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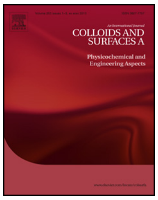

Isoelectric points of fresh and aged $Fe(OH)_2$

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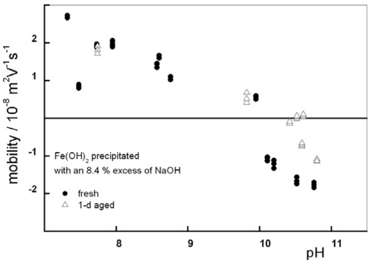
HIGHLIGHTS

- IEP of $Fe(OH)_2$ reported for the first time.
- Electrokinetic properties of Fe(II) precipitates are similar for different preparations.
- Electrokinetic properties of Fe(II) precipitates are rather insensitive to aging under anaerobic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Gray-green precipitates obtained from $FeCl_2$ solutions in basic medium in anaerobic conditions were studied in wet state. The results obtained by X-ray diffraction and Mossbauer spectroscopy suggest that $Fe(OH)_2$ is their main component. It is accompanied by wüstite, goethite, and $Fe(OH)_3$. The isoelectric point (IEP) of such precipitates falls at pH 10, which is a higher value than the IEP of iron (III) (hydr)oxides reported in the literature. Aging (for several days) had rather insignificant effect on the IEP.

1. Introduction

Iron (II) (hydr)oxides are important chemical compounds, but their surface chemistry is seldom studied. Iron (II) hydroxide is a primary corrosion product of iron, and it plays a significant role as a scavenger of metal ions under anaerobic conditions. The range of thermodynamic stability of $Fe(OH)_2$ is very narrow [1], and it is spontaneously converted into other compounds even under anaerobic conditions. For example the following Schikorr reaction:

$$3Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2H_2O \tag{1}$$

which occurs at room temperature does not involve oxygen as a reagent.

Precipitation of white or pale green hydroxide is a characteristic reaction for iron (II) used in qualitative analysis of metal cations. The precipitate becomes darker on aging, and the coloration is due to partial conversion of $Fe(OH)_2$ to magnetite (reaction (1)), wüstite (FeO), and to other compounds. Wüstite is a non-stiochiometeric compound with a variable Fe:O ratio [2].

In principle $Fe(OH)_2$ (solubility product, $[Fe^{2+}][OH^-]^2 = 4.87 \times 10^{-17}$) [3] is precipitated from water-soluble Fe(II) salts at basic pH irrespective of the anion, but the recipes for $Fe(OH)_2$ preparation recommend $FeSO_4$ as an iron precursor. Such recipes are not suitable for the present study, because sulfate anions adsorb specifically on the surfaces of metal (hydr)oxides, and they induce a shift in their isoelectric points IEP to low pH [4]. It is very difficult to remove sulfate anions from the surfaces of metal (hydr)oxides. Therefore we used $FeCl_2$ rather than $FeSO_4$ as an iron precursor.

The IEP is an important parameter characterizing particles in dispersions [5]. To the best knowledge of the present authors, a

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Table 1
The specimens used in the present study.

Specimen	Base	% excess of base	Aging
1	NaOH	8.4	None
2	NaOH	8.4	1 d
3	KOH	30	None
4	KOH	30	1 d
5	KOH	30	None
6	KOH	35.4	None
7	KOH	35.4	1 d
8	KOH	35.4	8 d
9	NaOH	17.7	3 d*
10	NaOH	17.7	None

* See Section 2.3.

reliable IEP of an iron (II) (hydr)oxide has never been published. Krause and Borkowska [6] used the term "isoelectric point" for the inflection point in the degree of oxidation vs. pH curve in their study of oxidation of $Fe(OH)_2$ in air. Their study (which is not related to electrokinetic phenomena) has been erroneously cited as IEP obtained by electroosmosis in several compilations of IEP of various materials, and it has been used to establish correlations between the IEP and other physical and chemical properties of metal oxides.

The IEP of metal oxides show negative correlation with the oxidation state of the metal, that is, higher oxidation state produces a lower IEP [7]. A similar relationship between the oxidation state and the acid–base properties is well-known in solution species [7]. The IEP of iron (III) hydroxides fall at pH about 9 [5]. Therefore an IEP at pH > 9 is expected for $Fe(OH)_2$. Interestingly enough, the IEP at pH 12 allegedly reported in Ref. [6] has been used to support the above correlation. The results reported for iron compounds are rather controversial in this respect. Contrary to expectations, most IEP reported for magnetite (iron II,III oxide) fall at pH < 9 [5]. Several studies report IEP of zero valent iron (ZVI) particles. Fresh particles had IEP at pH 6, and it shifted to lower pH on washing and aging [8,9]. ZVI particles can be considered as core–shell particles with a core composed of elementary iron and shell composed of magnetite. Thus, the surface of such particles is not composed of ZVI. This is why their IEP is relevant to the surface properties of magnetite rather than those of elementary iron.

2. Experimental

2.1. Preparation of Fe(II) precipitates and their composition

The precipitation was executed in a dry box purged with deoxygenized nitrogen. Water was Milli-Q, boiled and then stored under nitrogen. $FeCl_2·4H_2O$, NaOH, and KOH were reagent-grade chemicals from POCh (Poland). About 11 g of $FeCl_2·4H_2O$ were dissolved in 250 g of water. Solution of KOH or NaOH was added under stirring. The amount of base was always in excess of the calculated stoichiometric amount. The details of experimental conditions are summarized in Table 1.

The precipitate was filtered under vacuum and washed with water. The wet paste was collected into a plastic container, which was stored in the dry box for up to 8 d. A fraction of the precipitate was used directly after its preparation, and the remaining precipitate was stored for further use. The elementary analysis of the precipitate was carried out by means of ICP-OES JY 238 Ultrace spectrometer. To this end a specimen of wet paste (about 20% of dry mass) was mineralized in an Anton Paar Multiwave 3000 microwave in $HCl–HNO_3$ mixture at 22.4 bar and 211 °C.

2.2. XRD and Mossbauer spectroscopy

Samples of wet paste were studied. They were wrapped into air-tight plastic bags before taking them out of the dry box, and stored in those bags in course of the measurements. Empyrean from Panalitical was used in the XRD experiments. The Mossbauer measurements were carried out at room temperature in the standard transmission geometry using a source of ^{57}Co in a rhodium matrix. The reported isomer shifts refer to α-iron. The spectrum was collected in course of 1 week. This time was chosen as a compromise between sufficient signal-to-noise ratio (which requires long times), and possible chemical changes in the specimen.

2.3. Electrophoretic mobility

The electrophoretic mobility was measured by Malvern Zeta-Sizer at 25 °C using a transparent disposable cell. A few hundred milligrams of wet paste were transferred into plastic test tubes, each filled with 25 cm^3 of water. Six to twelve test tubes were prepared in the dry box. The sealed test tubes were transferred into an ultrasonic bath to disperse the particles. In specimen 9 (marked by * in Table 1), a concentrated dispersion was sonified in one test tube, and then it was diluted with water.

The pH was adjusted (in each test tube separately) by addition of NaOH solution. No special efforts were made to adjust the ionic strength. The wet paste contained substantial amount of NaCl or KCl (by-products of the precipitation reaction), which produced an ionic strength in excess of 10^{-3} M in the final dispersion. In course of the pH-measurement and of filling of the Malvern disposable cell, the test tubes were open to atmosphere, but these steps were quick and they were executed without excessive agitation to avoid oxidation of the precipitate. For each specimen of $Fe(OH)_2$, the pH and ζ potential measurements were carried out in the order from low-pH dispersions to high-pH dispersions. The time required to complete all measurements was usually much shorter than the age of the samples, and the time of the exposition to the atmosphere was approximately equal for all dispersions, irrespective of their pH.

The method of estimation of IEP from scattered data points is discussed in detail elsewhere [4,5].

3. Results and discussion

3.1. Color, stability, and chemical composition

The dispersions used in the electrokinetic measurements were gray-green. After the ultrasonic treatment the dispersions were stable against sedimentation for at least 1 h except for dispersions of pH about 9.5, which were unstable, and a layer of clear solution was visible within a few seconds on the top of the test tube. In several test-tubes reddish or brownish coloration has gradually built up in course of experiments carried out outside the dry box, indicating oxidation of iron (II) to iron (III).

The concentration of Ni in the Fe(II) precipitate was 1.2 ppm with respect to dry mass, and the measurements of Co concentration produced somewhat controversial results. The measurements via the spectral line 228.616 nm suggest 3.7 ppm of Co, while measurements via the spectral line 230.786 nm suggest 1.7 ppm of Co. Anyway, the concentrations of Ni and Co are too low to have a substantial effect on the IEP of the Fe(II) precipitate. The BET specific surface area of specimen 9 was 72.5 m^2/g. This should be emphasized that the sample was de-hydrated before the specific surface area measurement, and this might have resulted in chemical changes. Thus, the above value is not necessarily relevant to a