO$_2$ from Panzhihua ilmenite. Zhang et al.[18] have reported the effects of oxidation-reduction treatment and mechanical activation on HCl-leaching performance of Panxi (China) ilmenite. The method consists of (i) oxidation at 900 ℃ in O$_2$ for 15 min, (ii) reduction at 750 ℃ in H$_2$ for 30 min, (iii) ball milling for 2 h under N$_2$ atmosphere, (iv) ambient pressure leaching by 20% HCl for 10 h, (v) filtration and (vi) calcinations of the residue and the product containing 90.5% TiO$_2$, 1.37% Fe, 1% CaO and 1% MgO. The mechanical activations of ilmenite followed by 5 ~ 20% H$_2$SO$_4$ leaching[19] and by HCl leaching[20] have also been reported.

　　Using factorial design, the detrimental effect of pre-oxidation on dissolutions of Fe and Ti from an Iranian ilmenite by HCl leaching has been reported[21]. Panzhihua ilmenite has been leached under pressure with 40wt% H$_2$SO$_4$ at 150 ℃ and acid/ore mass ratio of 2 for 3 h to obtain a mass containing 85% titania[22]. A combined acid and alkali leaching of ilmenite has

been used[23] to synthesize high value TiO$_2$ nanowires. Rod shaped nano-sized titania （80% TiO$_2$) has been reported by double reductive HCl leaching of ilmenite[24]. Janssen and Putnis[25] have reported that the heat treatment of ilmenite at 700 ℃ in air results in the formation of hematite and rutile; and that hematite was less soluble in HCl. El-Hazek et al.[26] have demonstrated that the extent in leaching of 200 mesh ilmenite by 12 mol·L^{-1} HCl at S/L of 1/20 and 80 ℃ for 2.5 h was equal if 0.10 kg Fe as reducing agent was added per kg of ilmenite and S/L of 1/8 being used for 1.5 h.

　　A few works on ilmenite dissolution kinetics by acids are also reported. Sasikumar et al.[27] have reported the dissolution kinetics of Indian Manavalakurichi ilmenite in sulphuric acid (H$_2$SO$_4$) and HCl. According to Gireesh et al.[28] the rate constant for Fe-dissolution from ilmenite by 30% HCl at 700 r·min^{-1} and 70 ℃ was 5.18 × 10^{-3} min^{-1} and this value was increased to 6.15 × 10^{-3} min^{-1} by adding 100 mg gypsum to the system. Zhang and Nicol[29] found the dissolutions of Ti and Fe from ilmenite in moderately strong H$_2$SO$_4$ solutions in the presence and absence of reducing agents such as Ti(III) and SO$_2$. The rate data in the presence of reducing agent has been fitted to shrinking particle model and in the absence of reducing agent to shrinking core model.

　　Consequently, it appears that there is no method for complete dissolution of ilmenite or complete leaching out of Fe from ilmenite. The electrochemical dissolution of Fe from reduced ilmenite has been previously investigated[30-32], and the anodic dissolution of iron and cathodic reduction of oxygen occurred in NH$_4$Cl solution within 30 ~ 150 ℃. Zhang and Nicol[32] have reported the reduction and dissolution of ilmenite in 450 g·L^{-1} H$_2$SO$_4$ medium at an elevated temperature by an electrochemical study (the dissolution of ilmenite occurred at above 0.3 V due to reduction of hematite, while the dissolution processes for reduction of ilmenite to Ti(III) at negative potentials).

　　Ilmenite (p-type semiconductor) possesses electrical conductivities ranging from 0.016 to 0.38 Ω^{-1}·cm^{-1} depending on crystal orientation and hematite con-

tent[33]. Thus electrochemical studies can provide useful information on kinetics and mechanism of ilmenite dissolution. However, limited information is available due to non-availability of pure ilmenite.

As mentioned earlier, the electrical conductivity of ilmenite depends on the hematite content of the sample, and this report discusses the results based on the cyclic voltammetric analysis of Bangladeshi ilmenite concentrate produced by the BAEC pilot plant for heavy mineral exploration centre at Kalatoli, Cox's Bazar.

1　Experimental Procedure

1.1　Materials

Ilmenite fraction was collected from the BAEC pilot plant at Cox's Bazar. According to BAEC, the composition of the received sample was: 38.5% TiO_2, 25.62% Fe_2O_3, 29.75% FeO, 1.2% SiO_2, 0.03% P_2O_5, 1.2% MnO_2 and 1.08% Cr_2O_3. The ilmenite sand was dry-ground and sieved to collect particles of size < 53 μm. Carbon was collected similarly from the waste dry cells. All the other chemicals were of A.R. grade (E. Merck-BDH) products and used without further purification.

1.2　Preparation of Ilmenite Working Electrodes (Pellet)

Working electrodes were prepared as follows: A homogeneous paste was prepared by mixing powders of ilmenite and graphite with liquid paraffin in definite ratios by mass and placed in a steel holder of 3.3 cm in depth and 1.4 cm in diameter. A copper wire (10 cm long) was placed inside the mass of the holder. The holder was then placed in a pellet making machine to form a pellet on applying ~ 40 tons pressure. The pellet was covered by Araldite epoxy resin exposing the working surface area of 1.54 cm². The electrode surface was polished with 2000-grade SiC paper and rinsed with deionized water before each electrochemical measurement.

1.3　Electrochemical Measurements

Electrochemical investigations including potential step chronoamperometry, chronopotentiometry and cyclic voltammetry were carried out using a Hokudo Denko HAB-151 Potentiostat/Galvanostat,

Tokyo, Japan, equipped with a potential sweeper. Data were recorded in a computer through data acquisition system (USA) using WinDaq software. A three electrode system consisting of a working electrode, a platinum (50 mm × 10 mm × 0.1 mm) counter electrode and a AgCl-coated silver wire (dissolved in saturated KCl solution) reference electrode (SSE) was used in all electrochemical studies. The reference electrode was separated from the bulk solution by a fine porosity glass frit. The counter electrode was cleaned electrochemically in 1.5 mol·L⁻¹ H_2SO_4-1.5 mol·L⁻¹ H_3PO_4 mixture, rinsed with deionised water and acetone, and dried prior to use. All potentials in this work are quoted with respect to the Ag|AgCl reference electrode.

1.4　Electrochemical Dissolution of Ilmenite Fraction

Electrochemical dissolution of ilmenite fraction was carried out in 0.30 ~ 3.00 mol·L⁻¹ H_2SO_4 solutions under constant potential methods from -0.40 V to -1.20 V at temperature ranging from 30 to 85 ℃. Following each dissolution experiment, the resultant solution was analysed for Ti(IV) and Fe^{2+}/Fe^{3+} contents. Titanium and iron contents in solutions were analysed colorimetrically using a UV-visible Spectrophotometer (UV-1650 PC, Shimadzu, Japan). In the case of Ti(IV), the H_2SO_4-H_3PO_4-H_2O_2 method at 420 nm was used; whereas Fe(III) was estimated by the NH_4SCN method at 480 nm[35]. The later analysis was carried out without and after HNO_3 oxidation for determining Fe^{2+}/Fe^{3+} contents.

2　Results and Discussion

2.1　Characterization of Ilmenite Fraction by XRD and EDAX

X-ray diffraction analysis has been carried out with a Philips PW 1716 diffractometer using Cu K_α radiation (40 kV, 30 mA, scan speed: 0.01°·s⁻¹) to identify the compounds/phases existing in the ilmenite sample. The acquired diffraction pattern is shown in Fig. 1. The automatching indicates the presences of SiO_2, $FeTiO_3$, Fe_2O_3, TiO_2, (Fe, Mg)Ti_2O_5, Fe_2TiO_5 and $FeCr_2O_4$ in ilmenite. X-ray energy dispersive spectroscope (EDAX) analysis of ilmenite sample has

been carried out with Skyray Instrument Inc., EDX 3600B, UK and the analysis result is shown in Fig. 2. The Fe, Ti, Cr, Mn, Si and Zr were presented in the ilmenite fraction of the beach sand in Bangladesh and among them Fe content was of the highest amount. The EDAX analysis indicated the presence of iron beside its presence in ilmenite. The combined XRD and chemical analyses data indicated that the sample contained about 62.8% $FeTiO_3$, 16.35% Fe_2TiO_5 and 14.72% Fe_2O_3 (as free and also as $FeCr_2O_4$ and (Fe, Mg)Ti_2O_5).

2.2 Cyclic Voltammetric Studies of Pellets Made of Ilmenite-C-Paraffin Mixture in H_2SO_4

The cyclic voltammogram recorded on a pellet electrode made of 2:1:0.1 wt. ratio of ilmenite, carbon and paraffin mixture in 1 mol·L^{-1} H_2SO_4 solution at 30 ℃ with a scan rate of 10 mV·s^{-1} is shown in Fig. 3 as a solid curve. The rest potential was 0.12 V (vs. Ag|AgCl). The scan toward a negative direction (in the second cycle) consisted of the first and second reduction waves C_1 and C_2 with the current densities starting to increase at 0.52 V and -0.40 V, respectively. An additional reduction wave C_3 was observed with the increase of current density starting at -0.75 V. The reverse scan led to the first and second oxidation peaks P_{a1} and P_{a2} at -0.001 V and 0.70 V, respectively. Additional oxidation wave was observed starting at 1.37 V. The first reduction wave C_1 was absent
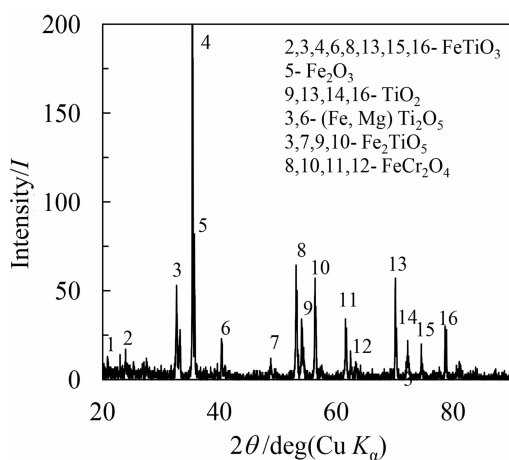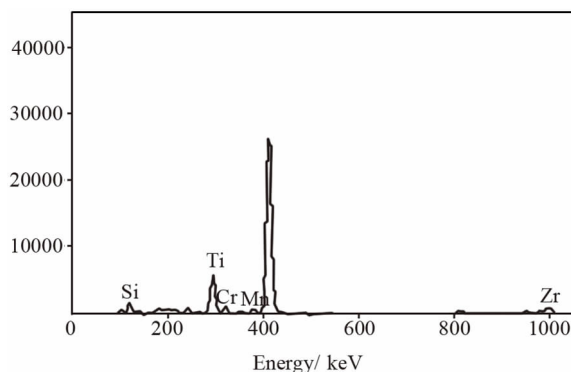

Fig. 2 EDAX profile of the ilmenite fraction

in the forward scan of the first cycle. However, in the first cycle, the magnitude of the current density in the second reduction wave C_2 was the same as that in the second cycle. On the other hand, the magnitudes of current densities in the first and second oxidation peaks (P_{a1} and P_{a2}) were increased in the second cycle.

Compared with the voltammogram obtained in the absence of ilmenite (the dashed curve in Fig. 3), the reduction peak appeared at -0.70 V corresponded to the reduction of H$^+$ in H_2SO_4 solution, while the oxidation peak at 1.35 V to the evolution of O_2 according to the following reactions:

$$2H^+ + 2e \rightarrow H_2\uparrow \quad \text{(at -0.70 V)} \tag{1}$$
$$2H_2O \rightarrow 4H^+ + O_2\uparrow + 4e \quad \text{(at 1.35 V)} \tag{2}$$

The voltammogram in the absence of carbon (the dotted curve in Fig. 3) did not exhitbit any reduction and oxidation waves. This indicated that the reduction of ilmenite was not possible in the absence of carbon due to the very low conductivity of ilmenite. The conductivity of ilmenite was increased by the addition of carbon in pellet. The solid curve in Fig. 3 indicated that the first and second reduction peaks were responsible for the reduction of ilmenite; whereas the first and second oxidation peaks were attributed to the oxidation of the reduced species of ilmenite in this solution.

Fig. 4 shows the effect of cathodic sweeping potential on the cyclic voltammogram recorded on a pellet electrode made of 2:1:0.1 wt. ratio of ilmenite: carbon:paraffin in 1 mol·L^{-1} H_2SO_4 solution at 30 ℃ with a scan rate of 10 mV·s^{-1}. It was readily seen that the first reduction wave C_1 corresponded to the sec-

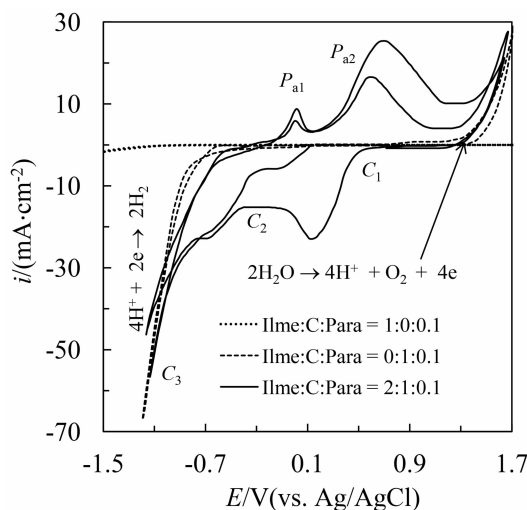Fig. 1 X-ray diffraction pattern of the ilmenite fraction of beach sand in Bangladesh

Fig. 3　Cyclic voltammograms recorded on a pellet electrode made of ilmenite, carbon and paraffin mixture in 1 mol·L^{-1} H$_2$SO$_4$ at 30 ℃ with a scan rate of 10 mV·s^{-1}
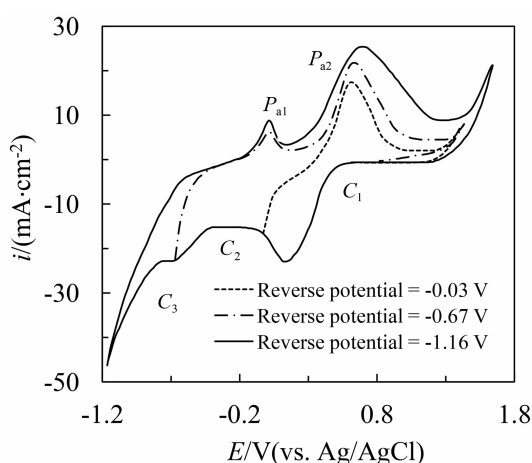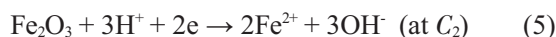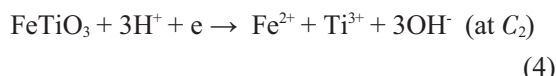

Fig. 4　Effect of sweeping potential on the cyclic voltammograms recorded on a pellet electrode made of ilmenite, carbon and paraffin mixture in 1 mol·L^{-1} H$_2$SO$_4$ at 30 ℃ with a scan rate of 10 mV·s^{-1}

ond oxidation peak P_{a2}. The second reduction wave C_2 corresponded to the both first and second oxidation peaks P_{a1} and P_{a2}. The first cathodic peak at about 0.13 V probably involved the reduction of Fe^{3+} to Fe^{2+} either in solution or in solid phase. The second reduction wave was possibly associated with the reductions of FeTiO$_3$ and Fe$_2$O$_3$ fractions to Ti^{3+} and Fe^{2+}; and furthermore, the first and second oxidation peaks were attributed to the oxidations of Ti^{3+} to Ti^{4+} and Fe^{2+} to Fe^{3+}, respectively, in solution as given below:

$$Fe^{3+} + e \rightarrow Fe^{2+} \quad (at\ C_1) \quad (3)$$
$$FeTiO_3 + 3H^+ + e \rightarrow Fe^{2+} + Ti^{3+} + 3OH^- \ (at\ C_2) \quad (4)$$
$$Fe_2O_3 + 3H^+ + 2e \rightarrow 2Fe^{2+} + 3OH^- \ (at\ C_2) \quad (5)$$
$$Ti^{3+} \rightarrow Ti^{4+} + e \ (at\ P_{a1}) \quad (6)$$
$$Fe^{2+} \rightarrow Fe^{3+} + e \ (at\ P_{a2}) \quad (7)$$

Similar results have been reported by Zhang and Nicol[18] for the electrochemical reduction and dissolution of ilmenite in H$_2$SO$_4$ solution. The dissolved solution obtained at a constant potential dissolution method (-0.80 V) contained Fe^{2+}, Fe^{3+} and Ti^{4+} ions.

The effect of ilmenite:carbon:paraffin ratio in pellets on the cyclic voltammogram (the 2nd cycle) recorded in 1 mol·L^{-1} H$_2$SO$_4$ solution at 30 ℃ with a scan rate of 10 mV·s^{-1} is shown in Fig. 5. It was seen that the current densities of the 1st and 2nd reduction/oxidation peaks were increased with the increase of ilmenite content in the pellets. It indicated that the 2:1:0.1 wt. ratio of ilmenite-C-paraffin mixture in the pellet would give higher dissolution rate of ilmenite fraction by constant potential and constant current methods.

Fig. 6 shows the effect of H$_2$SO$_4$ concentration ([H$_2$SO$_4$]) on the cyclic voltammograms （the 2nd cycle) recorded on a 2:1:0.1 (wt. ratio) ilmenite-C-paraffin mixed electrode at 30 ℃ with a scan rate of 10 mV·s^{-1}. The current densities of the reduction and ox
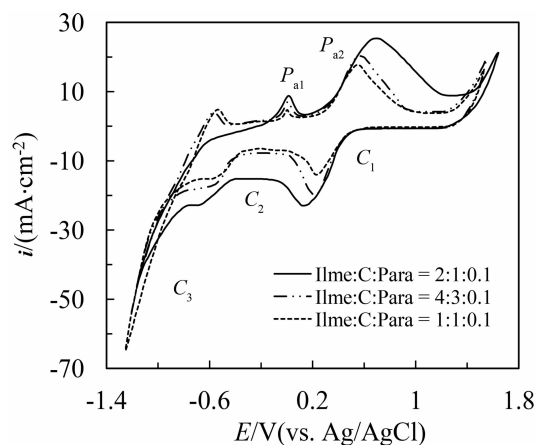

Fig. 5　The second cycle voltammograms recorded on a pellet electrode prepared using different ilmenite, carbon and paraffin mixtures in 1 mol·L^{-1} H$_2$SO$_4$ at 30 ℃ with a scan rate of 10 mV·s^{-1}
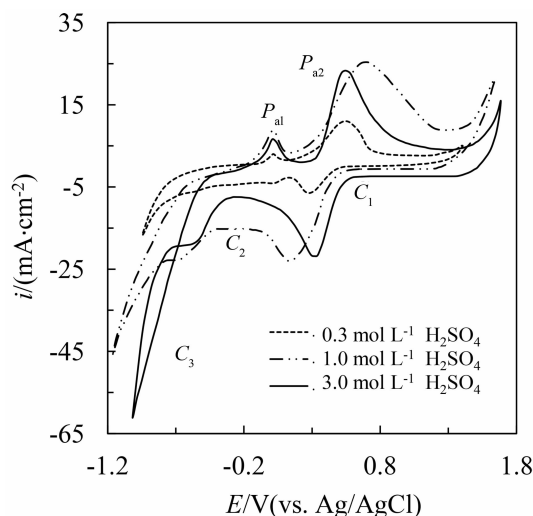
Fig. 6　The second cycle voltammograms recorded on a pellet electrode made of the 2:1:0.1 ratio of lilmenite:carbon:paraffin at 30 ℃ with a scan rate of 10 mV·s^{-1} in different H$_2$SO$_4$ concentrations.

Fig. 7　The second cycle voltammograms recorded on a pellet electrode consisted of the 2:1:0.1 ratio of lilmenite:carbon:paraffin in 1 mol·L^{-1} H$_2$SO$_4$ with a scan rate of 10 mV·s^{-1} at different temperatures

idation peaks in 1 mol·L^{-1} H$_2$SO$_4$ were larger than those in lower (0.3 mol·L^{-1}) and also higher (3 mol·L^{-1}) [H$_2$SO$_4$], which indicated that 1 mol·L^{-1} H$_2$SO$_4$ was suitable to obtain higher dissolution rate.

　　The effect of temperature on cyclic voltammogram (the 2nd cycle) recorded on a 2:1:0.1 (wt. ratio) ilmenite-C-paraffin mixed electrode in 1 mol·L^{-1} H$_2$SO$_4$ with a scan rate of 10 mV·s^{-1} is shown in Fig. 7. The current densities of the reduction and oxidation peaks were increased with the rise of temperature. It was, therefore, concluded that higher dissolution rate could be obtained from 2:1:0.1 (wt. ratio) ilmenite-C-paraffin mixed electrode in 1 mol·L^{-1} H$_2$SO$_4$ at 80 ℃.

2.3　Electrochemical Dissolution Study

　　Variation of ilmenite dissolution rate with time in 1 mol·L^{-1} H$_2$SO$_4$ at 80 ℃ from the 2:1:0.1 (wt. ratio) ilmenite-C-paraffin mixed pellet under constant potential method are shown in Fig. 8. The dissolution potentials were -0.80 V and -0.60 V (vs. Ag|AgCl). Initially, the dissolution rate of ilmenite fraction was sharply decreased with the increase of time up to 1 h and then slightly decreased afterwards. The dissolution rate of iron was about 5 times faster than that of titanium at both the applied dissolution potentials at a fixed time. Therefore, the dissolution time of 1 h has been select-
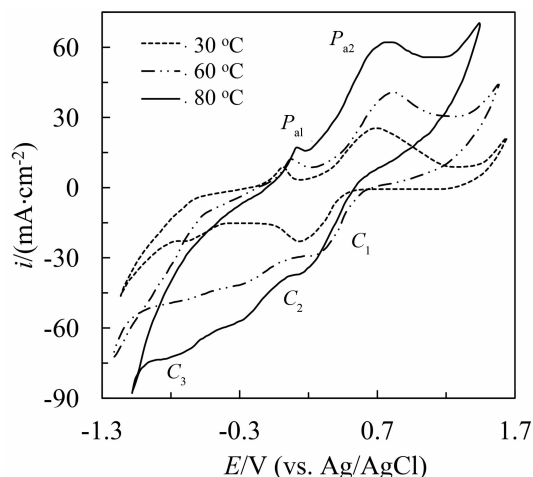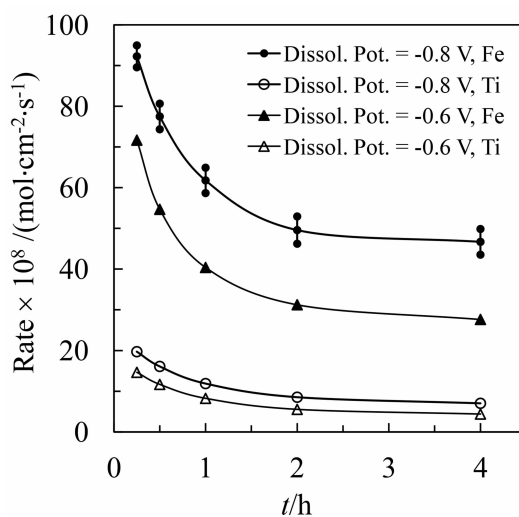

Fig. 8　Dissolution rates of iron and titanium as a function of time for a pellet consisted of the 2:1:0.1 wt. ratio of ilmenite:carbon: paraffin in 1 mol·L^{-1} H$_2$SO$_4$ at 30 ℃ and applied dissolution potential of -0.6 V or -0.8 V

ed in the subsequent electrochemical studies.

　　Fig. 9 shows the effect of temperature on the dissolution rate of ilmenite in 1 mol·L^{-1} H$_2$SO$_4$ from the 2:1:0.1 ilmenite-C-paraffin mixed pellets at different applied potentials. The dissolutions of ilmenite have been carried out in the potential range of -0.20 V to -1.0 V and the temperature range of 30 ℃ to 80 ℃. At the constant potential, the dissolution rate in-
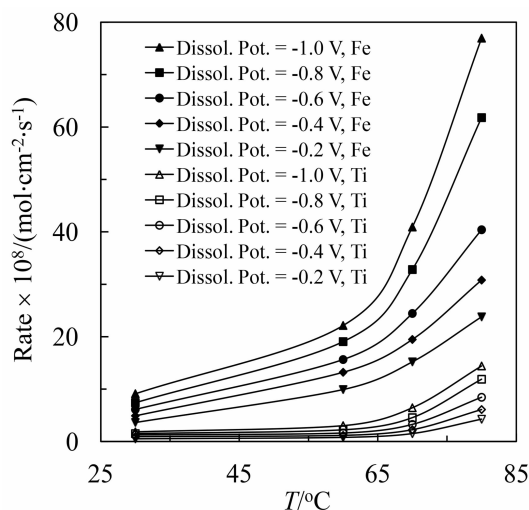
Fig. 9　Effect of temperature on the dissolution rates of iron and titanium for a pellet consisted of the 2:1:0.1 wt. ratio of ilmenite:carbon:paraffin in 1 mol·L^{-1} H$_2$SO$_4$ at different applied dissolution potentials

creased with the increase of temperature. The increasing rate became slow up to 60 ℃ and then sharply increased with the rise of temperature. The ratio of the iron dissolution rate to titanium dissolution rate at all applied dissolution potentials and temperatures was about 5.0.

　　The effect of H$_2$SO$_4$ concentration on the dissolution rate of ilmenite fraction at 80 ℃ from the 2:1:0.1 ilmenite-C-paraffin mixed pellets under constant potentials are shown in Fig. 10. At low applied reduction potentials (-0.20 V ~ -0.40 V), the dissolution rate was first increased up to 1 mol·L^{-1} H$_2$SO$_4$ solution and then the increasing rate was significantly slow with the rise of acid concentration. However, at more negative applied reduction potentials (> -0.40 V), the dissolution rate was first sharply increased up to 1 mol·L^{-1} H$_2$SO$_4$ solution and then decreased appreciably with the rise of acid concentration. At higher H$_2$SO$_4$ acid concentrations (> 1.0 mol·L^{-1}) and more negative applied reduction potentials (< -0.60 V), the dissolution rate of ilmenite fraction was decreased due to the starting of H$_2$ gas evolution which eventually reduced the active surface area of ilmenite pellet by adsorption.

　　The Arrhenius plots for the dissolution rate of

ilmenite fraction (lg$v$ vs. 1/T) at various dissolution potentials are shown in Fig. 11. It is evidently that the experimental data did not fall on a straight line; rather a curve was obtained. The slopes of the tangential lines at higher temperature region yielded the activation energy (E_a) of 50 ± 10 kJ·mol·L^1 and those at lower temperature region the E_a of ~15± 5 kJ·mol^{-1}. The values of E_a suggested the existence of a diffusion film which was destroyed at higher temperature. At lower temperature region, the process was diffu-
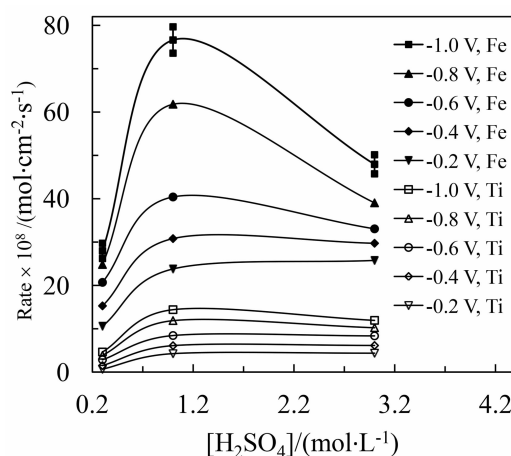

Fig. 10　Effect of H$_2$SO$_4$ concentration on the dissolution rates of iron and titanium for a pellet consisted of the 2:1:0.1 wt. ratio of ilmenite:carbon:paraffin at 80 ℃
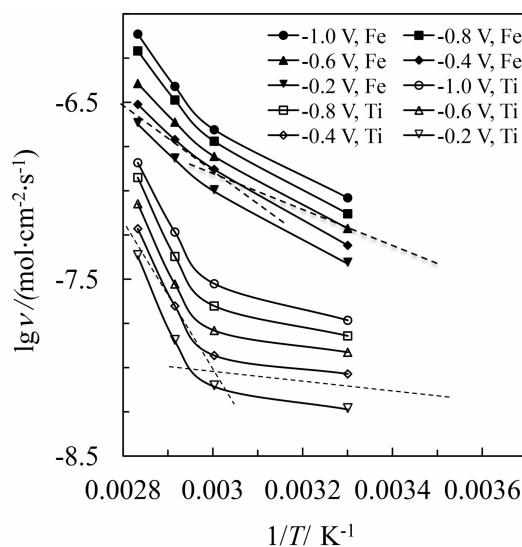

Fig. 11　Arrhenius plot: lg$v$ vs. inverse of absolute temperature (1/T) at various dissolution potentials. Ilmenite: carbon:paraffin = 2:1:0.1 and [H$_2$SO$_4$] = 1 mol·L^{-1}.

sion controlled and with the rise of temperature, the process became chemically controlled.

3 Conclusions

The dissolution of ilmenite fraction could not be obtained in H_2SO_4 solution without the addition of carbon due to the low conductivity of ilmenite fraction. The dissolution rates of ilmenite ($FeTiO_3$) and hematite (Fe_2O_3) were slow at low applied reduction potentials (< -0.40 V) and temperatures (< 60 ℃). At more negative potentials and higher temperatures, the dissolution rate of ilmenite was increased through the increasing rate in the reductions of ilmenite to Fe^{2+} and Ti^{3+}. The dissolution rate was also increased with the increasing acid concentrations up to 1 mol·L^{-1}. At higher acid concentrations and higher reduction potentials, the dissolution rate was decreased due to the starting of H_2 gas evolution which eventually reduced the active surface area of ilmenite pellet by adsorption. The hematite phase in the mineral had a higher dissolution rate than the ilmenite under reductive conditions. The values of E_a in the higher and lower temperature regions are 50 ± 10 kJ·mol·L^{-1} and ~ 15 ± 5 kJ·mol^{-1}, respectively, suggesting the existence of a diffusion film at lower temperature which was destroyed at higher temperatures. At lower temperature region, the process was diffusion controlled, and with the rise of temperature the process became chemically controlled.

Acknowledgement

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海沙钛铁矿在硫酸溶液中的电化学溶解研究

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摘要：采用电化学技术研究了孟加拉国海沙里钛铁矿在硫酸溶液中不同温度下的溶解行为. 循环伏安研究表明，在没有添加碳粉的条件下钛铁矿的溶解非常困难. 为探明钛铁矿的溶解过程，考察了钛铁矿-碳比例、硫酸浓度和温度对钛铁矿电化学溶解行为的影响. 结果显示，钛铁矿在低还原电位和低温下的溶解速率较慢. 施加更负的还原电位和在较高的温度下溶解速率加快. 增加硫酸浓度(最大浓度达到 1 mol·L⁻¹)也可提高溶解速率，但在较高的硫酸浓度和还原电位下，由于氢气析出导致钛铁矿的溶解速率降低且气体吸附，最后使得钛铁矿的活性表面积减小. 计算得到活化能数值在高温区间为 50 ± 10 kJ·mol⁻¹，而低温区间为 ~ 15 ± 5 kJ·mol⁻¹，说明低温区间为扩散控制过程，而高温区间为化学控制过程.

关键词：钛铁矿；循环伏安；电化学溶解；活化能；硫酸