



Electrochemical investigation on steel corrosion in iron-rich clay



Maocheng Yan*, Cheng Sun, Junhua Dong, Jin Xu, Wei Ke

Environmental Corrosion Center, Institute of Metal Research, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110016, China

ARTICLE INFO

Article history:

Received 22 October 2014

Accepted 16 April 2015

Available online 22 April 2015

Keywords:

A. Carbon steel

B. EIS

C. Acid corrosion

C. Kinetic parameters

ABSTRACT

The iron-rich clay mineral, such as the red soil, is found corrosive toward pipeline steel, which may partly attribute to the active Fe oxide constituents residing in the clay. Surface charge and electrokinetic properties of the red clay mineral were characterized and related to corrosion behavior of X80 steel in the soil. Results show that surface charge of the Fe-rich clay mineral is variable according to pH. Active clay minerals, especially Fe oxides, distinctly influence corrosion process of the steel. The dynamic redox cycle of Fe oxides promotes and sustains corrosion of the steel in contact with iron-rich clay environments.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

It is generally accepted that the presence of rust layer (Fe oxides) has significant influences on further corrosion of iron and steel. Various forms of Fe oxide corrosion products of iron or steel, especially ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), akaganeite ($\beta\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$), are electrochemically reactive and their redox behavior has potential for affecting atmospheric corrosion process of iron [1–4]. It has been widely accepted that reduction of Fe oxides participates in cathodic process, which generally demonstrates that Fe oxides do not suppress corrosion through shielding the steel surface from the corrosive environment but promote the corrosion process, especially during the initial stage. Except in atmospheric corrosion, phenomena so-called “Fe oxides facilitating corrosion” has also been reported in many other environments, such as in water or seawater [5,6] and in concrete [4,7].

In these researches, Fe oxides involved are corrosion products (rusts) pre-formed during corrosion. Meanwhile, Fe oxides are abundant in many nature sediments or minerals, like iron ores, soils and coals. Nature Fe oxides are redox active and play important roles in geological and biological processes. As contact with iron or steel, they should have potential for influencing or even altering corrosion behavior of metals. However, in most cases relating to nature Fe-rich environments, the presence of Fe oxides and their potential influence on corrosion have been neglected. For instance, it was reported that steel structures undergo severe corrosion attack in contact with iron ore or coal [8,9]. The mechanism

of Fe oxides promoting corrosion may have involved in these cases. However, such a mechanism has never been proposed or considered explicitly. In this work, we focus on the phenomena of “nature Fe oxide mineral facilitating steel corrosion”, and take the red clay soil as an example of Fe-rich materials or environments.

Red clay soils develop from a natural acidification process including intensive weathering and leaching favored by abundant precipitation and good drainage under warm, humid climate condition [10]. During this process, various soluble basic cations, such as Ca^{2+} , Mg^{2+} and K^+ , are washed away; whereas insoluble Fe oxides (from decomposition of original mineral) tend to accumulate on surfaces of fine clay minerals. This special soil forming process results in various inherent properties of the soil, such as low pH, relatively low ion contents and high resistivity [11].

The role of Fe oxides on metallic corrosion has been highlighted in our investigations. In a previous report, we observed that corrosion process of carbon steel tends to be facilitated by electrochemical active Fe oxides in the red soil [12]. However, so far very limited information is available on the electrochemical interaction between Fe oxides and steel.

Secondary clay mineral (soil particles less than $2\ \mu\text{m}$) is the colloidal size fraction of soils. Clay minerals generally possess a considerable amount of reactive surface sites and dominate a series of physicochemical natures of the bulk soil. Electrokinetic properties, including zeta potential (ζ), surface charge density and point of zero charge, are most important aspects of colloidal properties of clay minerals. ζ is the electric potential in the interfacial double layer at the slipping plane relative to a point in the bulk fluid. The point of zero charge (or called isoelectric point, pH_{PZC}) is regarded as the pH where $\zeta = 0$ [13].

* Corresponding author. Tel.: +86 24 2391 3195; fax: +86 24 2389 4149.
E-mail address: Yanmc@imr.ac.cn (M. Yan).

In the present work, electrokinetic properties of the colloidal fraction of the Fe-rich clay separated from a red soil and the corresponding soil with Fe oxide removed, as well as their corrosivity, were investigated. Special attention was given to the influence of electrokinetic property of clay minerals on electrochemical and corrosion process of API X80 pipeline steel in contact with the soil colloids. A possible mechanism of “soil Fe oxides facilitating corrosion” was proposed for the steel.

2. Experimental

2.1. Soil sample and treatment

The red soil was collected at Red Soil Ecological Experiment Station (28°15'20"N, 116°55'30"E) in Yingtan, China. The soil at this site is representative of red soils in Southern China. The sampled soil was taken at 1.2 m underground of a virgin area in nature state without any indication of pollution. The soil sample was sealed in airtight plastic bags and sent to laboratory for analysis. The moisture value of the soil at 1.2 m depth is about 29 wt% (dry weight basis). The red soil has the clay content (clay fraction of less than 2 μm) as high as 50 wt%. Some physicochemical properties and chemical compositions of the soil are given in Table 1. The soil was air-dried and ground to pass through a 16-mesh sieve before use.

A part of the soil sample was treated by a sodium citrate buffer (0.3 M sodium citrate + 0.05 M citric acid) containing 0.14 M sodium dithionite to remove Fe oxides in the soil [14,15], and the obtained soil was identified as the Fe-free soil. During the treatment, selective dissolution and removal of Fe oxides can be recognized as the typical red color of the soil changing to gray of the matrix minerals [16]. After the treatment, contaminant ions were removed by centrifugal separation. The detailed procedure of the treatment can be found in Ref. [12].

To study electrophoretic properties of a pure Fe oxide, goethite was synthesized following the procedure reported by Atkinson et al. [17]. NaOH solution (0.1 M) was dropped slowly into 0.5 M $\text{Fe}(\text{NO}_3)_3$ solution under stirring, adjusting pH to 12. The resultant product was collected and aged for 24 h at 60 °C. The synthetic goethite was electrolyzed and dried at 60 °C.

The clay mineral (clay fraction of less than 2 μm) was separated from the soil by a sedimentation procedure based on Stokes' law. The soil suspension was agitated and colloid particles in the upper portion of the suspension were collected at fixed intervals.

Table 1
Physicochemical properties of the Fe-rich red soil collected at Yingtan, Southern China.

Soil type	Ultisol
Organic matter ^a (wt%)	0.37
Total nitrogen (wt%)	0.025
pH (soil water ratio 1:2.5)	3.95
Total salt (wt%)	0.0042
Free Fe_2O_3 ^b g/kg	49
Exchangeable acid (cmol/kg)	3.93
Conductivity (soil water ratio 1:0.5) (mS/cm)	0.018
Conductivity of soil solution (mS/cm) (soil water ratio 1:5)	0.011
<i>Ionic composition (wt%)</i>	
NO_3^-	0.0006
Cl^-	0.0007
SO_4^{2-}	0.001
HCO_3^-	0.0011
Ca^{2+}	0.0004
Mg^{2+}	0.0002
K^+	0.0001
Na^+	0.0001

^a Organic matter, determined by dichromate method.

^b Determined by the dithionite–citrate–bicarbonate (DCB) method.

2.2. XRD and Mössbauer characterization

The Fe-rich clay separated from the red soil was analyzed by X-ray diffraction (XRD) and Mössbauer spectroscopy. XRD was conducted by a diffractometer (Rigaku D/max-2500/pc, Japan) equipped with a graphite diffracted beam monochromator using $\text{Cu K}\alpha$ radiation.

Mössbauer spectra were recorded at room temperature by a spectrometer with a proportional counter. $^{57}\text{Co}(\text{Rh})$ moving in a constant acceleration mode was used as the radioactive source. The Doppler velocity of the spectrometer was calibrated with respect to $\alpha\text{-Fe}$ foil. Samples were protected in Ar atmosphere during Mössbauer measurement. The spectra were fitted to a Lorentzian shape with a least-squares fitting procedure. In this way, Mössbauer parameters, such as the isomer shift (I.S.), the electric quadrupole splitting (Q.S.), the effective internal magnetic field (H_{eff}) and the relative areas of different Fe components, were determined.

2.3. Electrophoretic mobility measurement

Zeta potential of colloidal clay minerals was measured by a JS94H+ microelectrophoresis apparatus (Shanghai Huachen, China) following the procedure reported by Hou and Xu [18]. The suspension containing 2% clay particles in a dilute NaCl solution (0.001 M) as background electrolyte was dispersed ultrasonically at 40 kHz (300 W) for 30 min. The pH of the suspension was adjusted with HCl or NaOH solution to a desired value, and the suspension was kept standing for 1 h before measurement. For zeta potential measurement, the suspension was transferred to an electrophoresis vessel, in which migration of colloidal particles in 0.001 M NaCl solution under a potential gradient of 10 V cm^{-1} was monitored by a video system (40 \times). The electrophoretic velocity was obtained by timing 10 particles, first in one direction and then in the opposite direction by reversing the applied electrical field. Zeta potential was calculated based on Helmholtz–Smoluchowski equation.

2.4. Exposure test and electrochemical measurement

The test material was API X80 steel with composition as follows (wt%): C 0.07, Mn 1.82, Si 0.19, P 0.007, S 0.023, Cr 0.026, Ni 0.17, Cu 0.020, Al 0.028, Mo 0.23, Ti 0.012, Nb 0.056, V 0.002, N 0.004, B 0.0001, Fe balance. Coupons used for electrochemical measurements were embedded in epoxy resin to give a working area of 10 mm \times 10 mm. Coupons for weight loss test were in size of 25 mm \times 25 mm \times 3 mm. All working surfaces were abraded with SiC paper (from 400 to 1000 grit) followed by cleaning in acetone and alcohol and then air dried.

The soil exposure test and electrochemical measurement were performed in a cylindrical PMMA cell containing ca 2 kg water-saturated soil. Coupons were buried at 20 cm beneath the soil surface. The water-saturated condition was used based on the following considerations: First, in the water-saturated condition, dissolved O_2 in the sticky soil tends to be depleted quickly and O_2 diffusion through the soil is extremely slow [19], and hence the effect of dissolved O_2 can be neglected; Second, the water-holding capacity varies and hence the moisture state may be different for different soils with the same soil water content, and this can be avoided if both soils are saturated.

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were measured by an EG&G Parstat 2273 potentiostat using a traditional three-electrode system. The steel sample mounted in epoxy resin with an exposure area of 1.0 cm^2 was used as the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode (RE) and a graphite plate

Download English Version:

<https://daneshyari.com/en/article/7895277>

Download Persian Version:

<https://daneshyari.com/article/7895277>

[Daneshyari.com](https://daneshyari.com)