SKB TECHNICAL REPORT

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Part 2. Complexes with iron and calcium

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ACIDS. PART 2. COMPLEXES WITH IRON AND CALCIUM

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CONTENTS

ABSTRACT

An ultrafiltration technique combined with ion-selective-electrode and atomic absorption methods have been employed to obtain information on the complex forming properties of fulvic acid with iron and calcium. A model for interpreting complexation of metal ions to fulvic acid at any pH, medium ionic strength and metal to fulvic acid ratio developed earlier /1/ has been used in an attempt to predict the nature of iron and calcium interaction to Armadale Horizon Bh fulvic acid. Binding of calcium to fulvic acid which is enhanced at pHs greater than 6.0 has reasonably been predicted by the model taking into consideration complications due to the polyelectrolyte nature and the heterogeneity of the fulvic acid. The lack of agreement observed between the model predicted binding behavior and the experimentally observed results for the fulvic acid-iron system has been attributed to the formation of metal-induced aggregation. Reduction of Fe(III) to Fe(II) by the fulvic acid as reported by other workers is corroborated.

1. INTRODUCTION:

Studies of metal ion interactions to humic substances have been done over the past ·century employing a variety of techniques /2 - 5/. One approach involves the characterization of the metal ion in the humic substance-metal ion system while another kind of approach measures the ligand ie. humic substance in the system.
Examples of the first approach include ion-specific-electrodes (ISE) and anodic stripping voltammetry while an example of the second approach is fluorescence measurement of the humic substances. Literature survey indicates that studies of metal ion interaction to humic substances have been dictated by the complexity of the chemistry involved and the availability of techniques in speciation determinations. Whereas a reasonably large number of publication exists on metal-humate studies involving such metal ions as Cu^{2+}, Pb^{2+}, Cd^{2+} and Ca^{2+} due to the availability of ion specific electrodes, far fewer studies of the interaction of humic substances with metal ions such as iron, (Fe^{2+}/Fe^{3+}), manganese and aluminum have been published due to the complexity of their aqueous chemistry and the existence of different oxidation states for some of these metal ions.

2. EXPERIMENTAL

2.1 Protonation Enhancement

In this phase of the program, potentiometric behavior of fulvic acid with increasing amounts of metal ion Ca^{2+}, Fe^{2+} and Fe^{3+}, was studied. Standard potentiometric acid-base titration procedures were employed /6/. In the case of Fe^{2+} and Fe^{3+}, additional precautions were taken especially in the FA-Fe system. To prevent the oxidation of Fe^{2+} to Fe^{3+}, O_2 was scrubbed from the stream of N_2 passing over the reaction vessel by bubbling it through a solution of ammonium meta-vanadate, NH_4VO_3, dissolved in HCl and reduced with amalgamated Zn. To avoid the effect of light on the system, the reaction vessel was wrapped in aluminum foil during the course of the experiment.

2.2 Ultrafitration Experiments

An Amicon Ultrafiltration cell, model 8050 in

conjuction with the Amicon Diaflo membrane YM2 was used in these series of experiments. Initial experimentation with the membrane in dialysis experiments showed that the rate of diffusion of the metal ion through the membrane and the extent of its separation from water was a function of membrane usage. The membrane was conditioned by repeated transfer of water and salt ($NaNO_3$) until the concentrations of metal ion added to the system was unaffected during filtration; the filtrate and the retentate concentrations of metal ion were the same i.e. the rejection coefficient for the metal ion was equal to zero. The opening of pores in the membrane, however, remained small enough to prevent-any transfer of fulvic acid; ie. the rejection coefficient for the fulvic acid remained equal to unity. The rejection of any solute by a specified membrane may be expressed by the rejection coefficient, R, given by the following expression:

$$R = \ln\{C_f/C_o\}/\ln\{V_o/V_f\} \tag{1}$$

where C_f is the final macrosolute concentration in the retentate, C_o is the initial macrosolute concentration, V_o is the initial sample volume and V_f is the final retentate volume. For a freely permeable solute, $R = 0$ while for a material rejected by the membrane, $R = 1$.

A membrane was conditioned for use by repeated filtrations of a solution of the metal ion (5.0×10^{-3} M) to be used in the experiment. The experiments were carried out in a batchwise mode. In a typical experiment, solutions containing known initial amounts of FA and metal ion at a defined ionic strength had their pH's adjusted by the addition of standard NaOH. The solutions were allowed to come to equilibrium by storing them in a dessicator covered with aluminum foil for a period of about twenty hours. After equilibration about 10% of the solution was removed by filtration. The complete rejection of fulvic acid was observed in all experimental runs. The pH of each solution was measured before and after filtration. The filtrates were then analysed using an appropriate technique. The ultrafiltration experiments were performed for the Fe^{2+}/Fe^{3+}-FA and Ca^{2+}-FA systems as a function of ionic strength and FA-to-metal ion ratios. Atomic Absorption measurements were performed for Fe^{2+}/Fe^{3+} and Ca^{2+} using a Perkin-Elmer Atomic Absortion

Spectrophotometer, model 503. An acetylene-air flame was used. The Fe analyses were performed at λ = 247 nm in the ultraviolet region while Ca was analysed at λ= 209 nm in the visible region. In addition, Fe^{2+} was analysed spectrophotometrically by measuring the absorbance of the tris complex with 1,10-phenanthroline at λ = 508 nm in the visible region. A Cary 118 Spectrophotometer was used for such analysis.

2.3 Fe^{2+} Analyses In Presence of FA

In a number of experiments Fe^{2+} left in solution after equilibration of the Fe -FA system was measured. Aliquots of the Fe^{2+}-FA mixture (3ml) were withdrawn and added to 7.00 ml of 1.0 x 10^{-3} M solution of 1,10-phenanthroline in a 10 ml volumetric flask. A twenty four hour period was allowed for the color of the tris complex to develop before absorbance measurements were performed.

2.4 Ion-Specific Electrode Technique

An ion-specific-electrode was employed in studies of Ca^{2+} interaction to Armadale Fulvic acid at two different ionic strengths. Special precautions were taken in the calibration of the calcium electrode especially at lower pH values. To remove the significant perturbation caused by H^+, a family of calibration curves were obtained at selected pH's at and below 4.5 to ensure that Nertian responses were obtained. The pH below which the electrode response was non-Nertian was considered the lowest limiting pH. In our studies, the limiting pH was found to be 3.85 /7/.

3. RESULTS

3.1 Protonation Enhancement

The results of the protonation enhancement experiments for Fe^{2+} and Fe^{3+} are shown in Figures 1 and 2 respectively. In figure 1, the titration curve of Fe^{2+} alone shows two buffered regions. The first region appears around pH of 5.0 - 5.50 while the second region appears at around 7.5 - 7.80. The titration of Fe^{3+} alone, Figure 2 shows no such buffered regions. Some brownish precipitates were observed in instances where metal ion alone was titrated, i.e. Fe^{2+}-only and Fe^{3+}-only systems. The

first buffered region in the Fe^{2+}-only system may be attributed to the first stable hydroxy complex of the metal ion while the second may be attributed to the second stable hydroxy complex of Fe^{2+}. For the FA-Fe^{2+} mixture, the first buffered region disappears due to solubilization of the Fe^{2+} by the fulvic acid molecule but the second buffered region at around pH of 7.80 is observed. This buffered region was more pronounced with an increase in the Fe^{2+}/FA ratio. It is interesting to note, however, that for Fe^{2+}/FA ratios of 1.24 and 1.86, an identical curve is obtained (curves D & E; Fig. 1). Even for Fe/FA ratio of 2.48 on milliequivalent basis, the curve is identical to the earlier ratios ie. 1.24 and 1.86, until at about pH of 8.0 before breaking away (curve F; Fig. 1). The superimposability of the curves with increasing amounts of Fe^{2+} relative to FA below pH of 8.00, though not completely understood, may be visualized as a reaction between Fe^{2+} and FA which has surface sorption characteristics and is controlled by the quantity of FA present. After pH of 8.0, the excess Fe^{2+} becomes the controlling factor. These results suggest that Fe^{2+} interacts strongly with the chelating groups accessible in the Armadale fulvic acid.

The fact that there is 33% extra proton release instead of a possible high of 50% or a low of 25% is consistent with the fact that the chelating potential of the salicylic acid site is less for Fe^{2+} than for Cu^{2+} and larger than for Eu^{3+}. In the presence of excess Fe^{2+} the hydrolysis of free Fe^{2+} becomes the controlling factor in the pH profile.

The Fe^{3+}-FA system produced remarkably different curves (fig.2) from those of the Fe^{2+}-FA system. The Fe^{3+}-only titration produced a curve similar to a weak acid-strong base curve /6/. In the presence of FA and with increasing amounts of Fe^{3+} the curve was further displaced to the right indicating that more base was required to neutralize the system. The small buffering which occurred below pH of 4.0 may be attributed to the strong hydrolysing ability of Fe^{3+} as compared to Fe^{2+} /8/.

In the Fe^{2+}-only system, it is difficult to prevent the oxidation of Fe^{2+} to Fe^{3+} especially at higher pH values. The diferences in the shapes of the curves obtained suggest, however, that the reaction between Fe^{2+} and FA is characteristically different
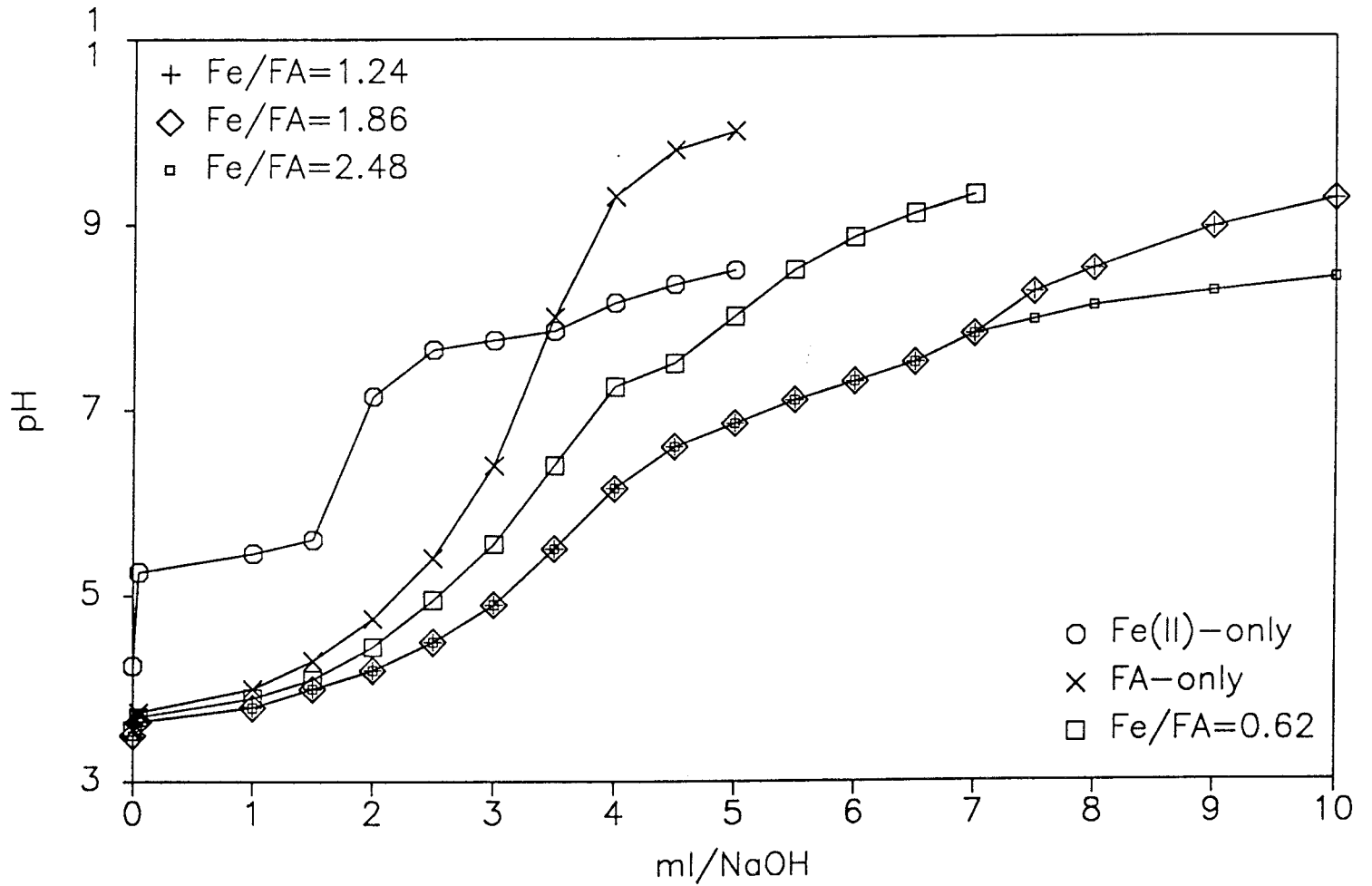
Figure 1. Potentiometric titration of Armadale
Horizon Bh FA with increasing amounts of
Fe(II). FA=7.0×10^{-4} M; I=0.100 M NaClO$_4$.
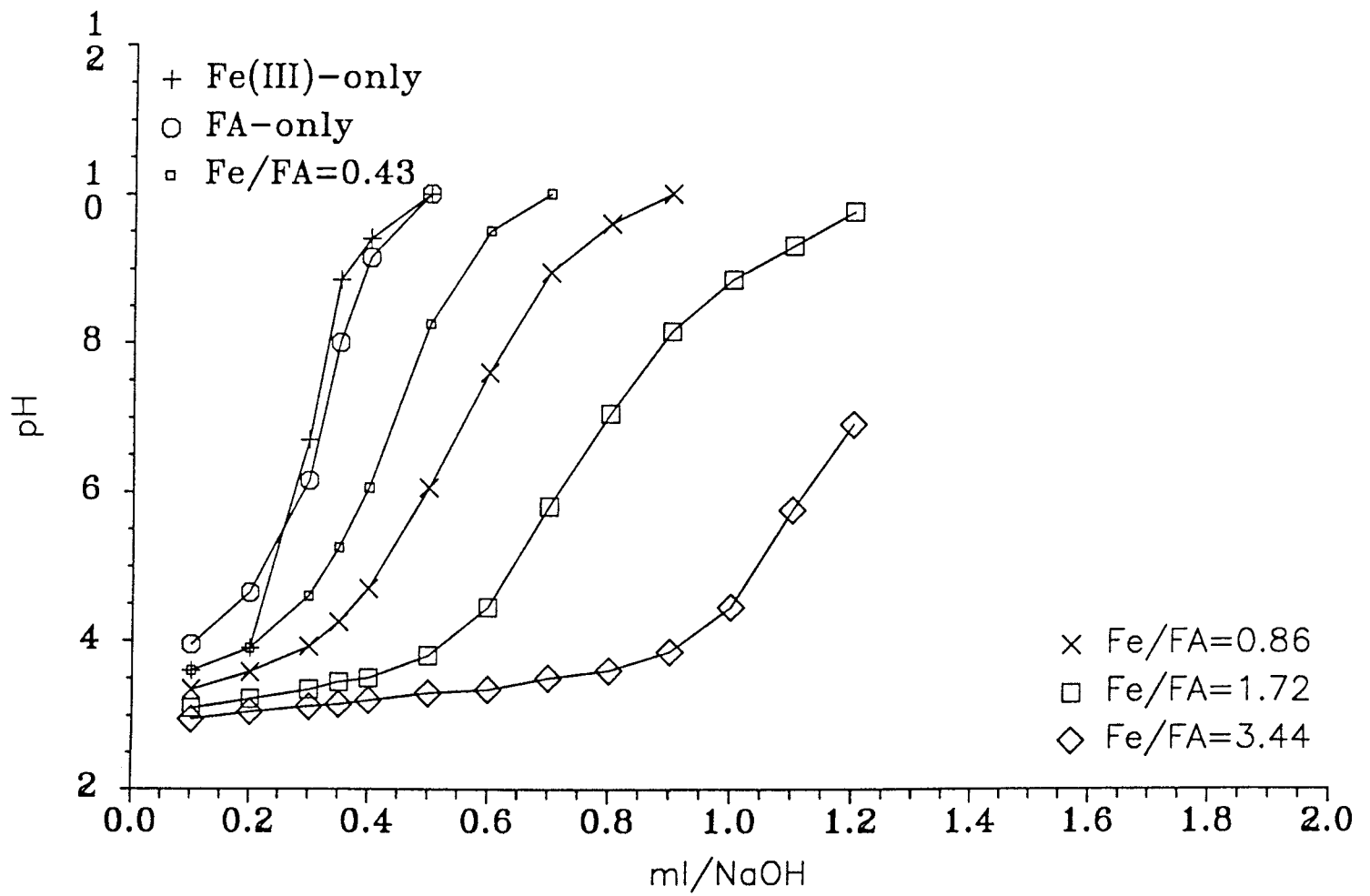
Figure 2. Potentiometric titration of Armadale Horizon Bh FA with increasing amounts of Fe(III); FA= 7.0×10^{-4} M; I=0.100 M NaClO$_4$.

from that between Fe^{3+} and FA.

Protonation enhancement studies /9/ with Ca^{2+} showed no significant extra acidity with increasing amounts of Ca^{2+}. This observation is consistent with the fact that no significant chelation takes place between Ca^{2+} and most mono-carboxylic acid functional groups /10/.

3.2 Ultrafiltration

Filtration of FA alone using the Amicon Diaflo membrane YM5 which has a cut-off molecular weight of 5000, yielded some fulvic acid in the filtrate. However, with a concentration of 4.0×10^{-4} M FA and 1.0×10^{-4} M Fe^{2+} in a mixture, filtration using the YM5 membrane yielded no fulvic acid molecule in the filtrate (ascertained by spectrophotometric analyses). This indicates that the FA molecule has fractions with an average molecular weight considerably smaller than 5000 to allow their passage through the membrane when filtered alone. In the presence of Fe^{2+} , however, the resultant mixture forms aggregates large enough to be held back by the YM5 membrane. Similar observation was made for FA-Fe^{3+} mixtures.

In the light of the above discussion, it is important to recognise that in the preceeding experiments, the fraction of metal ion which is retained upon filtration in the presence of FA is what is considered metal bound. Figs. 3 and 4 show that the rejection coefficients of the YM2 membrane for Fe^{2+} and Fe^{3+} respectively are both equal to zero. The figs. (3 & 4) show that the absorbances for the original, retentate and filtrate are all identical for initial metal ion concentration range of 1.0×10^{-4} M to 5.0×10^{-6} M.

Results for FA-Fe binding studies using the ultrafiltration technique are represented in Tables 1 and 2. In these tables, the results of the FA-Fe^{2+} and FA-Fe^{3+} systems at two ionic strengths (0.100 & 0.010 M $NaNO_3$) and for different fulvic acid to metal ion ratios are presented. The general observation was that for all the experimental sets, the amount of metal ion held back by the FA molecule increased with increase in pH. The tables show that the pH of the FA-Fe system does not change significantly in the course of the
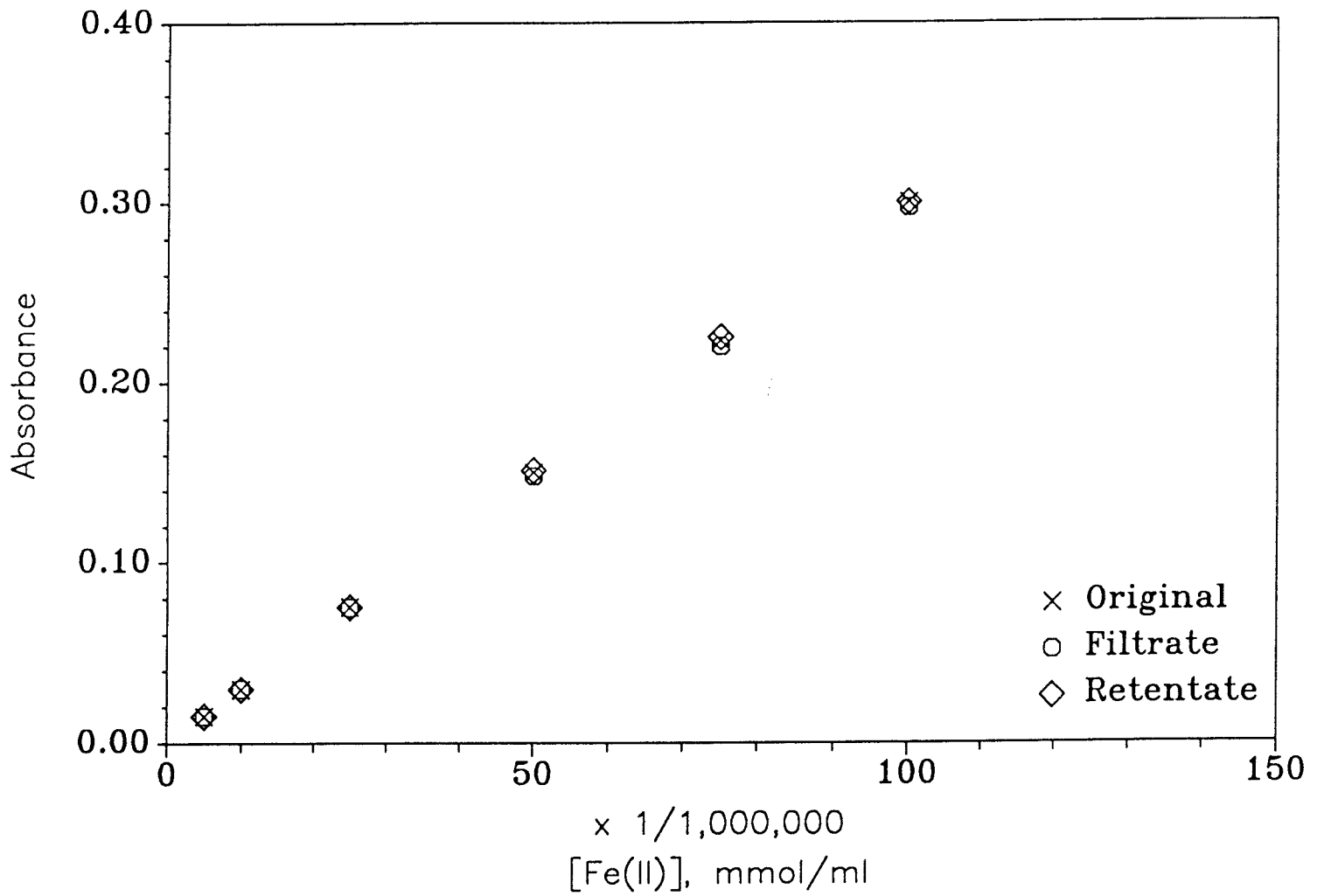
Figure 3. Retention of Fe^{2+} during filtration using Amicon YM2 Diaflo Membrane in conjunction with the Amicon 8050 ultrafiltration cell; $I=0.100$ M $NaClO_4$.
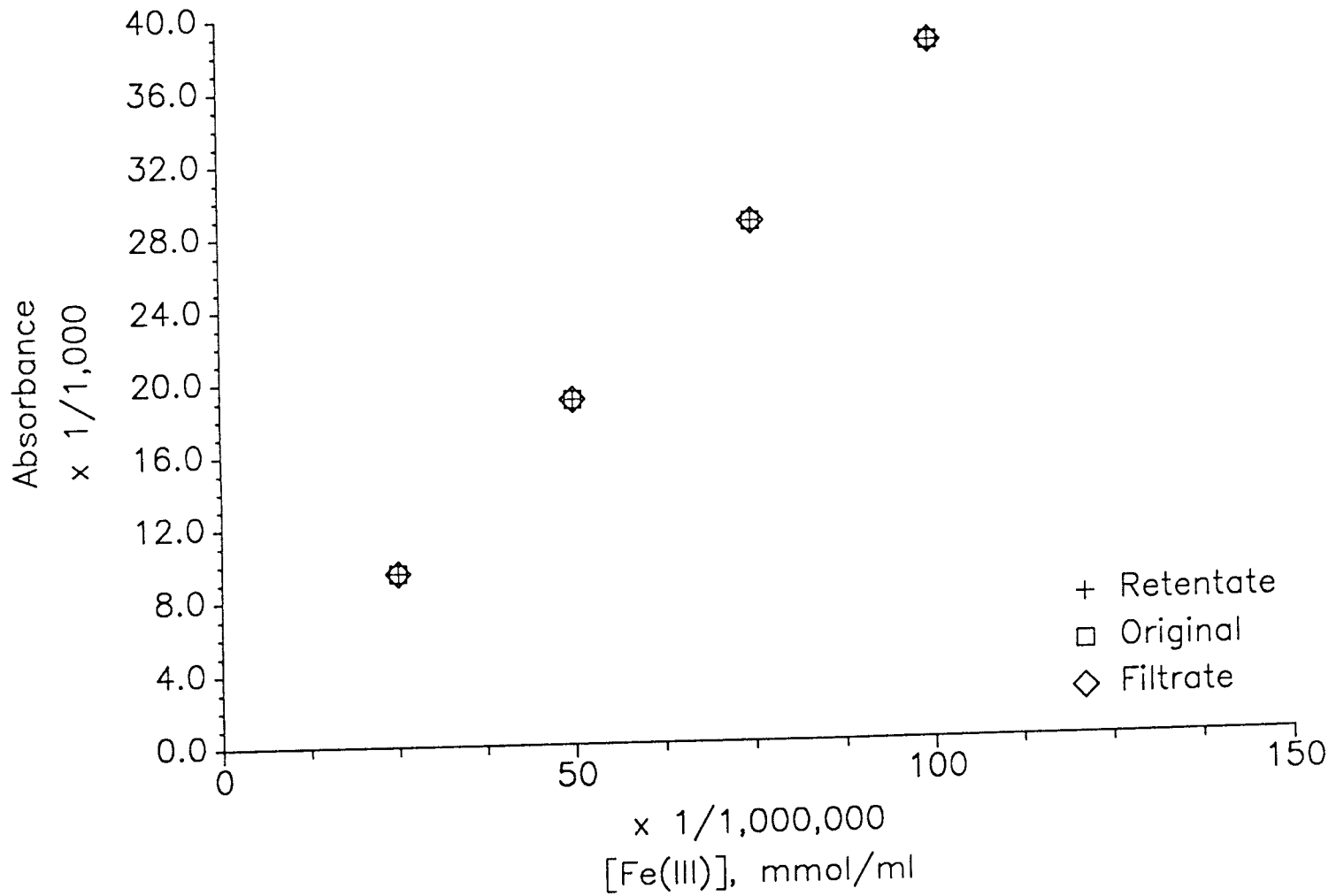
Figure 4. Retention of Fe^{3+} during filtration using the Amicon Ultrafiltration cell, model 8050, and the diaflo membrane, YM2; I=0.100 M $NaClO_4$.

filtration. This is due to the fact that even though the FA molecules were held back by the membrane since the H^+ had a rejection coefficient of zero, the pH of the system should not change appreciably if only a small volume of filtrate, V_f, as compared to the original volume, V_o, is collected. The proportion of metal bound increases with decrease in ionic strength and an increase in FA/Fe ratio. With a FA/Fe^{2+} ratio of 4 on milliequivalent basis, the proportion of metal bound in 0.10 M system at pH of about 3.5 is 33% (Table 1). This is significantly smaller than the proportion of metal bound in a $FA-Cu^{2+}$ system with similar ratio, (the proportion of metal bound is 62% at pH of about 3.5) and significantly larger than for the $Ca^{2+}-FA$ system. The proportion of metal bound for a FA/Fe ratio of 10 in 0.10 M $NaNO_3$ at pH of about 3.5 is 55% (Tab. 1-B). In 0.010 M $NaNO_3$ at a FA/Fe ratio of 4.6 (on meq. basis), the proportion of metal bound at pH of about 3.5 is 55% (Tab. 1-C). An increase in the FA/Fe^{2+} ratio to 11.5, results in a proportional increase of metal bound at pH of 3.5, i.e. 73% metal bound (Tab. 1-D). These values show significant increases as compared to values obtained in the 0.100 M $NaNO_3$ systems.

Results obtained in studies of $Fe^{3+}-FA$ mixtures in 0.10 and 0.01 M $NaNO_3$ are presented in Tab. 2. In these studies, a reduction of Fe^{3+} to Fe^{2+} was observed. The fraction of Fe^{3+} that was reduced and remained in solution was highly dependent on pH decreasing from 50 to 2% as the pH increased from 3 to 5.7. Analysis of the filtrates employing the 1,10-phenanthroline method (for Fe^{2+} only) yielded values similar (within experimental error) to those obtained by the atomic absorption analysis of total Fe ($Fe^{3+} + Fe^{2+}$). At pH's greater than or equal to 6.0, no Fe was detectable as Fe^{2+} or Fe^{3+}.

3.3 Experiments Without Fe^{2+} filtration

In Tab. 3 where the results of the direct analysis of Fe^{2+} is made without filtration, the quantity designated as metal bound ought to be considered as that portion of Fe^{2+} which was not released by the FA molecule for complexation with the 1,10-phenanthroline molecule. Because of competition between the FA molecule and the 1,10 phenanthroline molecule for Fe^{2+}, the values of Fe^{2+} measured as free is the highest limit that can possibly be

measured for the FA-Fe^{2+} system. As the pH increases, very little Fe^{2+} is left in solution to complex the 1,10-phenanthroline molecule. This pattern is observable in both 0.100 M and 0.010 M NaNO$_3$ systems. As a consequence of the above mentioned competition, the estimate of bound metal is significantly smaller than in the ultrafiltration method (Tab. 1).

3.4 Model-based computation of Fe^{2+}-FA Binding Studies

Computations of the Fe^{2+}-FA system using the model developed in this laboratory involving adequate characterization of the Armadale Bh Horizon fulvic acid and literature-based stability constants were effected /1/. The results of representative data in 0.100 M NaNO$_3$ shown in Tab. 4 indicate that the model-based computation of Fe^{2+}-bound is smaller than the experimentally observed Fe^{2+}-bound. The inability of the model-based predictions to describe the uptake of Fe^{2+} by Armadale fulvic acid is probably due to a number of factors among which are the following:

- possible metal induced aggregation of the fulvic acid in the presence of Fe^{2+}.

- complex aqua-complexation of the Fe^{2+} ion.

- nonavailability of concise literature-based stability constants.

3.5 Ca^{2+}-FA Binding Studies

Ca^{2+}-FA binding studies were done via two methods for comparison. These methods are:

- the direct measurement of Ca^{2+} in solution by an ion specific electrode (ISE)

- ultrafiltration of the Ca^{2+}-FA mixture followed by AA analysis of Ca^{2+} in the filtrate.

Sample results for both methods of study are presented in Tables 5 -7. Our model-based computations for different FA/Ca^{2+} ratios in 0.010 M NaNO$_3$ solutions are listed in the Tabs. In the ultrafiltration experiments with FA/Ca^{2+} ratio of 1.5, on milliequivalent basis, the results show that at pH of 4.00, 24% of the initial Ca^{2+} is

bound. However, for a similar FA/Ca^{2+} ratio in the ISE method, only 14% of the Ca^{2+} is bound at pH of 4.0. The two methods yield comparable results at higher pH values. In the ultrafiltration method with FA/Ca^{2+} ratio of 1.5, the proportion of Ca^{2+} bound at pH of 6.27 is 49% which compares well with the value of 48% for a similar FA/Ca^{2+} ratio at a pH of 6.29 in the ISE method.

In both ISE and Ultrafiltration studies of the fulvic acid-Ca^{2+} systems, the model based computations were smaller than the experimentally observed Ca^{2+} bound. This difference may be accounted for by considering the fact that some of the Ca^{2+} ions are only imbibed in the polymer domain and not necessarily bound to the polymer. Computations of the Ca^{2+} ions imbibed in the polymer domain may be effected by using the Donnan potential relationship as follows:

$$Ca_b = Ca_b^P + Ca_f^P \qquad (2)$$

where Ca_b is the total experimental Ca^{2+} bound, Ca_b^P is the real metal bound to the polymer and Ca_f^P is the free Ca^{2+} trapped in the polymer domain. The Donnan potential expression involving the free metal ion in the polymer domain and the bulk solution may be expressed as follows:

$$Ca_f^P/Ca_f = \{Na_f^P/Na_f\}^2 \qquad (3)$$

In the above expression the p represents the polymer domain. Ca_f is the activity of the free calcium ions in the bulk solution, Na_f is the activity of free sodium ions in the bulk solution, Na_f^P is the activity of sodium ions in the polymer domain which is related to the degree of neutralization of the polymer, α_{HA}, and Ca_f^P is the Ca^{2+} ions trapped in the polymer domain but not bound to the polymer. Computations of Ca_f^P may be effected by employing the computational procedure developed earlier using the Donnan potential approach /11/.

4. CONCLUSIONS

Rigorous analyses of the FA-Fe^{2+} data with our two phase model /1,11/, showed that the model-estimated metal bound was smaller than the experimentally-observed metal bound. However, in the FA-Ca^{2+} binding studies, there was considerable agreement

between metal bound experimentally and model-estimated. The failure of the model to predict the FA-Fe^{2+} system might be due to a combination of factors including the complex aqueous chemistry of the Fe^{2+} /Fe^{3+} couple and the high tendency of the Fe^{2+} hydrolysis products to induce aggregation.

The studies have shown, however, that there is considerable affinity of fulvic acid for Fe^{2+} and Fe^{3+} ions. The extent of Fe^{2+} complexation by the fulvic acid molecule which is dependent on the FA-to-metal ion ratio, the pH and the ionic strength of the system is slightly smaller than the complexation of Cu^{2+} to FA. There is binding of Ca^{2+} to fulvic acid but this is less significant at pH values below 6. Studies of FA-Ca^{2+} system in 0.100 M $NaNO_3$ indicated that binding is far much reduced especially at pH's below 4.5.

An additional problem with the FA-Fe^{2+}/Fe^{3+} studies is determining the oxidation state in which the metal ion is complexed to the fulvic acid molecule. In their studies of Fe^{3+} binding by humic materials, Senesi et al. /12/ concluded that all of the Fe^{3+} bound by the humic materials was in the tervalent state. This studies suggest that the Fe^{2+}/Fe^{3+} ion complexes to the fulvic acid molecule probably in both oxidation states. The reduction of Fe^{3+} to Fe^{2+} by humic materials has been reported by other researchers /13,14/.

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TABLE 1 -Armadale FA-Fe(II) Binding Studies - Ultrafiltration

A: System: $FA-Fe^{2+}$; I=0.100M $NaNO_3$; Fe_T^{2+} =0.005mmoles ;FA_T =0.04045meq.;VI=50ml

ml/NaOH	pH_{before}	pH_{after}	Fe^{2+}/M	Fe_b/mmoles
0.00	3.517	3.479	6.695×10^{-5}	1.653×10^{-3}
0.10	3.740	3.730	5.683×10^{-5}	2.153×10^{-3}
0.20	4.415	4.419	2.423×10^{-5}	3.784×10^{-3}
0.25	4.780	4.764	1.483×10^{-5}	4.255×10^{-3}
0.30	4.818	4.790	1.149×10^{-5}	4.423×10^{-3}
0.35	5.317	5.362	4.759×10^{-6}	4.760×10^{-3}
0.40	5.850	5.823	4.482×10^{-6}	4.774×10^{-3}

B: System:$FA-Fe^{2+}$; I=0.10 M $NaNO_3$; Fe^{2+}_T =0.002mmoles; FA_T=0.04012 meq.; V^I=50.0 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}/M	Fe_b/mmoles
0.00	3.472	3.457	1.793×10^{-5}	1.104×10^{-3}
0.10	3.732	3.722	1.266×10^{-5}	1.368×10^{-3}
0.15	3.926	3.968	1.100×10^{-5}	1.448×10^{-3}
0.20	4.223	4.223	4.897×10^{-6}	1.754×10^{-3}
0.25	4.567	4.583	4.655×10^{-6}	1.766×10^{-3}
0.30	5.021	5.012	2.056×10^{-6}	1.897×10^{-3}
0.35	5.790	5.860	1.571×10^{-6}	1.921×10^{-3}

C: System:$FA-Fe^{2+}$; I=0.010 M $NaNO_3$; Fe^{2+}_T =0.005mmoles; FA_T=0.04608 meq.; V_I=50.5 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}/M	Fe_b/mmoles
0.00	3.430	3.442	4.423×10^{-5}	2.767×10^{-3}
0.10	3.700	3.640	3.047×10^{-5}	3.458×10^{-3}
0.20	3.983	4.023	1.820×10^{-5}	4.077×10^{-3}
0.25	4.215	4.255	1.252×10^{-5}	4.365×10^{-3}
0.30	4.555	4.529	6.214×10^{-6}	4.684×10^{-3}
0.35	5.164	5.184	4.551×10^{-6}	4.769×10^{-3}
0.40	5.572	5.597	3.581×10^{-6}	4.818×10^{-3}

D: System:$FA-Fe^{2+}$; I=0.010 M $NaNO_3$; Fe^{2+}_T =0.002mmoles; FA_T=0.04608 meq; V_I = 50.2 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}/M	Fe_b/mmoles
0.00	3.463	3.480	1.072×10^{-5}	1.462×10^{-3}
0.20	4.117	4.114	3.205×10^{-6}	1.839×10^{-3}
0.40	6.074	6.145	1.404×10^{-6}	1.929×10^{-3}

TABLE 2- Armadale FA-Fe(III) Binding Studies - Ultrafiltration.

A: System:FA-Fe^{3+}; I=0.10 M NaNO$_3$; Fe$_T$ =0.005mmoles; FA$_T$=0.0350meq.;
V$_I$=51.0 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}+Fe^{3+}	Fe^{2+}	Fe$_b$/mmoles
0.00	2.938	2.919	4.844x10^{-5}	5.291x10^{-5}	2.530x10^{-3}
0.10	3.028	3.006	4.500x10^{-5}	4.813x10^{-5}	2.701x10^{-3}
0.40	3.456	3.435	3.812x10^{-5}	3.867x10^{-5}	3.041x10^{-3}
0.50	3.790	3.774	3.468x10^{-5}	3.486x10^{-5}	3.214x10^{-3}
0.60	4.362	4.364	2.093x10^{-5}	2.347x10^{-5}	3.920x10^{-3}

B: System:FA-Fe   ;   I=0.10M   NaNO^3;   FeT   =0.005mmoles;
FA^T=0.04702meq.,

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}+Fe^{3+}	Fe^{2+}	Fe$_b$/mmoles
0.00	3.334	3.325	4.167x10^{-5}	4.252x10^{-5}	2.896x10^{-3}
0.10	3.482	3.501	3.646x10^{-5}	3.296x10^{-5}	3.155x10^{-3}
0.15	3.634	3.638	3.021x10^{-5}	3.060x10^{-6}	3.470x10^{-3}
0.20	3.730	3.730	3.021x10^{-5}	3.150x10^{-5}	3.470x10^{-3}
0.40	4.821	4.830	8.333x10^{-6}	4.832x10^{-6}	4.576x10^{-3}
0.50	5.679	5.731	5.208x10^{-6}	1.576x10^{-6}	4.734x10^{-3}

C: System: FA-Fe^{3+}; I=0.10 M NaNO$_3$; Fe$_T$ =0.010mmoles; FA$_T$=0.04702 meq.;
V$_I$=51.0 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}+Fe^{3+}/M	Fe^{2+}	Fe$_b$/mmoles
0.00	3.245	3.242	1.031x10^{-4}	9.444x10^{-5}	4.742x10^{-3}
0.10	3.522	3.568	8.633x10^{-5}	7.313x10^{-5}	5.573x10^{-3}
0.40	4.114	4.136	5.967x10^{-5}	5.325x10^{-5}	6.933x10^{-3}
0.60	6.086	6.051	-	-	-

D: System: FA-Fe^{3+}; I=0.010 M NaNO$_3$; Fe$^{3+}_T$=0.005 mmoles; FA$_T$= 0.0403 meq
V$_I$=50.5 ml

ml/NaOH	pH^{before}	pH^{after}	Fe^{2+}+Fe^{3+}/M	Fe^{2+}/M	Fe$_b$/mmoles
0.00	3.354	3.376	3.225x10^{-5}	3.371x10^{-3}	
0.10	3.574	3.589	2.873x10^{-5}	3.546x10^{-3}	
0.15	3.716	3.714	2.284x10^{-5}	3.843x10^{-3}	
0.20	3.888	3.868	1.935x10^{-5}	4.019x10^{-3}	
0.30	4.418	4.473	2.931x10^{-6}	4.851x10^{-3}	
0.40	5.671	5.677	1.758x10^{-6}	4.910x10^{-3}	
0.45	6.003	6.114	-	-	
0.50	6.675	6.763	-	-	
0.60	8.219	7.921	-	-	

TABLE 3 - Armadale FA-Fe(II) Binding Studies- Analysis of Fe(II) Without Filtration.

A: System:FA-Fe^{2+}; I=0.010 M NaNO$_3$; Fe$^{2+}_T$ =0.020mmoles; FA$_T$=0.02991 meq.; V$_I$=52.0ml

ml/NaOH	pH	Fe^{2+}/M	Fe$_b$/mmoles
0.00	3.442	3.416×10^{-4}	2.150×10^{-3}
0.10	3.633	3.278×10^{-4}	2.923×10^{-3}
0.20	3.880	2.991×10^{-4}	4.385×10^{-3}
0.30	4.146	2.444×10^{-4}	7.217×10^{-3}
0.40	4.394	1.757×10^{-4}	1.079×10^{-2}
0.50	5.005	1.365×10^{-4}	1.284×10^{-2}
0.60	5.768	1.028×10^{-4}	1.459×10^{-2}
0.70	6.550	6.731×10^{-5}	1.645×10^{-2}
0.80	6.735	5.689×10^{-5}	1.700×10^{-2}

B: System: FA-Fe^{2+}; I=0.10 M NaNO$_3$; Fe$^{2+}_T$ =0.020mmoles; FA$_T$=0.03108 meq.; V$_I$=52.0 ml

ml/NaOH	pH	Fe^{2+}/M	Fe$_b$/mmoles
0.10	3.654	3.581×10^{-4}	1.344×10^{-3}
0.20	3.879	3.389×10^{-4}	2.307×10^{-3}
0.30	4.176	3.029×10^{-4}	4.158×10^{-3}
0.40	4.410	2.343×10^{-4}	7.724×10^{-3}
0.50	4.865	1.727×10^{-4}	1.094×10^{-2}
0.60	5.403	1.184×10^{-4}	1.377×10^{-2}
0.70	6.200	7.750×10^{-5}	1.592×10^{-2}
0.80	7.455	4.377×10^{-5}	1.769×10^{-2}

Table 4 - Model-based Calculations of Armadale FA-Fe(II) Binding Studies - Ultrafiltration

A: System: FA= 0.03108 mmoles; Fe^{2+}=0.02 mmoles; I=0.100 M KNO_3; V_I=52.0ml

ml/NaOH	pH	Fe_f/M	Fe_b-calc	Fe_b-exp
0.10	3.654	3.581×10^{-4}	3.879×10^{-4}	1.343×10^{-3}
0.20	3.879	3.389×10^{-4}	6.403×10^{-4}	2.309×10^{-3}
0.30	4.176	3.029×10^{-4}	1.031×10^{-3}	4.158×10^{-3}
0.40	4.410	2.343×10^{-4}	1.056×10^{-3}	7.723×10^{-3}
0.50	4.865	1.727×10^{-4}	1.244×10^{-3}	1.093×10^{-2}
0.60	5.403	1.184×10^{-4}	1.474×10^{-3}	1.377×10^{-2}
0.70	6.200	7.750×10^{-5}	2.504×10^{-3}	1.592×10^{-2}
0.80	7.455	4.377×10^{-5}	6.771×10^{-3}	1.769×10^{-2}

B: System: FA-Fe^{2+}; I=0.10 M KNO_3; FA=0.04012 mmoles; Fe^{2+}=0.002mmoles; V_I=50.0 ml

ml/NaOH	pH	Fe_f/M	Fe_b-calc	Fe_b-exp/mmole
0.00	3.472	1.793×10^{-5}	1.681×10^{-5}	1.104×10^{-3}
0.10	3.732	1.266×10^{-5}	2.482×10^{-5}	1.366×10^{-3}
0.15	3.926	1.100×10^{-5}	3.801×10^{-5}	1.448×10^{-3}
0.20	4.223	4.897×10^{-6}	3.483×10^{-5}	1.754×10^{-3}
0.25	4.567	4.655×10^{-6}	6.060×10^{-5}	1.766×10^{-3}
0.30	5.021	2.056×10^{-6}	6.335×10^{-5}	1.897×10^{-3}
0.35	5.790	1.571×10^{-6}	1.858×10^{-4}	1.921×10^{-3}

C: System: FA-Fe^{2+} ; I=0.100 M KNO_3; Fe^{2+}=0.005 mmoles; FA=0.04045 mmoles; V_I=50.0 ml

ml/NaOH	pH	Fe^{2+}_f/M	Fe_b-cal	Fe_b-exp
0.00	3.517	6.695×10^{-5}	7.090×10^{-5}	1.653×10^{-3}
0.10	3.740	5.683×10^{-5}	1.124×10^{-4}	2.153×10^{-3}
0.20	4.415	2.423×10^{-5}	2.234×10^{-4}	3.784×10^{-3}
0.25	4.780	1.483×10^{-5}	2.565×10^{-4}	4.255×10^{-3}
0.30	4.818	1.149×10^{-5}	2.184×10^{-4}	4.422×10^{-3}
0.35	5.317	4.759×10^{-6}	2.293×10^{-4}	4.760×10^{-3}
0.40	5.850	4.482×10^{-6}	4.586×10^{-4}	4.774×10^{-3}

Beta for third enol site = 1.00×10^5
Kexchange for amino groug= 0.00451
Kexchange for enol group = 0.001
Kexchange for salicylic chelate = 3.55×10^{-7}
Beta for acid with pK of 4.2 = 65
Beta for Salicylic unidentate = 25
Beta for acid with pK of 1.8 = 20
Beta for enol unidentate = 90

TABLE 5 - Ca(II)-Armadale Bh Horizon FA Binding Studies - Ultrafiltration

A: System: FA=0.03074 mmoles; Ca(II) =0.010 mmoles; I=0.100 M KNO_3; V_I=51.0 ml

ml/base	pH	pCa	Ca_b-calc	Ca_b-exp/mmoles
0.00	3.742	3.818	3.507×10^{-4}	2.245×10^{-3}
0.10	4.141	3.830	8.941×10^{-4}	2.442×10^{-3}
0.15	4.506	3.863	1.580×10^{-3}	2.988×10^{-3}
0.20	5.036	3.900	2.910×10^{-3}	3.554×10^{-3}
0.25	5.848	3.963	3.270×10^{-3}	4.419×10^{-3}
0.27	6.269	4.000	3.447×10^{-3}	4.873×10^{-3}
0.29	6.902	4.041	4.605×10^{-3}	5.333×10^{-3}
0.31	6.982	4.086	4.556×10^{-3}	5.791×10^{-3}

B: System: FA=0.03074 mmoles; Ca(II)=0.005 mmoles; I=0.010 M KNO_3; V_I=50.5 ml

ml/NaOH	pH	pCa	Ca_b-calc	Ca_b-exp/mmoles
0.00	3.606	4.140	1.169×10^{-4}	1.342×10^{-3}
0.10	4.100	4.187	3.984×10^{-4}	1.710×10^{-3}
0.20	5.168	4.323	1.543×10^{-3}	2.590×10^{-3}
0.25	5.984	4.475	1.551×10^{-3}	3.300×10^{-3}
0.27	6.266	4.569	1.468×10^{-3}	3.630×10^{-3}
0.29	6.499	4.638	1.543×10^{-3}	3.831×10^{-3}
0.31	6.797	4.638	1.693×10^{-3}	3.831×10^{-3}

C: System:FA=0.03074 mmoles; Ca(II)=0.003 mmoles; I=0.010 M KNO_3; V_I=50.3 ml

ml/NaOH	pH	pCa	Ca_b-cal	Ca_b-exp/mmoles
0.00	3.635	4.301	8.851×10^{-5}	4.848×10^{-4}
0.20	5.270	4.636	1.015×10^{-3}	1.832×10^{-3}
0.25	6.025	4.810	1.053×10^{-3}	2.217×10^{-3}
0.27	6.423	4.848	1.119×10^{-3}	2.282×10^{-3}
0.28	6.596	4.936	1.087×10^{-3}	2.414×10^{-3}
0.29	6.787	4.959	1.153×10^{-3}	2.444×10^{-3}
0.30	6.877	4.979	1.185×10^{-3}	2.469×10^{-3}
0.31	7.067	5.018	1.286×10^{-3}	2.514×10^{-3}

TABLE 6 - Ca(II)-FA Binding Studies ; Ion-Selective-Electrode Method

A: System: FA=0.03074 mmoles; Ca(II)=0.010 mmoles; I=0.010 M;
V_I=50.10 ml

ml/NaOH	pH	pCa	Ca_b-calc	Ca_b-exp/mmoles
0.10	4.016	3.767	7.726×10^{-4}	1.416×10^{-3}
0.12	4.149	3.789	9.832×10^{-4}	1.836×10^{-3}
0.14	4.284	3.803	1.237×10^{-3}	2.092×10^{-3}
0.16	4.463	3.818	1.607×10^{-3}	2.358×10^{-3}
0.18	4.661	3.833	2.782×10^{-3}	2.614×10^{-3}
0.20	4.893	3.840	3.046×10^{-3}	2.729×10^{-3}
0.22	5.167	3.863	3.236×10^{-3}	3.102×10^{-3}
0.24	5.476	3.897	3.343×10^{-3}	3.619×10^{-3}
0.26	5.849	3.941	3.392×10^{-3}	4.231×10^{-3}
0.27	6.047	3.959	3.453×10^{-3}	4.464×10^{-3}
0.28	6.287	3.989	3.533×10^{-3}	4.833×10^{-3}
0.29	6.543	4.026	3.723×10^{-3}	5.254×10^{-3}
0.30	6.874	4.048	4.458×10^{-3}	5.487×10^{-3}
0.31	7.271	4.082	5.728×10^{-3}	5.826×10^{-3}

B: System: FA=0.03074 mmoles; Ca(II)= 0.005 mmoles; I=0.010 M KNO$_3$;
V_I=50.05 ml

ml/NaOH	pH	pCa	Ca_b-calc	Ca_b-exp/mmoles
0.00	4.054	4.061	4.644×10^{-4}	6.422×10^{-4}
0.12	4.162	4.068	5.851×10^{-4}	7.101×10^{-4}
0.14	4.300	4.064	7.814×10^{-4}	6.687×10^{-4}
0.16	4.500	4.082	1.064×10^{-3}	8.429×10^{-4}
0.18	4.732	4.104	1.811×10^{-3}	1.047×10^{-3}
0.20	5.021	4.132	1.973×10^{-3}	1.292×10^{-3}
0.22	5.274	4.175	2.015×10^{-3}	1.640×10^{-3}
0.24	5.589	4.229	2.021×10^{-3}	2.032×10^{-3}
0.26	6.029	4.289	2.035×10^{-3}	2.414×10^{-3}
0.28	6.581	4.368	2.189×10^{-3}	2.843×10^{-3}
0.29	6.935	4.429	2.543×10^{-3}	3.125×10^{-3}
0.30	7.299	4.500	3.216×10^{-3}	3.408×10^{-3}

C: System: FA=0.03074 mmoles; Ca(II)=0.003 mmoles; I=0.010 M NaNO$_3$;
V_I=50.03 ml

ml/base	pH	pCa	Ca_b-calc	Ca_b-exp/mmoles
0.10	4.007	4.419	1.921×10^{-4}	1.090×10^{-3}
0.12	4.138	4.419	2.670×10^{-4}	1.089×10^{-3}
0.14	4.295	4.426	3.770×10^{-4}	1.119×10^{-3}
0.16	4.485	4.426	5.492×10^{-4}	1.118×10^{-3}
0.18	4.700	4.494	1.060×10^{-3}	1.389×10^{-3}
0.20	4.943	4.494	1.147×10^{-3}	1.574×10^{-3}
0.22	5.258	4.547	1.147×10^{-3}	1.574×10^{-3}
0.24	5.597	4.637	1.148×10^{-3}	1.840×10^{-3}
0.26	5.997	4.765	1.097×10^{-3}	2.136×10^{-3}
0.28	6.475	4.890	1.091×10^{-3}	2.352×10^{-3}
0.29	6.734	4.965	1.118×10^{-3}	2.455×10^{-3}

0.30	7.044	5.022	1.259×10^{-3}	2.522×10^{-3}
0.32	7.951	5.255	2.352×10^{-3}	2.720×10^{-3}
0.33	8.336	5.419	2.987×10^{-3}	2.808×10^{-3}

D: System: FA=0.03074 mmoles; Ca(II)=0.010 mmole; I=0.10 M $NaNO_3$; V_I=50.10 ml

ml/NaOH	pH	pCa	Ca_b-calc	Ca_b-exp/mmole
0.100	3.941	3.783	3.847×10^{-4}	1.726×10^{-3}
0.120	4.045	3.745	5.333×10^{-4}	9.661×10^{-4}
0.140	4.182	3.776	6.861×10^{-4}	1.585×10^{-3}
0.16	4.338	3.770	9.658×10^{-4}	1.465×10^{-3}
0.18	4.519	3.759	1.396×10^{-3}	1.242×10^{-3}
0.20	4.748	3.759	9.473×10^{-3}	1.239×10^{-3}
0.22	5.014	3.769	1.054×10^{-3}	1.435×10^{-3}
0.24	5.350	3.762	1.177×10^{-3}	1.292×10^{-3}
0.26	5.740	3.772	1.272×10^{-3}	1.487×10^{-3}
0.27	5.980	3.783	1.343×10^{-3}	1.698×10^{-3}
0.28	6.245	3.793	1.484×10^{-3}	1.886×10^{-3}
0.29	6.564	3.810	1.806×10^{-3}	2.196×10^{-3}
0.30	6.940	3.817	2.583×10^{-3}	2.319×10^{-3}

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[1] Starprog AB
[2] SKB AB
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[2] SKB AB
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Department of Nuclear Chemistry, Chalmers University of Technology, Gothenburg
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Lars Werme[1], Patrik Sellin[1], Roy Forsyth[2]
[1] Swedish Nuclear Fuel and waste Management Co (SKB)
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Ulla Bergström, Sture Nordlinder
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H D Schorscher[1], M E Shea[2]
[1] University of Sao Paulo
[2] Battelle, Chicago
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N Waber[1], H D Schorscher[2], A B MacKenzie[3], T Peters[1]
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N Waber
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M E Shea
Battelle, Chicago
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D C Holmes[1], A E Pitty[2], R Noy[1]
[1] British Geological Survey, Keyworth
[2] INTERRA/ECL, Leicestershire, UK
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Chemical and isotopic composition of groundwaters and their seasonal variability at the Osamu Utsumi and Morro do Ferro analogue study sites, Poços de Caldas, Brazil
D K Nordstrom[1], J A T Smellie[2], M Wolf[3]
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[3] Gesellschaft für Strahlen- und Umweltforschung (GSF), Munich
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Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

A B MacKenzie[1], P Linsalata[2], N Miekeley[3], J K Osmond[4], D B Curtis[5]
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Natural series nuclide and rare earth element geochemistry of waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

N Miekeley[1], O Coutinho de Jesus[1], C-L Porto da Silveira[1], P Linsalata[2], J N Andrews[3], J K Osmond[4]
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Chemical and physical characterisation of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Microbiological analysis at the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil

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Testing of geochemical models in the Poços de Caldas analogue study

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Testing models of redox front migration and geochemistry at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

J Cross[1], A Haworth[1], P C Lichtner[2], A B MacKenzi[3], L Moreno[4], I Neretnieks[4], D K Nordstrom[5], D Read[6], L Romero[4], S M Sharland[1], C J Tweed[1]
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L M Cathles[1], M E Shea[2]
[1] University of Cornell, New York
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December 1990

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Geochemical modelling of water-rock interactions at the Osamu Utsumi mine and Morro do Ferro analogue sites, Poços de Caldas, Brazil

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TR 90-24
**The Poços de Caldas Project: Summary
and implications for radioactive waste
management**

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TR 90-25
**Kinetics of $UO_2(s)$ dissolution reducing
conditions:
numerical modelling**

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TR 90-26
**The effect from the number of cells, pH and
lanthanide concentration on the sorption
of promethium on gramnegative bacterium
(Shewanella Putrefaciens)**

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TR 90-27
**Isolation and characterization of humics
from natural waters**

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