

KINETICS OF ELECTROCHEMICAL REDUCTIVE DISSOLUTION OF IRON(III) HYDROXY-OXIDES

Tomas GRYGAR

*Institute of Inorganic Chemistry,**Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic*

Received October 27, 1994

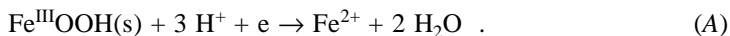
Accepted May 15, 1995

Abrasive stripping voltammetry was applied to the chronoamperometric and voltammetric investigation of the kinetics of reductive dissolution of synthetic and natural iron(III) hydroxy-oxides. Conditions were found under which the dissolution process can be described by equations derived for and applied to the surface reaction of the particles. The rate constants obtained were employed to compare the electrochemical and chemical reductive dissolution and to quantitatively evaluate the effect of adsorbing ions, pH, and working electrode potential.

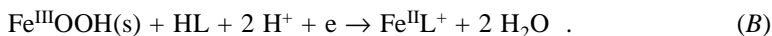
Reductive dissolution of iron(III) hydroxy-oxides is a phase-selective process, employed in the synthesis (separation of ferrihydrite or generally amorphous phases from synthetic goethite¹) and characterization of phases occurring in sediments and soils^{2,3}. Understanding the nature of this process is of importance for gaining insight into the cycle of iron and ions bound to Fe and Mn hydroxy-oxide particles, as well as for redox processes of organic substances, particularly in natural waters²⁻⁵. Use of the process to characterize synthetic hydroxy-oxides has found less extensive application, although its potential in this field is quite large. The complexity of the process actually poses problems: the rate of reductive dissolution of hydroxy-oxides is affected by the particle size and shape distribution, phase distribution, as well as by the dissolution system parameters such as the concentration of complexing and reducing substances, pH, and the many adsorbing ion species³⁻⁵.

The problems of the reductive dissolution can be classified into two categories: those of the process chemistry (interaction of ions, charge transfer) and those of the mechanical aspects (particle size and shape distribution).

The chemical reaction of dissolution of FeOOH giving rise to Fe²⁺ ions is generally described by the equation



In the presence of a complexant HL (or L⁻), the reaction is



Protonation or addition of a complexant precedes the charge transfer process, and only subsequently there follows removal of Fe^{II} from the FeOOH surface, hence, formation of Fe²⁺(aq) ions and their diffusion away⁴. Presumably, in dependence on the dissolution conditions, the reaction rate may be limited by protonation of FeOOH, charge transfer, and diffusion of Fe²⁺ away from the surface. In slightly acidic solutions containing a reductant such as ascorbic acid or sulfane, the formation of the Fe²⁺(aq) ion is the slowest step⁴. The FeOOH protonation equilibrium shifts in the presence of a ligand and/or other adsorbing ions. Chemical methods which are conventionally used in dissolution studies fail to discriminate the charge transfer reaction on its own.

The effect of the particle size and shape on the dissolution rate has been studied for the simple dissolution of calcium sulfate⁶ and hydroxyapatite⁷, and also for ferrihydrite in a reducing medium³. General kinetic equations of a particle surface reaction have been derived and tested in the form

$$J = -dn/dt = -k N_0 G(c)F(N_r/N_0) \quad (\text{I})$$

where $F(N_r/N_0)$ is the dependence of reactivity on the reactant particle size and shape distribution; for instance, the proportionality of $F(N_r/N_0)$ to the $(N_r/N_0)^s$ ratio has been experimentally verified. $G(c)$ is a function of the solution composition; if diffusion is the controlling phenomenon or if simple dissolution is involved, $G(c)$ can be a function of "solution unsaturation", as derived by Nernst, viz. $G = c_s - c$, where c_s is the concentration of the saturated solution of the product in the solution bulk and c is the actual concentration. For reductive dissolution this function is dependent on the concentrations of all reactants and on the adsorptive capacity of the substance, and if the reaction is conducted so that the solution composition at the surface of the solid particles does not change in time, the $G(c)$ function can be included in the constant k (ref.³). The reaction then can be regarded as one of the pseudo-first order, the dimension of the constant k being s⁻¹. This constant is typical of the phase, solution, and particle nature.

Electrochemical reduction of Fe(III) to Fe(II) in iron(III) hydroxy-oxides has been studied by many authors⁸⁻¹⁰. To our knowledge, electrochemical reductive dissolution has never been employed to analytically characterize the Fe(III) hydroxy-oxides or to compare the process with the chemical reduction.

In principle, two experimental approaches can be used for the electrochemical investigation of reactions of solid particles in aqueous solutions: the active paste method,

where the substance studied is mixed with graphite powder and a liquid binder^{8,9,11}, and the method where the solid sample is applied to an inert electrode, known as abrasive stripping voltammetry^{12,13} (AbrSV). Since the present work was conducted with a view to achieving a complete and irreversible analyte conversion on the electrode, as in chemical reductive procedures, the latter method was applied.

EXPERIMENTAL

Fe Oxides and Hydroxy-Oxides

Ferrihydrites were prepared by reacting $\text{Fe}(\text{NO}_3)_3$ with an alkali hydroxide at a constant pH (ref.¹⁴), viz. pH 3.9 for sample A and pH 7.3 for sample B.

Goethite (α - FeOOH) samples were prepared by transformation of ferrihydrite in a strongly basic solution at 20 °C (A), 60 °C (B), and 70 °C (C) following Schwertmann and Cornell¹, and by oxidation of Fe^{2+} in acid solutions (samples D and E). In addition, the commercial chemicals Bayer 920 (Bayer, Germany) (sample F) and SCP21 (Société Chimique de Provence, France) (sample G) were used. Phase purity of the samples was checked by Moessbauer spectroscopy at room temperature (min. 98%).

β - FeOOH was prepared by hydrolysis of FeCl_2 solution¹⁵, γ - FeOOH was obtained by oxidation of FeSO_4 in solution¹⁶, and δ - FeOOH and Fe_3O_4 were synthesized by oxidation of $\text{Fe}(\text{II})$ with H_2O_2 or KNO_3 (ref.¹).

Iron(III) oxides were commercial chemicals: Bayer 130 HB α - Fe_2O_3 (Bayer, Germany) and SCP21 γ - Fe_2O_3 (Société Chimique de Provence, France).

Natural sediments were represented by the Buffalo River Sediment (NIST, U.S.A.; certified total Fe content 4.11%) and the SL1 Lake Sediment (IAEA; certified total Fe content 6.74%). The samples served as examples of reaction continua with a phase composition which is not completely defined and with a considerable heterogeneity of the Fe hydroxy-oxide particles. In view of the sample treatment procedure it is possible that if the starting sediment contained amorphous hydroxide phases, a part at least can have transformed into more stable crystalline compounds.

The samples were characterized by their X-ray powder diffraction patterns (DRON 2.0, Burevestnik, U.S.S.R., equipped with a $\text{CoK}\alpha$ source and an Fe filter) and Moessbauer spectra (a KFKI 512-channel instrument, Hungary). The appearance of the samples was evaluated from their TEM photographs (a Tesla BS 242 E instrument, Czechoslovakia, with a 60 kV supply), and their specific surface area was determined by adsorption/desorption measurements using an $\text{H}_2 + \text{N}_2$ mixture.

Prior to their application to the electrode, the pure synthetic samples were ground in an agate mortar in the presence of a tenfold excess of silica gel (chromatography grade, Merck, Germany) so as to lower the probability of a mechanical contact of the reacting particles which complicates the course of the dissolution process. This hazard is particularly high for goethite, which is prone to agglomeration, a phenomenon that is beyond the scope of this study.

The voltammetric and chronoamperometric measurements of reduction of $\text{Fe}^{3+}(\text{aq})$ were performed with a solution of $\text{Fe}(\text{NO}_3)_3$ at a concentration of 1 mmol l^{-1} in the supporting electrolyte of choice.

Supporting Electrolytes for Electrochemical Measurements

The following buffers were used at concentrations of 0.05–0.2 mol l^{-1} : Sodium trichloroacetate–trichloroacetic acid (pH 1.6), potassium oxalate–oxalic acid (pH 2.5), potassium dihydrogen phosphate–phosphoric acid (pH 2.6), sodium chloroacetate–chloroacetic acid (pH 2.7), a mixture of acetate and chloroacetate buffers (pH 3.7), potassium hydrogen phthalate (pH 4.0), and sodium acetate–acetic

acid (pH 4.7). Reagent grade chemicals supplied by Lachema, Czech Republic, and Merck, Germany, were used for their preparation.

Electrochemical Measurements

Voltammetric and chronoamperometric measurements were performed with a PA-4 polarograph interfaced to a TZ-4620 recorder and an XY-4106 plotter (Laboratorni pristroje Praha, Czech Republic). Unstirred solutions were measured in vessels where the anode compartment was separated by a frit. The working electrode was prepared by vacuum impregnation of spectral graphite rods (Elektrokarbon Topolcany, Slovak Republic) with molten paraffin (m.p. 54–55 °C, Paramo Pardubice, Czech Republic) (PIGE). A saturated calomel electrode (SCE) served as the reference electrode, relative to which all potentials are reported in this paper. The working electrode surface was restored by polishing with a paste based on silicone oil and Si and Cr oxides. The samples were applied by rubbing the electrode vigorously against a suitable amount of sample mixtures with silica gel on a filter paper; loose particles were removed from the electrode surface by wiping with a cotton pad. The total charge for the sample reduction corresponded to an amount of $1 \cdot 10^{-7} - 2 \cdot 10^{-6}$ g, in dependence on the nature of the particles. It can be calculated that, given this quantity and the specific surface area concerned, the electrode coverage would be on the order of tens or units per cent if the particles were ideally dispersed over the surface.

RESULTS AND DISCUSSION

Effect of Conditions on the Electrochemical Reduction Rate

In the AbrSV mode, iron(III) hydroxy-oxides can be reductively dissolved from the working carbon electrode in a slightly acid medium at potentials that are to certain extent typical of the phase involved.

In dependence on the reaction conditions and on the sample nature, the sample can be completely converted on the working electrode in a time as short as a few minutes. Hence, the reaction rate is several orders of magnitude higher than during the acid reductive dissolution of the substances in solution, for which reaction periods as long as several hours have been reported³⁻⁵. If information about the particle properties is to be gained, the reaction conditions must be chosen such that the reaction rate is not governed by the velocity of reactant diffusion to the electrode. This requirement is equivalent to that of the $G(c)$ function in Eq. (1) being constant.

We found that exponential equations in the general form

$$I = a^* \exp(-bt) \quad , \quad (2)$$

derived for electrochemical reactions of solids (for the method and meaning of coefficients see refs^{11,17}), are not always well suited to the description of the chronoamperometric curves of the surface reaction. This is so because the reaction rate-determining variable involves more factors than merely the absolute amount of the substance (par-

ticle concentration in the active paste¹¹ or degree of coverage of the electrode surface¹⁷); in fact, the distribution of particle size plays a role as well. Equations of the type (2) are inapplicable if the reacting system of particles is too heterogeneous (see later). Hence, it is reasonable to apply Eq. (1), derived from a more general formulation of the reaction rate as a function of the reactant conversion. Modification of Eq. (1) gives

$$I = k Q_0 G(c) F(Q_t/Q_0) . \quad (3)$$

In agreement with the literature^{3,6,7} we found that in suitable conditions of dissolution of iron(III) hydroxy-oxides, function F in Eq. (3) can be regarded as proportional to a power of the unreacted-to-total amount ratio of the substance, and that the total amount of the substance and the constant factors (solution composition, electrode potential) can all be included in the constant k . The requirement of a constant solution composition at the reacting surface³ can be formulated as one of a sufficiently low reaction rate in comparison with the diffusion of the involved ions. Equation (3) then simplifies to

$$I = k Q_0 (Q_t/Q_0)^g . \quad (4)$$

The constant g has been interpreted by Postma³ as a factor characterizing a certain heterogeneity of the system: the more diverse the set of particles is (from the reactivity point of view), the higher the g value. In fact, Eq. (2) is only applicable if g approaches 1. It can be shown that this is not true of a set possessing a lognormal particle size distribution, to say nothing about a reaction continuum; it is Eq. (1) that actually describes their properties.

The applicability of Eq. (4) to the description of the chronoamperometric curves was verified for the dissolution of α -Fe₂O₃, α -FeOOH, γ -Fe₂O₃, γ -FeOOH, and Fe₃O₄ in a noncomplexing slightly acidic supporting electrolyte. If a complexing electrolyte is used, the behaviour of ferrihydrite, ammonium jarosite, and β -FeOOH can be described likewise. In some instances, positive deviations of the observed and approximated values were found at the beginning and at the end of the reaction. Equation (4) was employed if it was valid for the dissolution of the substance over a region of at least 10–90% of its total reacting amount.

Figure 1 shows the observed dependence of the rate constant of dissolution of goethite (C), ferrihydrite (A), and hematite on the working electrode potential. The linear dependence of the rate constant logarithm on the potential demonstrates that the charge transfer rather than the reactant diffusion is the rate determining step over the potential region used; the rate constant in Eq. (4) can be written as

$$k = k_0 \exp [-\alpha n F (E - E_0) / RT] \quad (5)$$

The observed charge transfer coefficients α are given in Table I.

Figure 2 shows the rate constants of dissolution of goethite (C) and ferrihydrite (A) in dependence on the pH of the supporting electrolytes, which were 0.05–0.2 M phthalate and chloroacetate buffers and dilute HNO₃. The rate constant logarithm vs pH plots possess sigmoid shapes, which indicates that, as suggested in the literature^{4,5}, the surface protonation products, which predominate at pH values lower than that of the zero charge of the surface, are the reduced species. In dependence on the kind of phase, the surface is neutral at pH 4–9 (ref.¹⁸).

The electrode reaction is accelerated appreciably by the presence of some ions in the supporting electrolyte (see Table II and Fig. 1). The mechanism of the effect of ions on the chemical reductive dissolution of Fe hydroxy-oxides has been presented by Biber and coworkers⁵. In general, the dissolution process is affected by all chemisorbing ions, from among which phosphate and sulfate and, to a lesser extent, borate, silicate and chloride are significant^{4,5,18}.

The presence of chemisorbing ions increases the rate of the electrochemical reduction of goethite (Table II), hematite, as well as ferrihydrite. This is demonstrated both by the increasing rate constants and by the anodic shifts of the voltammetric peaks. In this respect, there is a difference between the chemical and electrochemical dissolution: while during the chemical reduction of goethite with sulfane at a pressure of 100 Pa in a slightly acid solution, phosphate inhibits the reaction⁵ at a concentration as low as 10⁻³ mol l⁻¹, the rate of reaction of goethite during the electrochemical reduction

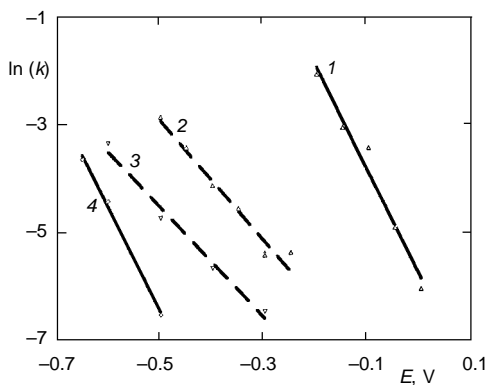


FIG. 1

Dependence of the logarithm of the electrochemical dissolution rate constant k on the working electrode potential E for ferrihydrite (A), goethite (C), and hematite. Curves: 1 ferrihydrite, 0.05 M chloroacetate; 2 goethite, 0.2 M chloroacetate + 0.5 M KCl; 3 goethite, 0.05 M chloroacetate; 4 hematite, 0.2 M chloroacetate

at pH 2.7, $E = -0.4$ V, is nearly an order of magnitude higher in the presence of 0.01 M phosphate. In the presence of 0.1 M sulfate or phosphate, the hematite reaction rate is also several times higher. Presumably, the chemisorbed ions facilitate the detachment of the Fe^{n+} ion from the hydroxy-oxide surface by weakening its bonding in the solid phase while posing no hindrance to the electrochemical reduction, which is not conditional on the simultaneous sorption of the reducing ion as in the chemical reaction. With respect to the rate-increasing effect on the reductive electrochemical dissolution of goethite, the ions examined can be arranged in the following descending order: phosphate > sulfate > oxalate > chloride > nitrate = chloroacetate.

Along with the increasing reaction rate constant of the electrochemical reduction due to the effect of sulfate and phosphate, the geometric factor g increases as well and the shape of the dissolution curve described by Eq. (4) distorts; the current behaviour, however, does not obey Cottrell's equation. On the contrary, if the reduction is con-

TABLE I

Observed charge transfer coefficients α for the electrochemical reduction of ferrihydrite, goethite, and hematite in a chloroacetate buffer solution

Phase (sample)	E , V	Medium	α
Ferrihydrite (1)	0 to -0.2	0.05 M chloroacetate	0.49
Goethite (3)	-0.2 to -0.6	0.05 M chloroacetate	0.25
	-0.2 to -0.5	0.2 M chloroacetate, 0.5 M KCl	0.28
Hematite	-0.5 to -0.65	0.2 M chloroacetate	0.50

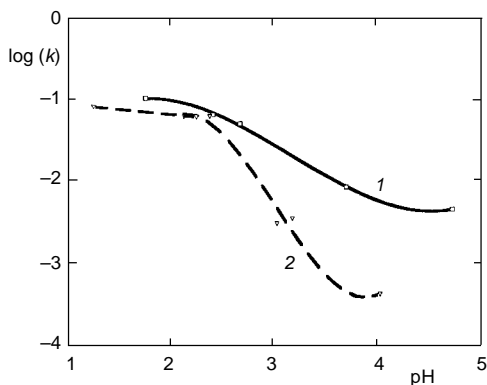


FIG. 2

Dependence of the logarithm of the rate constant k on the supporting electrolyte pH for ferrihydrite (A) and goethite (C). Curves: 1 ferrihydrite, $E = -0.15$ V; 2 goethite, $E = -0.4$ V

ducted in the oxalate medium, the g -factor value approaches 1 and is nearly invariably lower than in the chloroacetate buffer; the surface reactivity levels off.

As mentioned, the rate of a heterogeneous reaction is, in general, determined by the surface concentration of particles of the given phase, their specific surface area, protonation equilibrium constant, and pH. Figure 3 shows the rate constants of dissolution of several goethite samples with different particles in dependence on their specific surface

TABLE II
Effect of supporting electrolyte composition on the rate of dissolution of goethite (C) at -0.4 V

Supporting electrolyte	$k \cdot 10^{-3}, \text{s}^{-1}$			
	0.01 M	0.1 M	0.2 M	0.5 M
MCAc ^a		3.5	3.2	2.3
0.2 M MCAc +				
+ KNO ₃	3.1	3.6		
+ K ₂ SO ₄	13	20		
+ KCl		3.6	10	17
+ KH ₂ PO ₄	15	42	37 ^b	
+ oxalate	11	15 ^b		

^a Monochloroacetate buffer; ^b pure buffer (pH approaching that of the chloroacetate buffer, see Experimental).

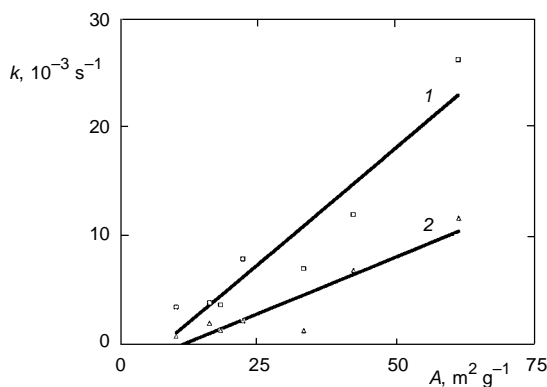


FIG. 3
Dependence of the logarithm of the dissolution rate constant k on the goethite specific surface area for samples A–G. Curves: 1 0.1 M oxalate buffer, $E = -0.2$ V; 2 2.1 M chloroacetate buffer, $E = -0.4$ V

area. At more negative working electrode potentials or in the presence of ligands the dependence is nearly linear, which indicates a unified reaction mechanism in the conditions applied. Differences between the easiness of reduction of the various crystal planes manifest themselves at more positive potentials^{19,20}.

Comparison of Reactivity of the Various Hydroxy-Oxides

The results of processing of the chronoamperometric curves for the reduction of the phases in the oxalate buffer are given in Table III. This electrolyte is best suited to finding the conditions of validity of Eq. (4) for the majority of phases examined. For instance, comparison of the reaction rates demonstrates that the reactivity at a working electrode potential of -0.2 V or -0.4 V decreases in order: ferrihydrite > goethites > hematite, which is consistent with the chemical reductive dissolution³⁻⁵. The SL1 and BRS samples rank among goethites with respect to the dissolution rate. The rather high g -values indicate that the iron hydroxy-oxides are not as reaction-homogeneous in them as in goethites. Table III, however, also displays large differences between the behaviour of the various goethite samples in dependence on their individual properties: the differences between the rate constants are not accounted for by the differences in the specific surface area solely. As shown previously²⁰, the particle size and the extent of development of the various crystal planes affect appreciably the reactivity of goethites as well. Such effects are particularly important at more positive working electrode potentials, at which the dissolution of goethites containing particles with well-developed (021) planes proceeds very slowly (with respect to their specific surface area). This anisotropy also manifests itself during the dissolution of goethite in acids¹⁹. Therefore, it is surprising to find that when the chemical reductive dissolution rates are compared in the literature, information on the crystallinity of the goethite samples mostly fails to be given³⁻⁵.

Table III also documents the relation between the voltammetric peak potential in a noncomplexing medium and the reductive dissolution rate: the faster the dissolution, the more negative the voltammetric peak potential (for identical charge transfer coefficients). Quantitative investigation of this relation will be the subject of a forthcoming study.

It follows from the voltammetric peak potential values (Table III) that the soluble Fe^{3+} ion cannot be the electroactive species in the reduction of the rather stable α -phases. Since the $\text{Fe}^{3+}(\text{aq})$ reduction peak potential is affected by the presence of the solid phase, reduction via $\text{Fe}^{3+}(\text{aq})$ is improbable for more reactive phases as well. However, the appreciable cathodic shift of the half-wave potential of the $\text{Fe}^{3+}(\text{aq})$ species in the presence of a solid phase on the working electrode points to the possibility of interactions of the various iron species in the solid phase and in the solution.

Comparison of the Electrochemical and Chemical Reductions

The phase selectivity of the electrochemical reduction in oxalate buffer with respect to the discrimination of ferrihydrite, goethite, and hematite is considerably lower than in the conventional chemical reductive dissolution. In a slightly acid medium during the reduction with ascorbate or sulfate, the reduction rate has been found to be about two orders of magnitude lower for ferrihydrite than for hematite or goethite³. The differences between those phases in the electrochemical reduction increase somewhat if a

TABLE III

Values of the k and g parameters in the kinetic equation (4) for the dissolution of the phases in the 0.1 M oxalate buffer at working electrode potentials of -0.2 and -0.4 V vs SCE, and the voltammetric half-wave and peak potentials in 0.1 M chloroacetate buffer; scan rate 10 mV s⁻¹

Phase (sample)	-0.2 V		-0.4 V		$E_{1/2}$, V
	$k \cdot 10^{-3}$, s ⁻¹	g	$k \cdot 10^{-3}$, s ⁻¹	g	
Ferrihydrite (A)	45	1.32	>100	–	0.00
(B)	33	1.38	>100	–	-0.10
α -FeOOH (A)	26	1.15	22	1.36	-0.34
(B)	8.0	1.18	15	1.13	-0.49
(D)	3.8	1.18	6.9	1.28	-0.53
(E)	7.1	1.17	5.9	0.93	-0.55
(F)	4.0	1.01	5.6	1.38	-0.50
(G)	3.6	1.38	–	–	-0.47
β -FeOOH	4.1	0.88	^a	–	-0.16 ^b
γ -FeOOH	55	1.35	>100	–	-0.01
δ -FeOOH	43	1.31	>100	–	0.00
Fe ₃ O ₄	65	1.98	>100	–	-0.02
α -Fe ₂ O ₃	0.6	1.12	2.7	1.04	-0.56
γ -Fe ₂ O ₃	63	2.62	>100	–	-0.08
Sediments: BRS			15	3.31	^c
SL1	16	1.73	16	2.81	^c
Fe ³⁺ (aq) ^f	reduction process obeying Cottrell's equation				-0.08 ^d +0.30 ^e

^a Chronoamperometric curve is not monotonous; ^b broad peak, slow current decrease after the maximum; ^c no clear maximum, slowly rising wave; ^d clean electrode surface; ^e electrode surface with deposited FeOOH; ^f $c_{\text{Fe}} = 1 \text{ mmol l}^{-1}$.

noncomplexing medium is used. For instance, the reduction of ferrihydrite (A) in the chloroacetate buffer at a potential of 0 V obeys the kinetic equation

$$I/Q_0 = 2.2 \cdot 10^{-3} (Q_t/Q_0)^{0.92}, \quad (6)$$

whereas for the reduction of ferrihydrite in 0.01 M ascorbate at pH 3 (the redox potential of this solution measured with the PIGE is between 0 and +0.1 V), Postma³ reported the relation

$$J/N_0 = 4 \cdot 10^{-4} (N_t/N_0)^{1.1}. \quad (7)$$

The difference in the rate constant can be partly explained by the somewhat higher pH value and somewhat more negative potential during the electrochemical reduction, but still it is clear that the results of the two methods are in an acceptable agreement for ferrihydrite.

The rate constant of the electrochemical dissolution of goethite (C) calculated from Eq. (5) for the potential of 0 V is $7.6 \cdot 10^{-5} \text{ s}^{-1}$, which is about 30-fold less than for ferrihydrite. Taking into account the specific surface area of ferrihydrite, which is approximately half an order of magnitude higher, the difference in the electrochemical reduction rate of goethite (C) and ferrihydrite (A) relative to their reacting surface areas is about one order of magnitude. Hence, the rate of electrochemical reduction of goethite in the conditions applied is considerably higher ($4 \cdot 10^{-8} \text{ mol s}^{-1} \text{ m}^{-2}$) than that of its chemical reductive dissolution at pH 3 with the goethite surface saturated with ascorbate (initial dissolution rate $1.8 \cdot 10^{-11} \text{ mol s}^{-1} \text{ m}^{-2}$, ref.⁴). As it seems, while the reaction rate during the electrochemical reduction is determined by the charge transfer rate solely, the effect of steric factors in the surface adsorption layer is considerably more significant during the chemical reduction. In practice, the electrochemical reduction of goethite will be best conducted at rates characterized by the rate constant lying within the range of 10^{-7} – $10^{-5} \text{ mol s}^{-1} \text{ m}^{-2}$ (for Eq. (4) being valid over a wide region of particle conversion and within times which do not exceed tens of minutes for a complete conversion).

CONCLUSIONS

The electrochemical and chemical dissolution of iron(III) hydroxy-oxides proceeds by similar mechanisms: reduced are either protonated groups occurring on the reacting surface (the process is a highly phase-specific reduction of, e.g., well-crystalline hematite or goethite) or some Fe(III) species which are in equilibrium with the protonated

particles (presumably in the case of amorphous and thermodynamically less stable phases, where the reaction is considerably less specific). In both cases, experimental conditions can be adjusted such that the simple kinetic equation (4), derived for a chemical reaction or a simple dissolution, is obeyed and charge transfer is the rate determining step, which allows the dissolution process to be electrochemically monitored. Kinetic equations of the surface reaction of particles can be employed to evaluate the reactivity of particles of both the pure phases and their mixtures as during the use of the chemical reaction³. In contrast to the chemical reductive dissolution, the electrochemical alternative is not so appreciably affected by the steric effect of adsorbed ions^{4,5} but only by the extent to which the ions affect bonds in the surface layer of the hydroxy-oxide phase, so that the phenomena can be in principle separated. In view of the possibility of affecting the reaction rate over a wide region through the choice of the pH, working electrode potential and supporting electrolyte ionic composition, dissolution experiments can be performed in times which are by orders of magnitude shorter than during the chemical reductive dissolution.

SYMBOLS

A	specific surface area, $\text{m}^2 \text{g}^{-1}$
E	working electrode potential, V
$E_{1/2}$	voltammetric half-wave or peak potential, V
g	geometric factor in the surface reaction kinetic equation for a set of particles ^{3,6,7} , defined by Eq. (4)
J	mass flow, $J = -dn/dt$ (mol s^{-1})
k	rate constant of the pseudo-first order reaction, s^{-1}
N_0	total amount of substance of reacting particles
N_t	instantaneous amount of substance of reacting particles in time t
Q_0	total charge passed during the reaction (corresponding to N_0)
Q_t	charge corresponding to the amount of substance N_t
α	charge transfer coefficient

REFERENCES

- Schwertmann U., Cornell R. M.: *Iron Oxides in the Laboratory*. Verlag Chemie, Weinheim 1991.
- Tessier A., Campbell P. G. C., Bisson M.: *Anal. Chem.* **51**, 844 (1979).
- Postma D.: *Geochim. Cosmochim. Acta* **57**, 5027 (1993).
- Zinder B., Furrer G., Stumm W.: *Geochim. Cosmochim. Acta* **50**, 1861 (1986).
- Biber M. V., Afonso M. S., Stumm W.: *Geochim. Cosmochim. Acta* **58**, 1999 (1994).
- Christoffersen J., Christoffersen M. R.: *J. Cryst. Growth* **35**, 79 (1976).
- Christoffersen J.: *J. Cryst. Growth* **49**, 29 (1980).
- Hickling A., Ives D. J. G.: *Electrochim. Acta* **20**, 63 (1975).
- Bauer D., Gaillochet M. P.: *Electrochim. Acta* **19**, 597 (1974).
- Mancey D. S., Shoesmith D. W., Lipkowski J., McBride A. C., Noel J.: *J. Electrochem. Soc.* **140**, 637 (1993).
- Brainina Kh. Z., Vydevich M. B.: *J. Electroanal. Chem.* **121**, 1 (1981).

12. Scholz F., Nitschke L., Henrion B.: *Naturwissenschaften* **76**, 71 (1989).
13. Scholz F., Lange B.: *Trends Anal. Chem.* **11**, 359 (1992).
14. Subrt J., Stengl V., Skokanek M.: *Thermochim. Acta* **211**, 107 (1992).
15. Weisser H. B., Mulligan W. O.: *Inorg. Synth.* **2**, 215 (1962).
16. Solcova A., Subrt J., Hanousek F., Holba P., Zapletal V., Lipka J.: *Silikaty* **24**, 133 (1980).
17. Lovric M., Komorsky-Lovric S., Bond A. M.: *J. Electroanal. Chem.* **319**, 1 (1991).
18. Datta N. C.: *J. Scient. Ind. Res.* **40**, 571 (1981).
19. Cornell R. M., Posner A. M., Quirk J. P.: *J. Inorg. Nucl. Chem.* **36**, 1937 (1974).
20. Grygar T., Subrt J., Bohacek J.: *Collect. Czech. Chem. Commun.* **60**, 950 (1995).