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Iron (Fe^{2+}, Fe^{3+}) in Systems with Organic Substances

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Abstract. Relationships in systems of Fe^{2+} and Fe^{3+} - selected organic substances (humic and fulvic acids; amino acids - alanine, cysteine and glycine; saccharides and polysaccharides - D-glucose, cellulose, saccharose and starch; carbon acids - citric, acetic, oxalic and tartaric) were subjected to experimental research. The research investigated conditions under which soluble Fe complexes are formed, the conditions for Fe migration, and the conditions for the formation of insoluble complexes causing deposition of iron. The research showed that these relationship are very complex, depending upon the degree of oxidation of Fe, the pH values of the environment, the intensity of light and, in case of humic and fulvic acids, also upon the locality or origin of matter that the substances were extracted from.

Keywords: Fe^{2+}, Fe^{3+}, organic substances, soluble and insoluble complexes

Introduction

The role of organic substances (OS) in processes of migration of chemical elements has been accepted in geochemical theories for more than three-quarters of the 20th century. This research was stimulated through simple experiments by Harrar (1929), in which he an observed increased solubility of iron in environment where acetic acid is present. These observation and data about the natural presence of acetic acids in the environment were base for his theory about the influence of acetic acid on iron migration. It is important to mention that in chemical-analytical practice acetic acid has been used since a long time ago as an agent suppressing the formation of insoluble Fe^{3+} hydroxides and Al^{3+} hydroxides; however, in geochemical processes it had not been taken into account.

Looking at the influence of humic acids on Fe and Al migration has a very interesting history. We have not succeeded in finding the original or indirect references of who the author was of the often mentioned assumption because this phenomenon was proved for the first time by experiments only in in the 1970-ies. We assume that earlier mentioned of it was only based on empirical observation, supported mainly by experiences and the wide spread presence of humic acids in various sediments, soils etc.

In the frame of systematic experimental research of the relationship between OS and the chemical elements we have also paid attention to compounds of Fe^{2+} and Fe^{3+}. We found that the relationships among these systems are significantly more complex than was originally assumed. We proved that besides the migration, OS under certain condition also cause the accumulation of Fe and that in such case degree of oxidation of Fe is also important. The results of our experimental research of the relationships of Fe^{2+} and Fe^{3+} with selected OS are subject of this paper.

Brief Overview of Literature Research

Despite the fact that in chemical-analytical practice, the relationships of several Fe-OS systems are well known now for several decades, the research in their geochemistry and related scientific branches only started only in the1960-ies and mainly in the 1970-ies. For example, Schnitzer and Khan (1972) have proved the generation of soluable Fe^{+3} complexes by humic acids (HA) and fulvic acid (FA) in the environment with pH 3 and 5. Fox (1984) observed that insoluble Fe^{3+} compounds do not precipitate even in strongly alkaline solution when HA is present. These observations were also confirmed by our introductory experiments (Babčan and Ševc, 1989). It is noteworthy that we have not proved the formation of soluable Al complexes with HA and FA.

The experimental research of relations between Fe and OS has become very wide spread in seventies. Hermann and Gerke (1992) proved the formation of Fe^{3+} complexes in the presence of humic substances in a wider range of pH values (2.5 - 6.4). Pandeya (1993) reported about the formation of soluable Fe^{3+} complexes in presence of FA and citric acid in solution with pH value of 5 and 8.5. Geetha et al. (1995) described saccharide Fe^{3+} complexes with glucose, sorbose, fructose, mannose, galactose, lactose and maltose. Tomasik et al. (1995) reported about the formation of easily hydrolyzable starch - Fe(O)(OH) complex.

Jersak et al. (1992) assign a good leakage of Fe from forest soils to oxalates. Gerke (1992) observed a strong time dependence (he reached a maximum of the release of Fe after 90 days) during leaching of Fe from soils by citric acid. Knocke et al. (1992) leached Fe from soils by humic and fulvic acids and then by tannic and oxalic acids. These acids have strong complex-making effects on Fe^{2+}, and the newly formed complexes prevent its oxidation.

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Ochs et al. (1993) compared the Fe leaching from rock decomposition and from soils, and stated that the most effective Fe leaching from soil-root system is reached at a pH of 3-4. Izeferis and Agatzinileonaardou (1994) investigated the release of Fe from laterite. From all investigated OS the most effective acid was oxalic acid, (except for Ni it was citric acid). Methoxyacetic, formic, acetic and salicylic acids were ineffective. The effect of oxalic acid was also confirmed by Cajuste et al. (1996).

At present many authors pay attention in their researches to redox reactions of Fe in systems with OS. Deng and Stumm (1993) investigated the kinetics of the reduction of Fe^{3+} by fulvic acids (optimum should be at pH 7.5). On the other hand, Liang et al. (1993) observed that, beside glutamate, FA also accelerates the oxidation of Fe^{2+}. Carter (1995) includes among strong Fe reducing agents glutamate, ascorbite and tocopherate. Karlsson et al. (1995) reported that in near-surface layers (with access to light) of waters of northern lakes the Fe^{3+} photo-reduction is running optimally at pH 4. Fe^{3+}. It is not being reduced in deeper layers but, due to an alkaline environment, the iron is segregated in the form of hydroxides. Volker and Sulzberger (1996) reported that fulvic complexes of Fe^{2+} are oxidized faster by hydrogen peroxide than by aqua-complexes. Pehkonen et al. (1993) investigated photo-reduction of Fe oxides and hydroxides in the presence of formaldehyde, formic salts, acetate, oxalate and butyrate. They observed that the pH of the environment and the wave length of light used are important factors of photo-reduction (a maximum of reduction accrued at a wave length of 330 - 405 nm.

Method of the Research

The primary goal of the experimental research was to investigate the influences of individual OS on soluable Fe compounds ($FeCl_2$, $FeCl_3$); and particularly to figure out what are the conditions when soluable, insoluble and transient Fe compounds are formed in pH ranging from 1 to 12. Further more, we investigated the redox effects of used OS on both Fe oxidation degrees. The systems with Fe^{2+} were investigated in the internal environment and excluding light.

The basic substances used in the research were natural (humic and fulvic) acids and artificial substances i.e. factory products with purity p.a. (amino acids - alanine, cysteine and glycine, saccharides - D-glucose and cellulose, acids - citric, acetic, oxalic and tartaric - all products of the factory Lachema, Brno, the starch from factory in Boleráze, saccharose from a factory in Sereď). Humic and fulvic acids were extracted from peat from the localities of Cérová and Hroboňovo. A detail description is given in the report by Babčan and Ševc (1989). The operating procedure itself consists of several operations, which repeatability was verified by two series of experiments. Accurate setting of required pH values of solutions (the so called starting pH values) in range from 1 to 12 occurred as a specific problem. On the basis of preliminary experiments, we adopted the following technique.

Given amount of OS (100 mg) was added into approximately 80 ml of distillated water (in case of experiments with Fe^{2+}, CO_2 and another gasses were removed by boiling) and the required pH was set by adding HCl or HaOH. 1 millimole (mmol) of $FeCl_2$ or $FeCl_3$ solution was added into the prepared solution, then the pH of the solution environment was re-adjusted and the volume of the solution was filled up to 100 ml. The samples were stored and occasionally stirred for 24 hours, then the coagulum that formed was removed by centrifuge. Finally, the Fe content was measured in a proportional part of the solution. Fe^{3+} was determined by complex-metric titration according to Přibil (1997), Fe^{2+} was determined from the difference after prevailing oxidation of Fe^{2+} to Fe^{3+}. The content of Fe in insoluble compounds corresponds to the difference between the initial Fe content in solutions and the Fe content in the final respective solutions. In the attached graphs the Fe contents in solutions (after recalculation to volume 1000 ml) represents soluable Fe form of the given oxidation degree and at given pH conditions.

In case of experiments with Fe^{2+}, the tests were done in internal atmosphere of Ar or N_2, with and without access to light (Erlenmeyer flasks were wrapped in foil and inserted into closed cabinet). The repeatability of setup of initial as well as final pH values of solutions and repeatability of determination of individual Fe oxidation degrees in the systems with tartaric acid in solutions with two different pH values are shown on the graphs given in figures 1 and 2. Statistical data of mentioned tests are summarized in table 1. The test on reproducability of setup of pH values 5 and 7 showed that the value of standard deviation was 0.6 to 0.8%.

Result Overview and Discussion

The observed experimental values from the research of the systems Fe^{2+}, Fe^{3+} - organic substances are given on figures 3 to 33. The graphs show the relationships between soluble and insoluble forms of Fe^{2+} and Fe^{3+} compounds in solutions containing given organic substances and at given pH conditions. More Fe in solution means a more soluble system; values close to the X axis refer to insoluble or lightly soluble systems (bonds) of iron.

1. Fe Systems Without Organic Substances

A study of the so called "solely water" Fe systems, i.e. systems without OS, served as the standard for judgment of Fe compounds behavior in given a environment. In the case of Fe^{3+} compounds the data for water only systems are given in figures 5, 6 and 22. Data for Fe^{2+} are on figures 3 and 4. Data regarding water only Fe^{3+} systems usually approximate values published in analytical reference books. Data from Fe^{2+} systems are original, with the observation that in strongly acid medium only small portion of Fe^{2+} is oxidized and also with the observation that the forming of insoluble Fe^{2+} compounds is shifted toward higher pH values when light is absent.

Table 1 Statistical data from tests on repeatability of setup and changes of pH values in solution environment, and determination of Fe forms in systems Fe^{2+} - tartaric acid.

Designed setup of pH	Number of tests	Set values of pH	Reached pH of solution	Sum of Fe (mmol) after test	Content of Fe^{2+} (mmol)
5.0	5	5.03 ± 0.03	4.23 ± 0.09	10.04 ± 0.54	8.80 ± 0.46
7.0	7	7.20 ± 0.06	6.17 ± 0.24	8.80 ± 0.30	7.00 ± 0.42

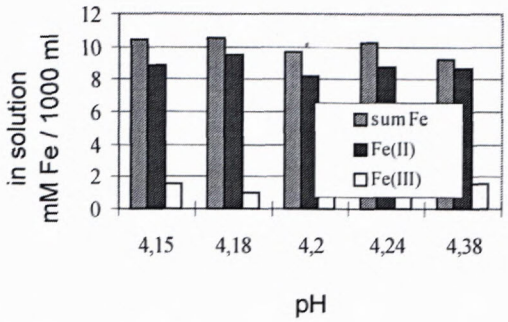

Fig. 1 Repeatability of setups of pH values, and determination of Fe in systems Fe^{2+} - tartaric acid (designed setup pH = 5, without access of light)

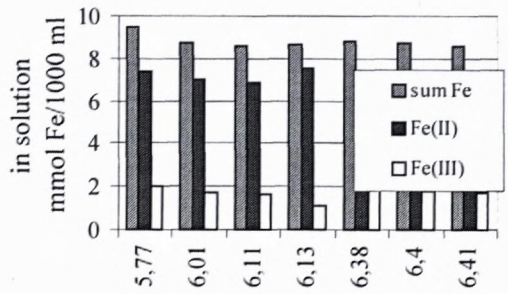

Fig. 2 Repeatability of setups of pH values and determination of Fe in systems Fe^{2+} - tartaric acid (designed setup pH = 7, without access of light)

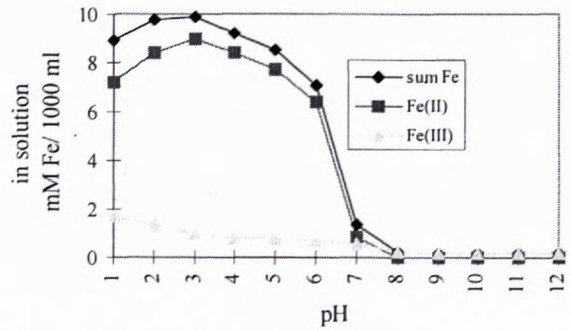

Fig. 3 Systems Fe^{2+} – water (with access of light)

According to summary values of Fe content in solutions, the systems Fe^{2+} - HA (with access of light) and Fe^{2+} - FA (without access of light) are alike. However in the case of systems with HA and access of light, the participation of Fe oxidation forms is different. In the systems without access of light some oxidation of Fe^{2+} could took place during the mechanical manipulation (centrifuge, pipette, etc.) that we could not avoid.

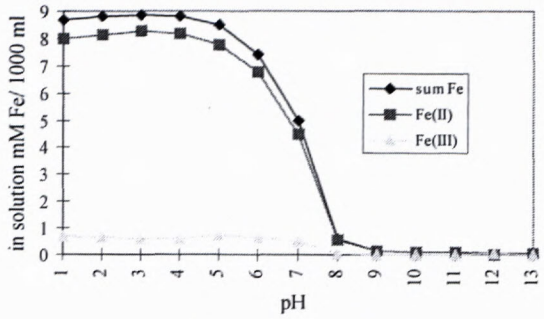

Fig. 4 Systems Fe^{2+} – water (without access of light)

2. Systems with Humic and Fulvic Acid

Figures 5 and 6 show the relationships in the systems Fe^{3+} - humic and fulvic acids. Results of the study of HA and FA from two localities are significantly different, which supports the opinion that the effect of these substances is dependent upon their origin. At the same time this observed phenomena can be the reason for the differences in the conclusions about mentioned systems reported by various authors. The differences are probably caused by structural singularities of HA and FA from given localities. It is obvious that HA and FA from the Cérova locality have a different function groups as from Hroboňové.

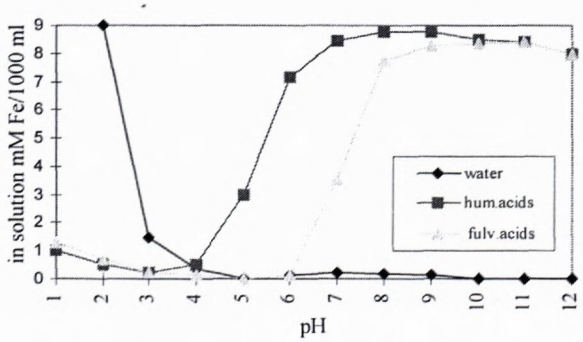

Fig. 5 Systems Fe^{3+} – water - humic and fulvic acids

3. Systems with Amino Acid

Out of three investigated amino acids (alanine, cysteine, glycine) cysteine had the most significant influence on systems with Fe^{3+} (Figs. 9 and 10). Probably due to sulfur present in cysteine molecule, there was an outstanding reduction of Fe^{3+} (with access of light), as show by the results presented in figure 9. The effects of the

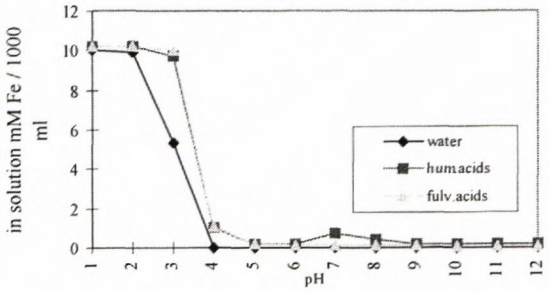

Fig. 6 Systems Fe^{3+} – water - humic(HA) and fulvic acids (FC), (Hroboňovo)

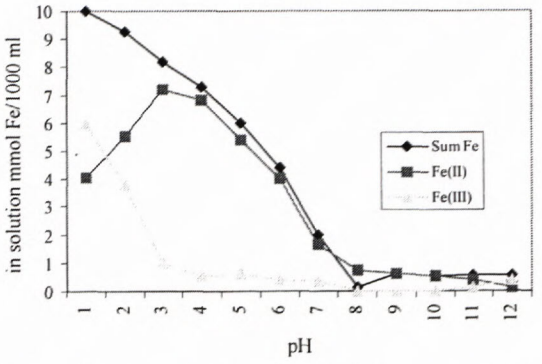

Fig. 7 Systems Fe^{2+} – humic acids (with access of light)

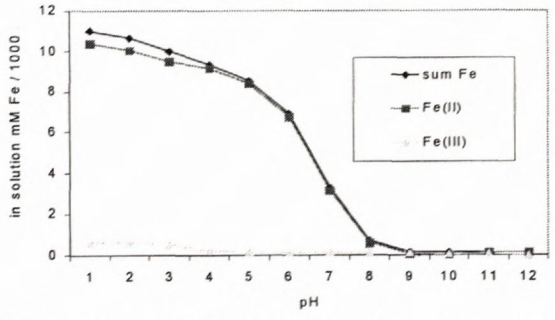

Fig. 8 Systems Fe^{2+} – fulvic acids (without access of light)

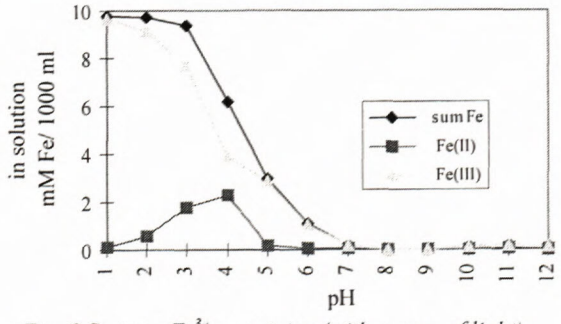

Fig. 9 Systems Fe^{3+} – cysteine (with access of light)

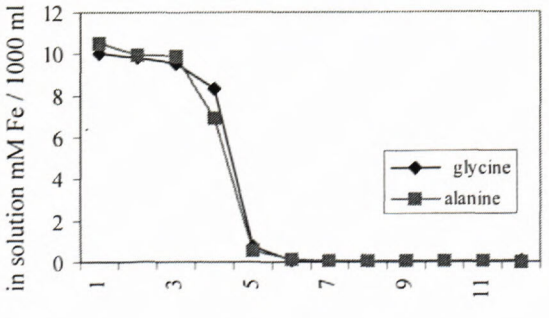

Fig .10 Systems Fe^{3+} – alanine and glycine (with access of light)

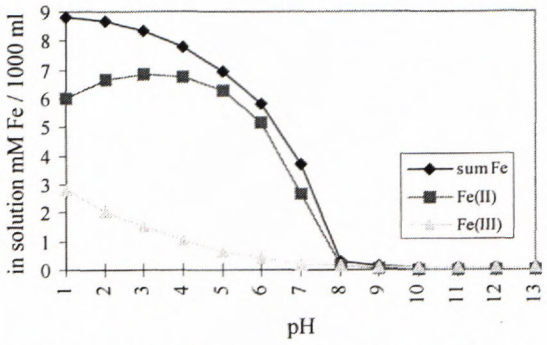

Fig. 11 Systems Fe^{2+} – glycine (with access of light)

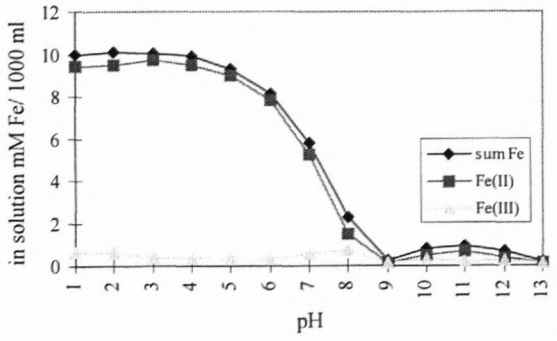

Fig. 12 Systems Fe^{3+} – glycine (without access of light)

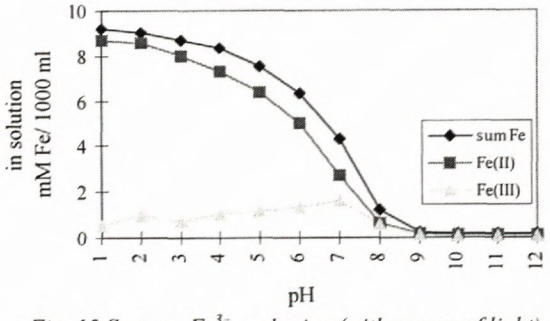

Fig. 13 Systems Fe^{3+} – alanine (with access of light)

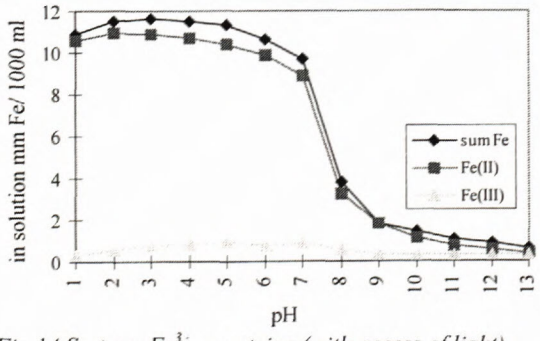

Fig.14 Systems Fe^{3+} – cysteine (with access of light)

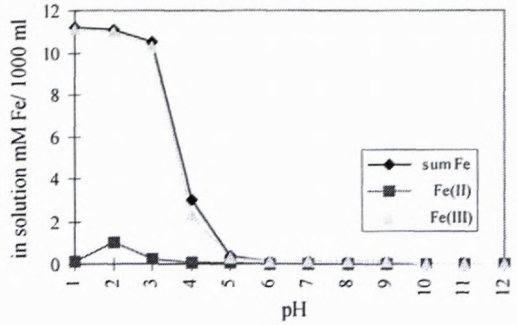

Fig. 15 Systems Fe^{3+} – cellulose (with access of light)

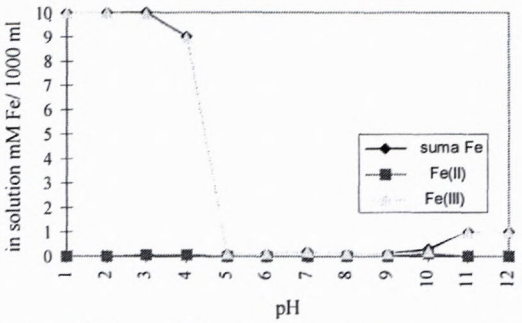

Fig. 16 Systems Fe^{3+} – D-glucose (with access of light)

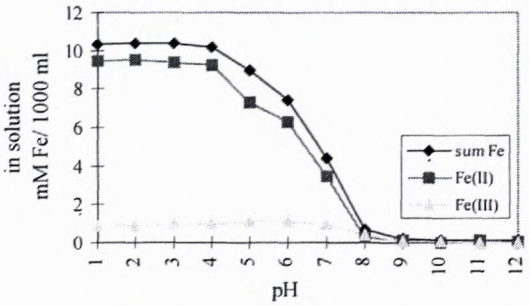

Fig. 17 Systems Fe^{2+} – cellulose (with access of light)

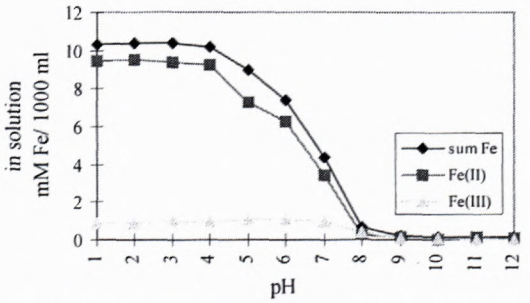

Fig .18 Systems Fe^{2+} – cellulose (without access of light)

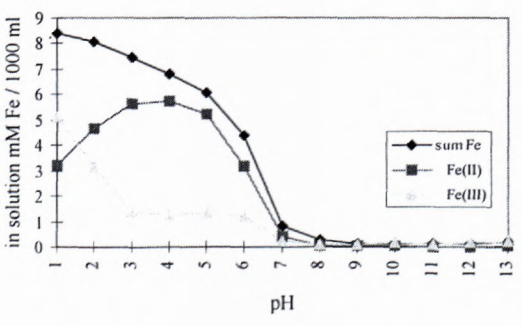

Fig. 19 Systems Fe^{2+} – D-glucose (with access of light)

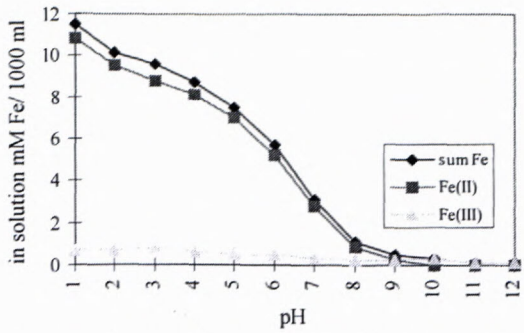

Fig. 20 Systems Fe^{2+} – D-glucose (without access of light)

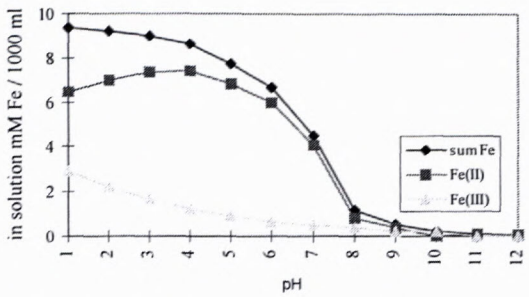

Fig. 21 Systems Fe^{2+} – starch (with access of light)

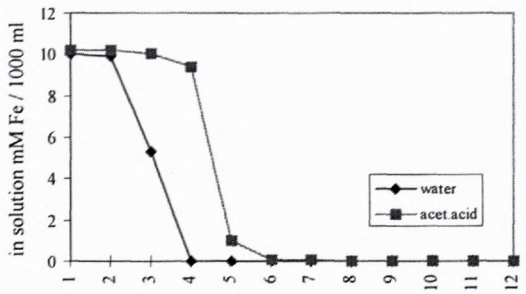

Fig. 22 Systems Fe^{3+} – water and acetic acid (with access of light)

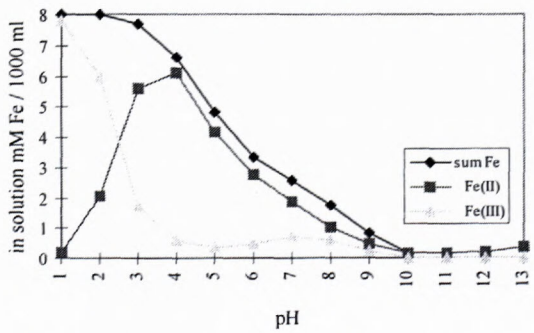

Fig. 23 Systems Fe^{2+} – acetic acid (with access of light)

other two acids differ from solely water systems only by shifting of pH values when formation of insoluble compounds occurs (Fig. 10).

Glycine in the systems with Fe^{2+} behaves differently when light is present or absent. In an acid medium (Fig. 11) stronger oxidation of Fe^{2+} occurs; however, if light is blocked out (Fig. 12) this effect is markedly suppressed. The light influences the oxidation of Fe^{2+} also when alanine is present (Fig. 13), whereas in case of cysteine the oxidation of Fe^{2+} is suppressed.

4. Saccharides and Polysaccharides

Fe^{3+} in systems with various saccharides and polysaccharides behaves very similarly, except for a few cases. A little reduction occurs only in the environment with cellulose (Fig. 15), when formation of insoluble compounds is shifted toward higher pH values. The shift of formation of insoluble bonds was also observed in a case of glucose. Interesting is also the reduction of Fe^{3+} in a strongly alkaline medium.

Fe^{2+} systems are markedly oxidized in the presence of glucose and light (Fig. 19). Fe^{2+} systems with starch behave a little less markedly in this way (Fig. 21).

5. Carbonic Acids

Each of the investigated carbonic acids (or their salts) behaves in a specific way in relation to the Fe^{3+} and Fe^{2+} systems. Although much is known of these domains from analytical chemistry, many of our observations are new; these will be useful in explaining of the geochemical, pedological biological and other phenomena.

Acetic acid in systems with Fe^{3+} significantly shifts the formation of insoluble iron compounds to the alkaline zone (Fig. 22). In the case of acetic acid systems with Fe^{2+}, the almost quantitative oxidation of Fe in a strongly acid medium with access of light (Fig. 23) is significantly different from the solely water systems (Figs. 3 and 4). The difference is also rather significant without access of light to the system (Fig. 24).

Dicarbonic oxalic acid slightly reduces Fe^{3+} (Fig. 25) and, in comparison to the solely water systems, it shifts the formation of insoluble Fe^{3+} compounds to the alkaline zone more moderately than does acetic acid, for instance. The acetic acid invokes significant changes in systems with Fe^{2+}. When light is present (Fig. 26) there is significant oxidation of Fe^{2+} and so there is also formation of soluble Fe compounds (Fig. 25). When light is blocked out (Fig. 27), the oxidation of Fe^{2+} is minimal, however the solubility of Fe^{2+} compounds is significantly decreased due to formation of insoluble iron oxalate.

Another dicarbonic acid, but with two hydroxyl groups in a structure, is tartaric acid. It has unusual influence on both Fe forms. It reduces Fe^{3+} compounds when air is present (Fig. 28), namely in two maxima - in the pH range of 4 to 5 - and a little bit more intensively in the pH range of 9 to 10. A second significant influence is a shift of the insoluble Fe^{3+} compounds formation to the strongly alkaline zone (Fig. 28).

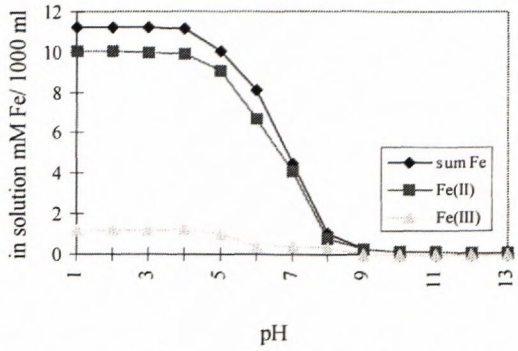

Fig. 24 Systems Fe^{2+} – acetic acid (without access of light)

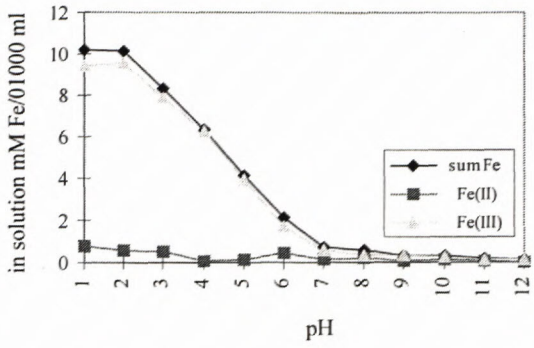

Fig. 25 Systems Fe^{3+} – oxalic acid (with access of light)

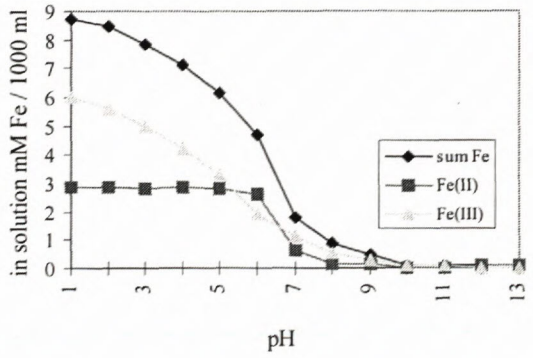

Fig. 26 Systems Fe^{2+} – oxalic acid (with access of light)

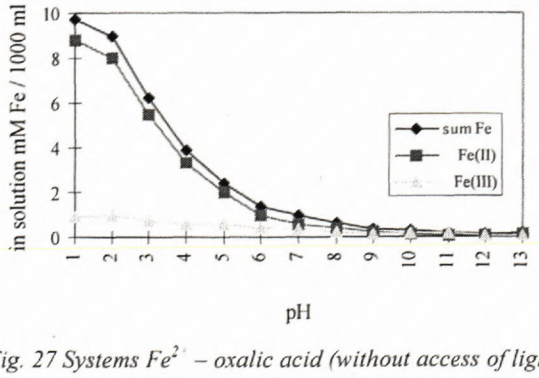

Fig. 27 Systems Fe^{2+} – oxalic acid (without access of light)

In the presence of tartaric acid the oxidation of Fe^{2+} compounds respond whether the system is in the light or dark (Figs. 29 and 30). Soluble compounds formation is shifted toward alkaline zones in these systems; however, a little bit less than in systems with Fe^{3+}.

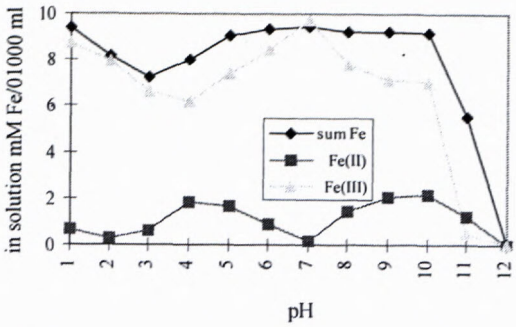

Fig. 28 Systems Fe^{2+} –tartaricacid (with access of light)

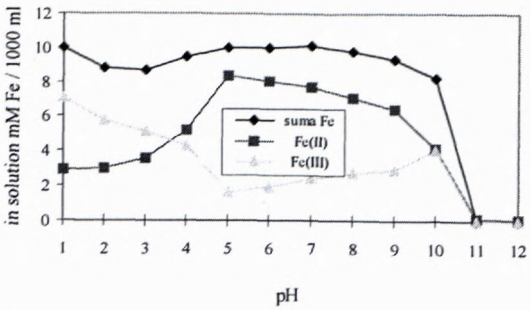

Fig. 31 Systems Fe^{2+} – citric acid (with access of light)

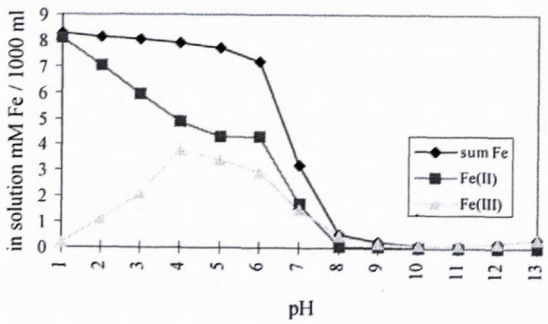

Fig. 29 Systems Fe^{2+} – tartaric acid (with access of light)

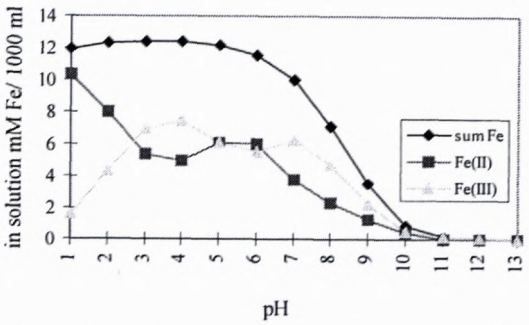

Fig. 32 Systems Fe^{2+} – citric acid (with access of light)

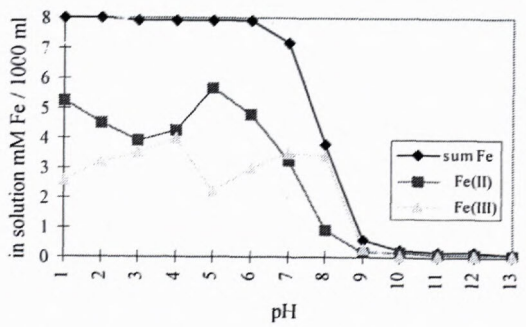

Fig. 30 Systems Fe^{2+} – tartaric acid (without access of light)

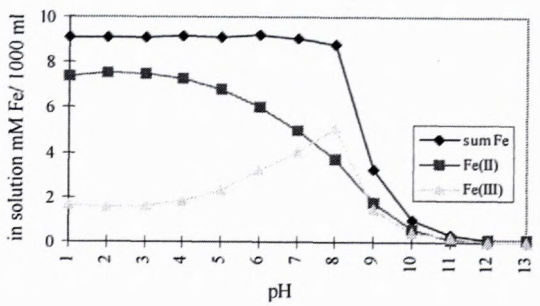

Fig. 33 Systems Fe^{2+} – citric acid (without access of light)

Tricarbonic citric acid in presence of light very strongly reduces Fe^{3+} compounds, with a maximum in the slightly acid to the alkaline zone (Fig. 31). The shift of formation of insoluble iron compounds is striking, up to strongly alkaline zone. The formation of insoluble compounds in the presence of citric acid is also shifted towards the alkaline zone in systems with Fe^{2+}(Figs. 32 and 33). Oxidation of Fe^{2+} interestingly occurs with or without light.

Conclusions

The experiments confirmed that the relationships in systems of Fe^{2+} and Fe^{3+} and organic substances (OS) are very complex. It was revealed that the formation of soluble and insoluble Fe and OS complexes as a condition of migration or accumulation of iron depends upon the degree of oxidation of Fe, the pH values of the environment, access to light and, in case of humic and fulvic acids (HA, FA), also upon the origin of the matter from which these acids were extracted. Even small change in the conditions may lead toward changes in the character of Fe - OS systems.

1. Significant by different results were obtained in the case of HA and FA extracted from peat obtained from two localities. When light was present, neither HA nor FA prevents the oxidation of Fe^{2+}.

2. Neither amino acid alanine and glycine suppresses oxidation of Fe^{2+} when light is present; however, under these conditions cysteine reduces Fe^{3+}.

3. Cellulose reduces Fe^{3+} in an acid environment, with access to light. D-glucose and starch do not prevent oxidation of Fe^{2+} when light is present. All these substances form with soluble complexes Fe^{2+} and Fe^{3+} and shift formation of insoluble Fe compounds toward higher pH values.

4. Carbonic acids have various influences on Fe compounds. In the systems with Fe^{3+} they shift the formation

of insoluble complexes towards the strongly alkaline zone, tartaric and citric acids also reduce Fe^{3+} in presence of light, and at the same time they do not suppress the oxidation of Fe^{2+}, neither in either light or in dark conditions (acetic, tartaric, citric acids). Oxalic acid prevents the oxidation of Fe^{2+} when light is blocked out and it forms insoluble oxalate $Fe(COOO)_2$ even in acid environment.

The information gathered from these study of systems Fe^{2+}, Fe^{3+} - selected OS may explain many problems of iron migration in the geochemical, pedological, biological and others processes.

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