COPRECIPITATION OF IRON AND ALUMINUM DURING TITRATION OF MIXED Al\(^{3+}\), Fe\(^{3+}\), AND Fe\(^{2+}\) SOLUTIONS

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Abstract—Potentiometric titration analysis was used to examine the hydrolysis behavior of Fe\(^{2+}\), Fe\(^{3+}\), and Al\(^{3+}\) in pure solution and in mixture, in order to evaluate the potential for coprecipitation and mixed solid-phase formation. Mixtures of Fe\(^{3+}\) and Al\(^{3+}\) did not interact during neutralization; base consumed in their respective buffer regions was equivalent to the total metal added. Fe\(^{2+}\)-Al\(^{3+}\) solutions, however, showed excess base consumption in the Al\(^{3+}\) buffer region, indicating hydrolysis of Fe\(^{2+}\) at lower than normal pH. Ferric/ferrous iron analyses of systems at the Al endpoint (pH 5.5) showed amounts of oxidized Fe equivalent to the excess base consumption (~10% of total Fe), with substantial amounts of Fe\(^{2+}\) sorbed to or occluded within Al polymers present. Increased electrolyte levels or the presence of SO\(_4^{2-}\) inhibited oxidation and sorption of Fe\(^{2+}\) on Al surfaces, suggesting that Fe hydrolysis and oxidation was catalyzed at the surfaces. Increasing Al\(^{3+}\):Fe\(^{2+}\) ratios in the titrated solutions also increased the amount of Fe\(^{2+}\) coprecipitation, supporting a surface-mediated reaction mechanism. Ferrous iron oxidation was sensitive to O\(_2\) levels, which also affected the amount of coprecipitation. These findings suggest that surface-facilitated oxidation of Fe\(^{2+}\) may be important in the formation of mixed Fe-Al mineral phases in dilute soil solutions.

Key Words—Aluminum, Hydrolysis, Iron, Oxidation, Potentiometric titration.

INTRODUCTION

The formation of solid phases containing both Fe and Al by either cationic substitution or formation of mixed oxyhydroxides has been documented both in laboratory preparations and in nature (Schwertmann and Taylor, 1977; Taylor and Schwertmann, 1978). Laboratory syntheses have produced mixed Fe\(^{3+}\)-Al\(^{3+}\) solid phases by neutralization of solutions containing Al salts and either Fe\(^{3+}\) or Fe\(^{3+}\), the former of which is oxidized during the neutralization process. Fey and Dixon (1981) suggested that processes involving oxidation of Fe\(^{2+}\) in the presence of Al\(^{3+}\) is more conducive to formation of mixed phases, resulting in a higher degree of Al substitution in goethite than aging of Fe\(^{3+}\)-Al\(^{3+}\) solutions. In nature, Fe\(^{3+}\) released in primary mineral weathering and through alternating oxidation/reduction cycles is the predominant soluble iron species, and is therefore most likely to be involved in mixed phase formation during pedogenesis (Gerstl and Banin, 1980). Hydrolysis and oxidation of Fe\(^{2+}\), and resultant mineral phase characteristics, have been shown to be strongly influenced by solution parameters, such as concentration, associated ions, and O\(_2\) levels (Misawa et al., 1973; Sugimoto and Matijevic, 1980).

Most mineral synthesis studies have used high concentrations of metals and rapid neutralization with concentrated base to obtain sufficient solid phase for study. During mineral genesis in soils, a slow neutralization of much more dilute solutions probably takes place; the composition of the resultant phases will be dependent upon how the aqueous components interact during this neutralization. Potentiometric titration analysis is capable of studying this process by using relatively slow base addition to dilute metal solutions and quantifying base consumption as a function of solution pH. In the current study, titration analysis was used to examine the interactions of the acidic cations, H\(^+\), Al\(^{3+}\), Fe\(^{3+}\), and Fe\(^{2+}\), in mixture during neutralization in order to identify interactions suggesting coprecipitation of mixed phases. Particular attention was given to the behavior of Fe\(^{2+}\) in the Fe\(^{2+}\)-Al\(^{3+}\) system, to assess the effects of solution chemistry on Fe\(^{2+}\) hydrolysis and oxidation.

MATERIALS AND METHODS

Solution preparation

Solutions nominally containing 1 meq/liter of H\(^+\), Fe\(^{3+}\), Al\(^{3+}\), or Fe\(^{2+}\) were prepared by diluting stock solutions of the ions in their chloride forms. Stock solutions were prepared fresh daily at a concentration of 100 meq/liter by adding weighed salts (or concentrated HCl) to polyethylene volumetric flasks that were continually purged with high-purity N\(_2\) to exclude oxygen. CO\(_2\)-free, Milli-Q water was used to prepare all solutions. The concentration of the HCl stock solution was determined by titration with standardized NaOH, the Fe\(^{3+}\) and Fe\(^{2+}\) concentrations by the o-phenanthroline spectrophotometric method (Stucki and Anderson,
1981), and the Al$^{3+}$ concentrations by the 8-hydroxyquinoline method (Barnhisel and Bertsch, 1982). Where required, N$_2$-saturated KCl or K$_2$SO$_4$ solutions were added during dilution to provide background electrolyte.

**Titration methodology**

Potentiometric titration analyses were performed using a Radiometer recording titration system equipped with a PHM 84 pH meter, a TTT 80 titrator unit, an ABU 80 autoburette with 2.5-ml burette (accuracy of 0.001 ml), and an REC 80 Servograph recorder with the REC 160 titrigraph module. For most titrations settings on these instruments were maintained at 14-min full-scale deflection (on REC 160), 5% burette delivery speed (on ABU 80), and 0.05 proportional band (on TTT 80). All titrations were conducted with the TTT 80 instrument set in a "stepped" titration mode, whereby the rate of titrant delivery is varied based on the rate of pH change (i.e., base is added more rapidly when the pH is changing slowly and vice versa). This mode of operation maintains near equilibrium conditions during the titration and allows more accurate identification of endpoints, compared with traditional methods using a fixed rate of base addition.

The NaOH employed as the titrant in this study was standardized regularly with 1 meq/liter potassium hydrogen phthalate. The NaOH concentrations used were within the range 20-50 meq/liter. The glass and reference electrodes were standardized with pH 4.01, 7.00, and 10.00 buffers before each titration. During titrations, H$_2$O-saturated N$_2$ gas was used to purge the air space within the titration vessel at a flow rate of 20 cm$^3$/min. In certain studies the N$_2$ injection rate was increased to 150 or 300 cm$^3$/min, or compressed air was substituted for the N$_2$, at a rate of 300 cm$^3$/min.

Titration of solutions containing either the proton or individual metals (Fe$^{2+}$, Fe$^{3+}$, or Al$^{3+}$) were performed using aliquots containing 20-50 μeq of total metal. The endpoint of a titration was determined as the inflection point on the chart record. Replicate determinations showed the precision of the analyses at these concentrations to be ± 0.05 μeq NaOH.

**Titration of mixed H-Al-Fe solutions**

Titrations of 2-, 3-, and 4-component systems were performed using equi-equivalent amounts of the proton and three metals, with experimental conditions maintained as described above. Amounts of metal titrating within individual buffer regions were determined by reading amounts of NaOH consumed between inflection points on the chart recordings. Based on these results, study of the Fe$^{2+}$-Al system was initiated to investigate interaction of these metals during neutralization. The following individual experiments were conducted on this mixed system:

**Redox measurements.** A titration of 20 μeq each of Al$^{3+}$ and Fe$^{2+}$ was performed using standard procedures, but with a redox electrode (connected to an Orion Ionanalyzer) inserted into the titration vessel. Redox potential (Eh) values were continually recorded during the titration and corrected to pH 7. The same procedures were followed for separate titrations of 20 μeq of Al$^{3+}$ and 20 μeq of Fe$^{2+}$ for comparison.

**Varying Fe$^{2+}$-Al$^{3+}$ ratios.** Titrations were performed on mixed Fe$^{2+}$-Al$^{3+}$ solutions containing 5 μeq Fe$^{2+}$, and 5-20 μeq Al$^{3+}$. The amount of Fe$^{2+}$ coprecipitation with Al was determined by measuring the excess base consumed in the Al buffer region, which was attributed to hydrolysis and/or oxidation of Fe$^{2+}$.

**Fe$^{2+}$ partitioning.** To examine the interaction of Fe$^{2+}$ with Al, titrations of mixed Fe$^{2+}$-Al solutions were stopped at the Al inflection point (e.g., pH ≈ 5.5), at which time essentially all the Al had reacted with base, but Fe$^{2+}$ had not begun to hydrolyze. The solution in the reaction vessel was rapidly transferred to a 0.2-μm polycarbonate filter apparatus and maintained under an N$_2$ atmosphere while being filtered. The filtered solution was analyzed for Fe$^{2+}$ and Fe$^{3+}$ by the o-phenanthroline method. The precipitate on the filter was then washed with 50% ethanol solution and leached with 25 ml of 0.005 M MgCl$_2$ to displace surface-adsorbed Fe. Ferric and ferrous forms were analyzed in this solution as well. After another ethanol wash, 3 M HCl was added to the filter apparatus to dissolve the precipitate; ferrous/ferric analysis was then performed on this solution. Because some oxidation of Fe$^{2+}$ in the filter apparatus was observed during this last extraction, an independent method was used to determine the Fe$^{2+}$ : Fe$^{3+}$ ratio within the precipitate. Immediately after stopping the titration, an aliquot of the suspension was removed from the titration vessel, dissolved in 3 M HCl, and assayed using o-phenanthroline. Amounts of soluble and Mg-displaceable Fe$^{2+}$ and Fe$^{3+}$ were subtracted from these values to give accurate estimates of Fe$^{2+}$ occluded within the precipitate or oxidized to Fe$^{3+}$.

**Effect of anion and ionic strength.** To investigate the effect of anion and ionic strength on electrical double layer properties that may have affected Fe$^{2+}$/Al interactions, titrations were performed on equi-equivalent mixed solutions of Fe$^{2+}$ and Al$^{3+}$, initially made up with either chloride or sulfate salts, using methods described above. Additional KCl or K$_2$SO$_4$ was added to give electrolyte concentrations of 0.1 or 1.0 M for the chloride system, or 0.1 M for the sulfate salt.

**RESULTS AND DISCUSSION**

**Titration of individual metals**

Solutions of Al$^{3+}$, Fe$^{3+}$, Fe$^{2+}$, or H$^+$ titrated individually yielded curves such as those shown in Figure 1. Each metal showed a buffer region at a unique pH...
corresponding to hydrolytic consumption of hydroxyls. Ferric iron titrated at a lower pH than Al$^{3+}$, and Al$^{3+}$ was a stronger acid than Fe$^{2+}$. The inflection point of these curves, taken at the point of maximum slope where pH changed most rapidly with base addition, was used as the endpoint of titration. The number of microequivalents of NaOH added at that point corresponded to the analytically determined amounts of metals added (by spectrophotometric methods) to within 1% (Figure 1).

Ferrous iron titrated with a 20 cm$^3$/min N$_2$ injection rate, as in Figure 1, resulted in the formation of a red solid, which suggests that the iron had oxidized. The pH of the buffer region was also lower under these conditions than that reported in the literature (Baes and Mesmer, 1976). Titrations on 20 μeq of Fe$^{2+}$ with varying N$_2$- and air-flow rates showed a pronounced effect of oxidizing environment on the resultant titration curves (Figure 2). Both air injection and 20 cm$^3$/min N$_2$ allowed sufficient O$_2$ into the titration vessel to cause rapid oxidation of the Fe$^{2+}$ at pHs of 6.0-6.5 in this relatively dilute Fe$^{2+}$ solution. Purging with 150 cm$^3$/min N$_2$ resulted in a small buffer region at pH 6.5, with some red floc formation, but most of the Fe$^{2+}$ titrated at pH 8.0-8.5 to form a blue-gray precipitate. If 300 cm$^3$/min N$_2$ was used, essentially all the Fe$^{2+}$ titrated at pH 9 as a blue-green solid. This ferrous product, described previously as “green rust” (Misawa et al., 1973; Schwertmann and Taylor, 1977) was formed more readily at higher Fe$^{2+}$ concentrations than that reported in the literature.

Analysis of titration curves obtained using various combinations of the four metals gave the following generalized results:

1. Fe$^{3+}$ and H$^+$, as strong acids, were indistinguishable in mixture, both titrating at low pH (2.5-4).
2. In mixtures containing Al$^{3+}$ and Fe$^{3+}$, each metal titrated quantitatively in a distinct buffer region; inflection points between buffer regions could be used to quantify the amounts of each individual metal.
3. Fe$^{2+}$ in mixture with either Fe$^{3+}$ or Al$^{3+}$ did not titrate quantitatively in separate regions, but rather showed an increase in base consumption in the more acidic buffer region.

This last observation, illustrated for the Fe$^{2+}$-Al$^{3+}$ system in Figure 3, suggests that Fe$^{2+}$ oxidized in the presence of the other metals and thereby titrated at a lower pH. In this system, in which all solutions were flushed extensively with N$_2$ and which utilized high N$_2$ flow rates during titration, about 10% of the titer was...
shifted from the high-pH Fe$^{3+}$ region to the lower pH Al$^{3+}$ region. Less complete purging with N$_2$, or lower N$_2$ flow rates, increased the amount of coprecipitated Fe to as much as 25% in some experiments (data not shown). The presence of colloidal surfaces has been proposed to catalyze the hydrolysis and oxidation of Fe$^{2+}$ (Arden, 1950; Chen and Davidson, 1955; Tronc and Jolivet, 1984). Taylor and Schwertmann (1978) noted greater base consumption to pH 7 (and more oxidation of Fe$^{2+}$) in the presence of Al$^{3+}$ than in its absence. Based on these observations, the formation of many mixed Fe-Al solids at low pH may have involved surface reactions that facilitated the oxidation of Fe$^{2+}$, thereby resulting in coprecipitation of the two metals as previously proposed for Fe$^{2+}$ in the presence of ferrimagnetic oxide dispersions (Tronc and Jolivet, 1984).

Redox measurements

Redox potentials made during titrations of 20 μeq solutions of AlCl$_3$, FeCl$_2$, and mixed AlCl$_3$-FeCl$_2$ (20 μeq each) solutions, showing relative areas under redox curves.

Partitioning of Fe$^{2+}$/Fe$^{3+}$

To determine Fe$^{2+}$ oxidation more directly in mixed Fe-Al systems, suspension samples were taken from the titration vessel after titrating to the Al endpoint (pH 5.5) and analyzed for Fe$^{2+}$ and Fe$^{3+}$ after acid digestion. This analysis was performed on titrations conducted for varying salts, and excess base consumption in the Al region was determined on the basis of inflection points. The percentage of Fe$^{2+}$ oxidized and excess base consumption (Table 1) agree closely. From the close correlation of these separate determinations, excess base consumption in the Al region may have been due solely to neutralization of oxidized Fe. In the Cl$^-$-H$_2$O system, the value of ~12% oxidation also agrees closely with the 10% value obtained from the redox curves in Figure 4. The rather high standard deviations of the data in Table 1 reflect slight changes in O$_2$ environment between replicate titrations, and emphasize the importance of standardized purging techniques in conducting titrations of oxidizable species.

The effect of anion type and ionic strength (μ) on Fe oxidation is shown in Table 1. In the Cl$^-$-system, increasing μ to 0.1 M decreased oxidation by 50% of the value in water, and 1.0 M salt inhibited oxidation com-
Table 1. Fe\textsuperscript{2+} coprecipitation/oxidation with Al\textsuperscript{3+} at the Al endpoint as determined by spectrophotometric and titrimetric methods.\textsuperscript{1}

<table>
<thead>
<tr>
<th>System</th>
<th>Fe\textsuperscript{2+} oxidized (o-phenanthroline)</th>
<th>Fe coprecipitated (base consumption)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage of total Fe added</td>
<td></td>
</tr>
<tr>
<td>Cl\textsuperscript{−}, H\textsubscript{2}O</td>
<td>12.9 ± 0.9</td>
<td>11.7 ± 1.2</td>
</tr>
<tr>
<td>Cl\textsuperscript{−}, 0.1 M</td>
<td>6.8 ± 1.7</td>
<td>6.8 ± 1.3</td>
</tr>
<tr>
<td>Cl\textsuperscript{−}, 1.0 M</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2−}, H\textsubscript{2}O</td>
<td>5.5 ± 0.7</td>
<td>5.9 ± 0.4</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2−}, 0.1 M</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

\textsuperscript{1} 5 × 10\textsuperscript{-4} N solutions of Fe\textsuperscript{2+} and Al\textsuperscript{3+} titrated to pH 5.5.

Completely. Also, oxidation was decreased at low $\mu$ (water only) in the SO\textsubscript{4}\textsuperscript{2−} system to less than half of that in the Cl\textsuperscript{−} system, and was completely halted at 0.1 M. Other studies (Sung and Morgan, 1980; Millero, 1985) have shown the effect of activity and complexation on Fe\textsuperscript{2+} oxidation rates, but calculations on the solutions used in Table 1 by the speciation model GEOCHEM (Sposito and Mattigod, 1980) did not show large enough differences in Fe\textsuperscript{2+} activity to account for observed differences in oxidation. For example, in H\textsubscript{2}O systems Fe\textsuperscript{2+} activity was 3.9 × 10\textsuperscript{-4} with Cl\textsuperscript{−} anion and 3.6 × 10\textsuperscript{-4} with SO\textsubscript{4}\textsuperscript{2−}.

A more complex partitioning of Fe\textsuperscript{2+}-Fe\textsuperscript{3+} was used on a subsequent series of titrations to characterize soluble, surface-adsorbed, and occluded Fe in samples removed from the titration vessel at the Al endpoint (Table 2). Unexpectedly, filtering of these suspensions showed that only 65% of the total Fe was present in the solution phases of the low $\mu$ Cl\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−} systems, with 85% soluble in 0.1 M salt solutions. Oxidized Fe was confined to the occluded (acid-soluble) fraction and corresponded closely with the values reported in Table 1. The remainder of the insoluble Fe\textsuperscript{2+} was present either in a surface-adsorbed (Mg\textsuperscript{2+}-displaceable) or occluded (acid-soluble) form. At low ionic strength, 20% of the Fe was surface sorbed as Fe\textsuperscript{3+} in either Cl\textsuperscript{−} or SO\textsubscript{4}\textsuperscript{2−} systems, but decreased to 2% at 0.1 M $\mu$. Occluded Fe\textsuperscript{2+} varied with anion: for Cl\textsuperscript{−}, about 8% was occluded, whereas for SO\textsubscript{4}\textsuperscript{2−} the value was ~14%, at both levels of $\mu$.

These results support a surface-mediated mechanism for Fe\textsuperscript{3+} oxidation in the presence of Al. Poorly crystalline, high surface area Al polymers formed during neutralization apparently adsorbed significant amounts of Fe\textsuperscript{2+} or its hydrolysis products, thereby concentrating Fe\textsuperscript{2+} on the Al surface where oxidation was more prevalent (Figure 5). Increased rates or amounts of Fe\textsuperscript{2+} hydrolysis at the surface possibly were due to the presence of loosely held hydroxyls in the positively-charged double layer of the Al polymers. The first-order rate constants for Fe\textsuperscript{2+}, Fe(OH)\textsuperscript{2+}, and Fe(OH)\textsuperscript{3+} oxidation have been reported to be 6 × 10\textsuperscript{-5}, 1.7, and 4.3 × 10\textsuperscript{5}/min, respectively, with this difference resulting from the facilitated d\textsubscript{z} electron transfer from Fe\textsuperscript{2+} to O\textsubscript{2} when hydroxyls are in the inner coordination sphere (Millero, 1985). Thus, a surface-facilitated hydrolysis should have had a significant influence on the Fe\textsuperscript{2+} oxidation rate. Higher electrolyte concentration inhibited adsorption and resultant oxidation, either by displacing Fe\textsuperscript{2+} and/or OH\textsuperscript{−} from surface sites, or by coagulating the Al polymers, thereby reducing available surface area. The proportionately greater effect of SO\textsubscript{4}\textsuperscript{2−} in reducing oxidation may be ascribed to the more efficient flocculating action of SO\textsubscript{4}\textsuperscript{2−} due to specific adsorption, which caused surface area reductions and increased occlusion of Fe\textsuperscript{2+}, and/or to displacement of adsorbed and double-layer hydroxyls on the polymer surfaces, which reduced Fe\textsuperscript{2+} hydrolysis.

**Effect of Fe\textsuperscript{2+}:Al\textsuperscript{3+} ratio**

As the amount of Al varied from 5 to 20 $\mu$eq, with a constant 5 $\mu$eq of Fe\textsuperscript{2+} in the titrated solutions, the amount of coprecipitated Fe (determined by excess base consumption in the Al region) increased sharply with increasing Al in the Cl\textsuperscript{−} system containing no added electrolyte (Figure 6). These observations likely represent the availability of more surface area for surface-induced hydrolysis and oxidation of Fe\textsuperscript{2+}. Sulfate had an increasingly depressive effect on coprecipitation of Fe\textsuperscript{2+}.
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Figure 6. Effect of varying additions of Al^{3+} on coprecipitation of Fe^{2+} in Cl^- and SO_4^{2-} systems; initial Fe^{2+} = 5 \mu\text{eq}.

Fe^{2+} as the amount of added Al was increased, as noted above (Figure 6).

Mechanisms of coprecipitation

Previous studies of the formation of mixed Fe^{2+}-Al^{3+} solids have suggested mechanisms involving soluble species reacting to form mixed hydroxides, such as, e.g., Fe^{2+}-Al^{3+} hydroxide, which has a pyroaurite-type structure (Taylor and McKenzie, 1980; Taylor, 1984):

\[
3 \text{Fe(OH)}^+ + \text{Al(OH)}_4^- + 2 \text{H}_2\text{O} \rightarrow 3 \text{Fe(OH)}_2^0 \cdot \text{Al(OH)}_6^0 + 2 \text{H}^+.
\]

Although this or similar reactions may occur at the higher pH and under more anoxic conditions used in the above-cited studies, the results of the present study show that the presence of Al solids strongly influenced the behavior of Fe^{2+} during neutralization, most likely by catalyzing the hydrolysis and subsequent oxidation of Fe^{2+} on the surface of the solid. It should be emphasized that the relatively slow neutralization rates and dilute solutions used in this study do not allow direct comparison with other research, but are likely to be more similar to those in actual soil solutions.

Taylor (1984) demonstrated the rapid formation of double hydroxide salts, generally having the pyroaurite-type structure, by mixing a precipitated hydroxide with solutions of a second metal cation at pHs below which it would normally hydrolyze. Although not explicitly stated, the induced hydrolysis in this experiment presumably involved the interaction of the soluble unhydrolyzed metal with partially hydrolyzed polymers or the fully hydrolyzed precipitate, resulting in the formation of such phases as takovite, Ni_6Al_2(OH)_{16}CO_3 \cdot H_2O, and hydrotalcite, Mg_6Al_2(OH)_{16}CO_3 \cdot H_2O. Surface-induced hydrolysis has also been proposed to explain multiple buffer regions in potentiometric titrations of Fe^{3+} solutions in the presence of Fe^{3+} oxide colloids (Tronc and Jolivet, 1984).

The importance of Fe^{3+} oxidation in mixed solid-phase formation has been appreciated in laboratory synthesis studies (Schwertmann and Taylor, 1977; Fey and Dixon, 1981), and is also demonstrated in the results presented here. The equivalence of analytically measured Fe^{3+} and base consumption by titrimetry implies that only Fe^{3+} was incorporated within the solid produced under the conditions used; considerable Fe^{2+} was, however, sorbed to or occluded within the precipitate. The effect of electrolyte concentration, type of anion, and Al solid-phase surface area on Fe oxidation/coprecipitation and the amounts of sorbed Fe suggests surface-catalyzed hydrolysis and oxidation to be a major mechanism in mixed solid phase formation in the dilute Fe^{2+}-Al^{3+} system studied here.

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REFERENCES


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