ICW note 1772

March 1987

nota
instituut voor cultuurtechniek en waterhuishouding, wageningen

IMPORTANT IONS AND ION-PAIRS IN SOLUTIONS OF ACID SULFATE SOILS AND THE INFLUENCE OF THE REDOXPOTENTIAL, CO$_2$ PRESSURE AND ACIDITY ON THEIR ACTUAL CONCENTRATIONS

drs. C.J. Ritsema

CONTENTS

1. INTRODUCTION

The wish to calculate the activities of ions and ion-pairs in solutions of acid sulfate soils makes it necessary to extend the original version of the model COMPLEX as been formulated by ABDEL KHALIK and BLÖMER (1984).

The original version of COMPLEX, a computer program for solving chemical equilibria, calculates the ion activities of 19 major components and species. ABDEL KHALIK and BLÖMER (1984) distinguish respectively the components Na^+, Ca^{2+}, Mg^{2+}, H^+, Cl^-, HCO_3^-, SO_4^{2-}, OH^- and the species $NaCO_3^-$, $NaHCO_3^o$, $NaSO_4^-$, $CaCO_3^\circ$, $CaHCO_3^+$, $CaSO_4^\circ$, $MgCO_3^\circ$, $MgHCO_3^+$, $MgSO_4^\circ$, CO_3^{2-}, $H_2CO_3^\circ$. This range of components and species is not sufficient for describing solutions found in acid sulfate soils. For example in saline acid sulfate soils concentration of chloride can be as high as $0.33\ mol.l^{-1}$ (VAN BREEMEN, 1976), which means that important complexation with this ion is to be expected. Furthermore redox-reactions, which are one of the most important phenomena in acid sulfate soils, have been neglected in COMPLEX.

Aim of this study is to investigate which ions and ion-pairs have to be incorporated in COMPLEX to achieve a complete and accurate computerprogram for solving chemical equilibria in solutions of acid sulfate soils. Preliminary calculations with concentration data gathered by VAN BREEMEN (1976) for saline acid sulfate soils in Thailand resulted in fulfilment of this aim.

2. THEORY

Some of the main characteristics of acid sulfate soils are the:

1. occurence of pyrite;
2. sometimes high ionic strengths, especially in saline acid sulfate soils;
3. alternating oxidised and reduced conditions;
4. alternating CO_2 pressure in soil. Under oxidised conditions PCO_2 equals rougly 0.003 atm, under submerged conditions it can be as high as 0.8 atm;
5. fluctuating pH. The pH has low values at oxidised conditions and relatively high values under submerged circumstances.

2.1. Occurence of pyrite

The ionic composition of soil solutions can vary largely both in time and space. Firstly this is caused by the enormous variety of minerals found in soils, each with its own resistance against physical and chemical weathering processes. Secondly the continuous release of ions into the soil solution as a result of these weathering processes does not garrantee a definite ionic composition because for instance also adsorption, precipitation, complexation and transport processes, do take place. However, the ionic composition of most soil solutions can be explained by the behaviour of one or a couple of minerals which are present in relatively large amounts. Sometimes a mineral which is present only in minor amounts, such as pyrite in acid sulfate soils, can influence soil chemical behaviour in particular.

Pyrite is stable only under submerged conditions. Oxidation of this mineral can cause a seriously decrease in soil pH (RITSEMA, 1986) so knowledge of the stability of pyrite if essential in understanding the occurence of such processes. In figure 1 a stability diagram is shown from which it can be concluded that pyrite is stable under a wide range of pH but only under low pe conditions. The parameter pe expresses the negative logarithm of the electron activity. A high value of pe corresponds with strongly oxidised conditions, a low one with reduced. The relations and assumptions used in constructing figure 1 are summarized and worked out in appendix 1. Further it can

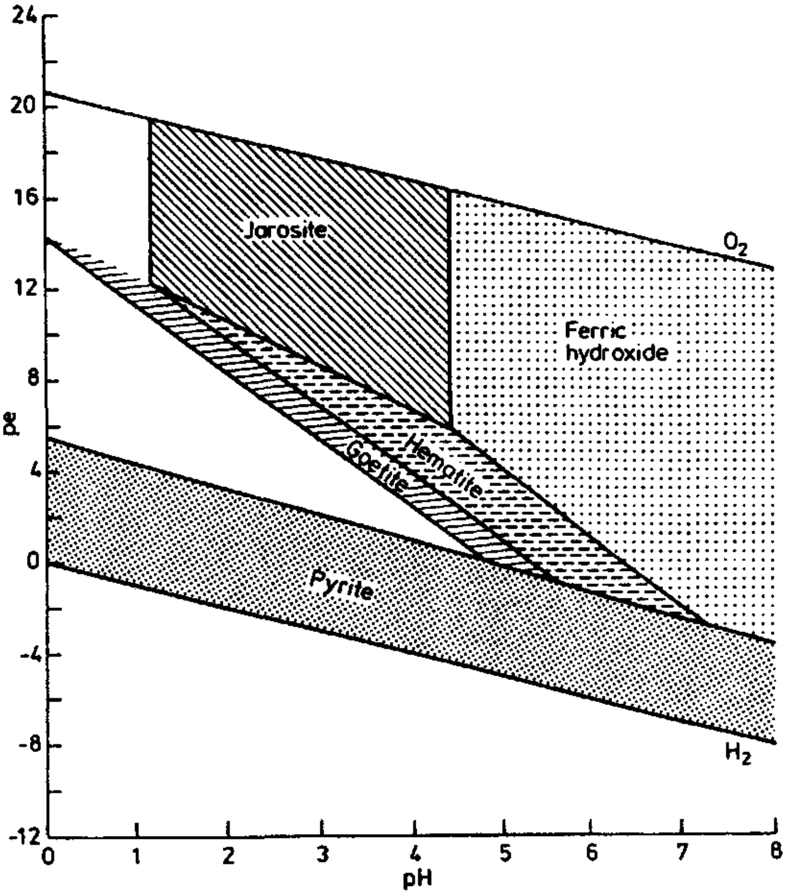

Fig. 1. Stability diagram of pyrite, goetite, hematite, ferric hydroxide and jarosite at 25°C

be seen from figure 1 that jarosite, which is commonly found in association with decomposing pyrite, can only be formed under strongly acid, oxidised circumstances. Goetite is produced by the oxidation of ironbearing minerals such as pyrite or magnetite. Goetite has a wide distribution, ranging from the tropics to the artic and is one of the main colouring substances in soils. Hematite has a widespread occurence in sedimentary rocks in which it may be of primary origin or as a secondary mineral, precipitated from iron-bearing percolating waters and replacing other minerals such as pyrite. Transformation of goetite to hematite is a very slow process (LANGMUIR, 1971). Hematite varies in colour between steel-grey to bright red and occurs chiefly in soils of tropical and subtropical areas in old geological formations. Ferrichydroxide, an amorphous yellowsh-brown substance, occurs in many non-acid soils in the initial stages of formation.

Field values of redoxpotential and pH can be added to figure 1 in order to investigate which mineral(s) are stable under the measured conditions.

BAAS BECKING et al (1960) have reported numerous redox measurements made in natural environments. Those most frequently measured for soils are shown by the enclosed region on figure 2.

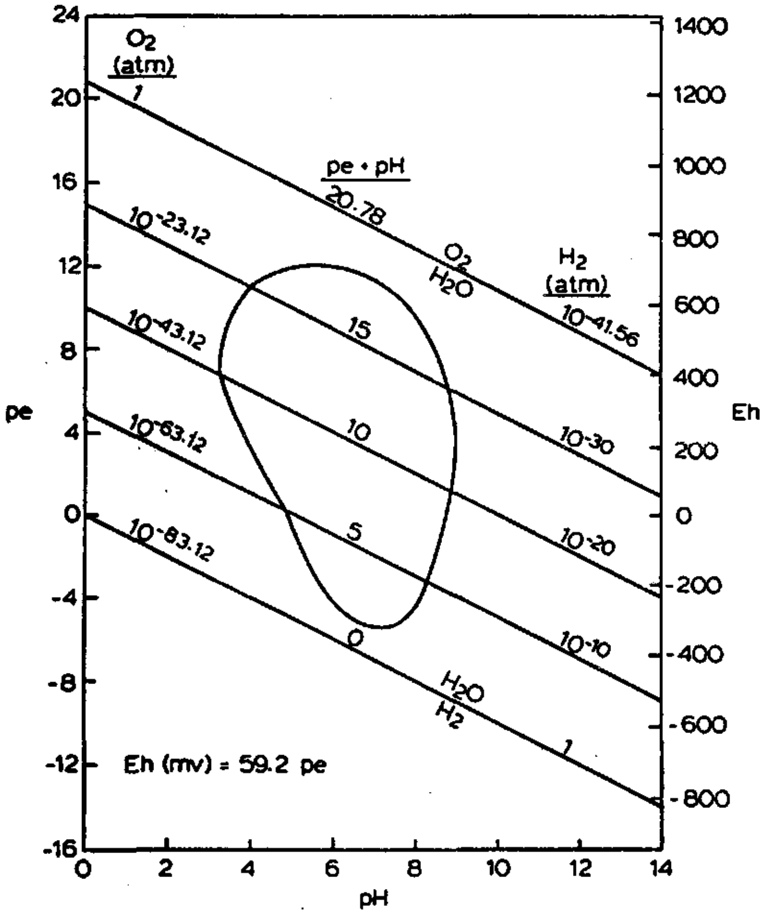

Fig. 2. Equilibrium redox relationships of aqueous systems. The inscribed area was adopted from BAAS BECKING et al (1960) and is representative of most soils (after LINDSAY, 1979)

The parameter pe can be converted to Eh according to:

$$59.2 * pe = Eh \qquad (1)$$

Most soils fall in the pH range of 3.5 to 9 and in the pe range of -6 to +12. The pe + pH range of most soils lies between 2 and 18.

2.2. Ionic strentgh

Soil solutions of, for instance saline, acid sulfate soils can possess high ionic strengths. These soils can be found in coastal lowlands and brackish lagoons in the humid tropics.

Under such conditions equilibrium calculations should be carried out in terms of activities instead of concentrations. Activity coefficients of individual ions, in solutions with low or high ionic strength, can be calculated according to the relations formulated by RITSEMA and BLÖMER (1986).

2.3. Redoxpotential

As a result of alternating oxidised and reduced conditions redox reactions play an important role in the chemical behaviour of acid sulfate soils.

Lowering of the redoxpotential after submergence (and the influence of the temperature on this phenomena) have been measured experimentally by CHO and PONNAMPERUMA (1971) for two different soils (see figure 3).

Reduction of soil components proceeds in the following sequence: O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, CO_2, N_2 and H^+. KOWALIK (1985) constructed a figure showing the limits of stability of some of the soil compounds (see figure 4). Especially iron and manganese redoxreactions are important in acid sulfate soils (VAN BREEMEN, 1976) and should be incorporated in the model COMPLEX.

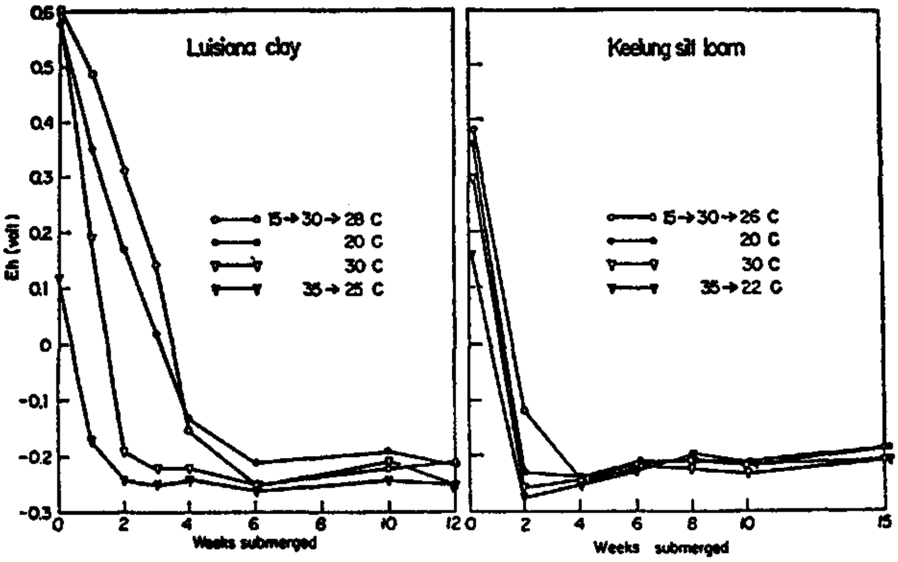

Fig. 3. Influence of submergence (and temperature) on the redoxpotential in two soils (after CHO and PONNAMPERUMA, 1971)

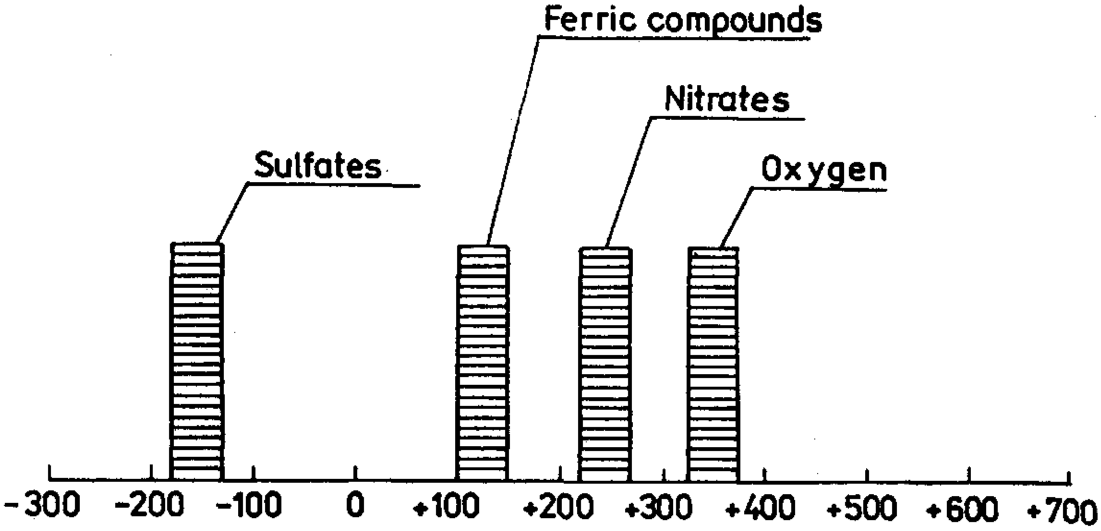

Fig. 4. Approximate values of redoxpotentials (Eh_7) in millivolts and the limits of stability of some of the soil compounds (after KOWALIK, 1985)

2.4. CO_2 pressure

The partial pressure of CO_2 in a soil increases after submergence, reaches a peak of 0.2-0.8 atm 1-3 weeks later and declines to a fairly stable value of 0.05-0.2 atm (IRRI, 1964). Cho and Ponnamperuma did measure the influence of submergence (and temperature) on the partial pressure of CO_2 (see figure 5).

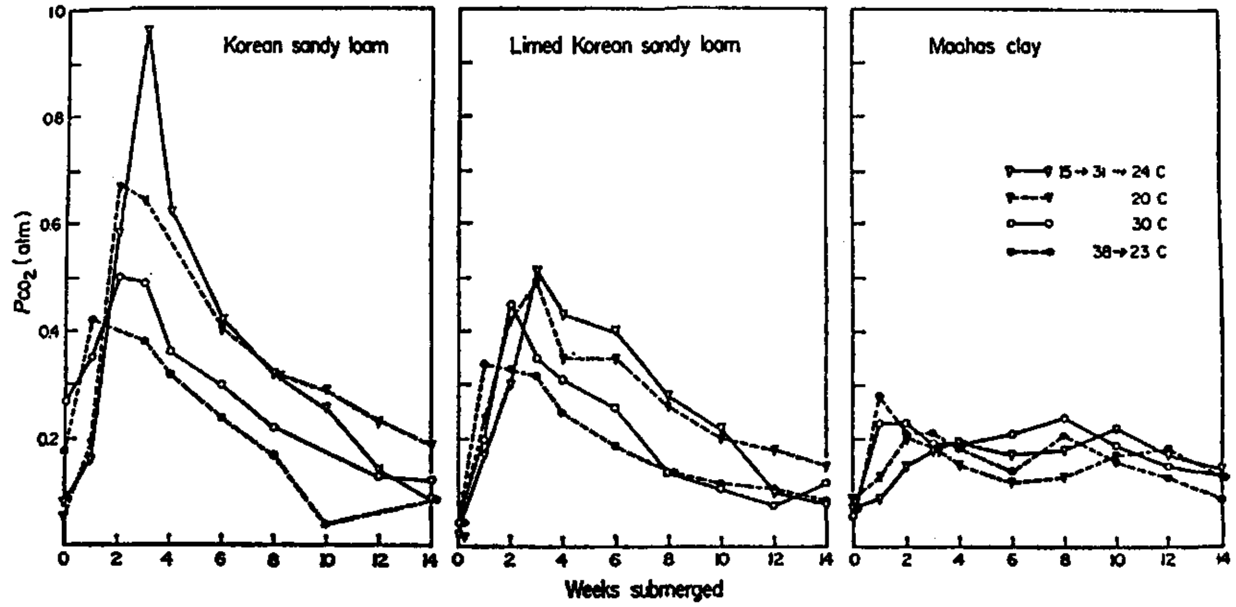

Fig. 5. Influence of submergence (and temperature) on the partial pressure of CO_2 (after CHO and PONNAMPERUMA, 1971)

Acid soils high in organic matter but low in iron and manganese show a rapid increase in P_{CO_2} to about 0.5 atm within 1-2 weeks of flooding followed by a slow decline to about 0.3 atm. Acid soils high in both organic matter and iron build up P_{CO_2} values as high as 0.8 atm, but the peaks are followed by a rapid decline to a fairly constant value of about 0.1 atm. Sandy soils tend to give higher mean P_{CO_2} values than clay soils of comparable organic matter content.

The decrease in P_{CO_2} after 1-4 weeks of submergence is due to escape, leaching, removal as insoluble carbonates and bacterial reduction of CO_2 to CH_4. Since low temperature retards methane production P_{CO_2} tends to be high when the temperature is low (CHO and PONNAMPERUMA, 1971).

The practical implications for rice culture are that CO_2 injury may occur in acid soils low in iron, that organic matter or low temperature aggrevate this injury, that high P_{CO_2} values are short lived in ferruginous soils, and that planting should be delayed at least 2 weeks after flooding to avoid CO_2 injury.

2.5. Acidity

Soils and sediments that undergo alternate flooding and drying show reversible pH changes. The overall effect of submergence is an increase of pH of acid soils and a decrease of pH for sodic and calcareous soils (see figure 6).

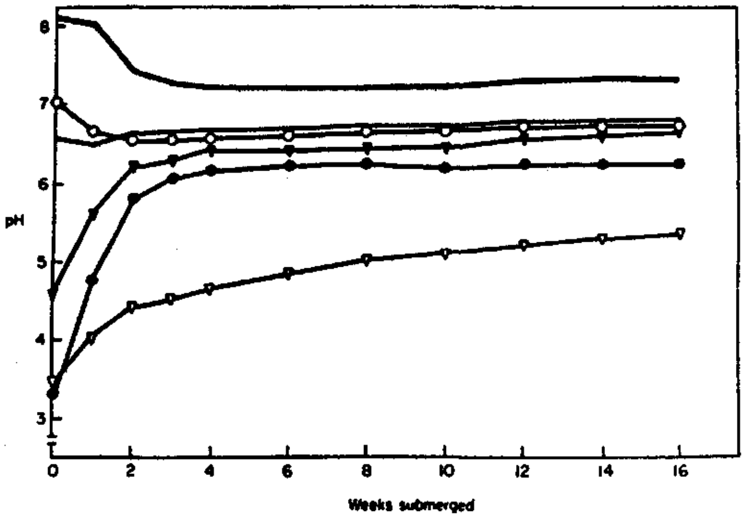

Fig. 6. Influence of submergence on pH of acid and calcareous soils (after PONNAMPERUMA, 1972)

The increase of pH of acid soils is due to soil reduction (PONNAMPERUMA et al, 1966) of components mentioned in the foregoing paragraph. The decrease in pH shortly after submergence of sodic or calcareous soils is probably due to the accumulation of CO_2 produced by respiration of aerobic bacteria (NICOL and TURNER, 1957).

The pattern of changes in figure 6 are markedly unfluenced by soil properties (and temperature). Soils high in organic matter and reducible iron attain a pH of about 6.5 within a few weeks of submergence. Acid soils low in organic matter or in active iron slowly attain pH values which are less than 6.5. In fact, acid sulfate soils low in iron may not attain a pH of more than 5 even after months of submergence. Low temperature or the presence of nitrate retards the increase in pH.

The increase in pH of acid soils is one of the benefits of flooding rice soils because it eliminates aluminium toxicity, minimizes iron toxity, and increases the availability of phosphorus.

3. METHODS

In order to investigate which ions and ion-pairs are relatively important in solutions of acid sulfate soils and how pe, pH and P_{CO_2} affects their actual concentrations, graphics were constructed with help of (mean) fielddata of saline acid sulfate soils gathered by VAN BREEMEN (1976) in Thailand.

The actual ionic composition of a soil solution is the result of a range of complex processes that did take place in history. Sometimes it is obvious that the concentration of one or some of the major ions in solution is controlled by the behaviour of a certain soil-mineral. For most of the major ions this is not that simple because a variety of minerals can control their concentrations as is the case with Na^+, K^+, Ca^{2+} and Mg^{2+}. For these ions it has been assumed that their concentrations are controlled by a hypothetical 'soil-cation' mineral according to:

$$\text{'soil-cation'} \rightleftarrows \text{cation} \qquad (2)$$

Roughly 50 samples were used for calculating mean concentration values of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and $SO_4{}^{2-}$ for soil solutions of saline acid sulfate soils. It has been assumed that these values, which are summarized in table 1, are more or less representative for such soils.

Table 1. Mean ion concentrations in soil solutions of saline acid sulfate soils (calculated from data gathered by VAN BREEMEN, 1976)

Ion	Concentration (mole.l^{-1})
K^+	0.004
Na^+	0.167
Ca^{2+}	0.002
Mg^{2+}	0.008
Cl^-	0.185
$SO_4{}^{2-}$	0.004

The value of the solubility product of the 'soil-cation' mineral equals the mean value of the cation concentration as been given in table 1.

However, not all the cation concentrations in soil solutions are controlled by a variety of minerals. For instance according to VAN BREEMEN (1973, 1976) and VAN MENSVOORT et al (1985) Al^{3+} concentrations in acid sulfate soils are controlled by the mineral jurbanite, $AlOHSO_4$ (with pK_{SO} = between 10 and 17). Furthermore the concentration of Fe^{3+} is usually controlled by the most soluble oxide present. Common found Fe^{3+}-oxides in soils are $Fe(OH)_3$, γ-Fe_2O_3, γ-FeOOH, α-$Fe(OH)_3$ (hematite) and n-FeOOH (goetite). In this range $Fe(OH)_3$ is the most soluble Fe^{3+}-oxide, α-FeOOH the least. Only in well-drained, highly weathered soils not subject to frequent reductions hematite and goetite are expected to lower the solubility of Fe^{3+} towards their equilibrium levels. The solubilities of hematite and goetite are nearly identical, but goetite is generally considered the ultimate weathering product of iron in soils. According to PONNAMPERUMA (1972) the solubility of iron in submerged paddy soils is controlled by the $Fe(OH)_3$-Fe^{2+} equilibrium system. According to VAN BREEMEN (1976) near-equilibrium with amorphous $Fe(OH)_3$ is observed only during oxidation experiments in calcareous pyritic soils which maintained a pH between 7 and 8. In submerged acid sulfate soils in Thailand iron solubility is controlled by goetite (VAN BREEMEN, 1976). The electron activity in soils controls the ratio of Fe^{2+} to Fe^{3+} in solution. As soils are reduced the concentration of Fe^{2+} increases. An unimpeded increase in concentration of Fe^{2+} after submergence of an iron-rich soil is possible until the solubility of a more reduced iron mineral is exceeded. The reduced mineral then becomes the stable phase. If the electron activity is low enough SO_4^{2-} can be reduced to S^{2-} and, eventually, FeS_2 can be formed.

If manganese is present in soil solutions concentrations are usually controlled by pyrolusite, MnO_2 (LINDSAY, 1979). This mineral is also mentioned by VAN BREEMEN (1976) as a possible controlling factor in the ionic composition of solutions of calcareous pyritic soils. In older acid sulfate soils Mn^{2+} may be present mainly in exchangable and dissolved form (VAN BREEMEN, 1976).

In appendix 2 an example is given how calculations of sulfate, chloride and hydroxil Fe^{2+} ion-pairs have been carried out. To simplify calculations for this development activity coefficients were taken as unity. The activities of these ion-pairs have been expressed as function of pe, pH and/or P_{CO_2}. The constructed graphics presented in the next chapter are based on such relations. These graphics makes it easy to conclude which ions and ion-pairs are presumably present in relatively 'large' quantities in solutions of (saline) acid sulfate soils and thus have to be incorporated in model COMPLEX (keeping in mind the assumed conditions!).

4. RESULTS

A series of figures (7 up to 11) showing the activities of ions and ion-pairs as functions of pe, pH and/or P_{CO_2} is presented in this chapter.

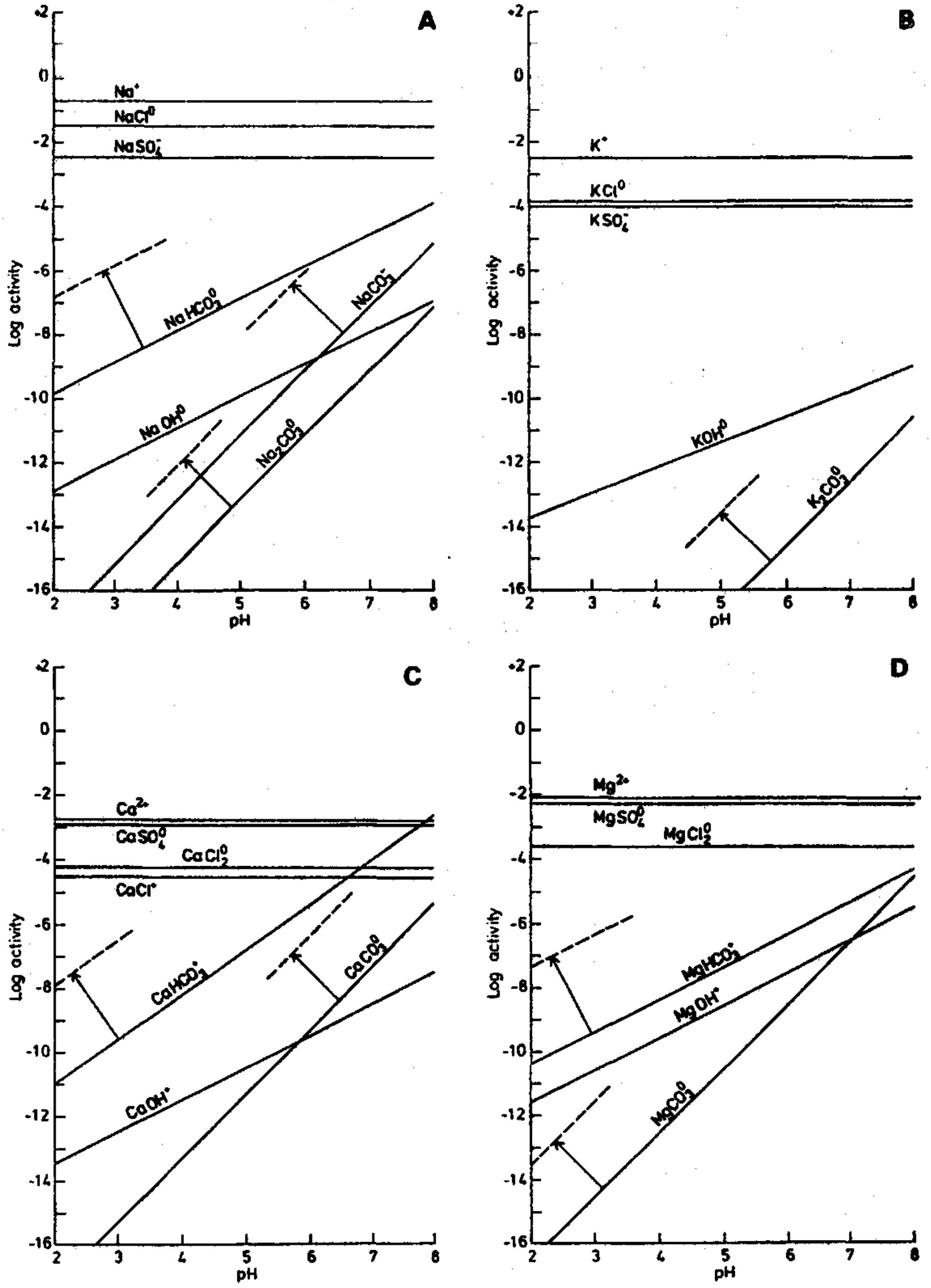

Fig. 7. Sulfate, chloride, bicarbonate and hydroxyl complexes in equilibrium with soil-cation* and the influence of acidity and CO_2 pressure on their actual concentrations. Combined solid and broken lines correspond respectively with a P_{CO_2} of $10^{-3.52}$ and $10^{-0.52}$ atm

*(a) in equilibrium with soil-Na (c) in equilibrium with soil-Ca

(b) in equilibrium with soil-K (d) in equilibrium with soil-Mg

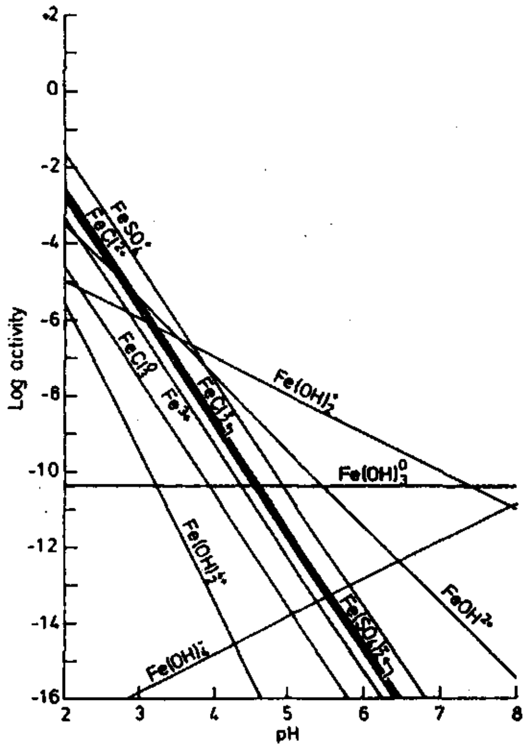

Fig. 8. Fe^{3+} sulfate, chloride and hydroxyl complexes in equilibrium with goetite (FeOOH) and the influence of acidity on their actual concentrations

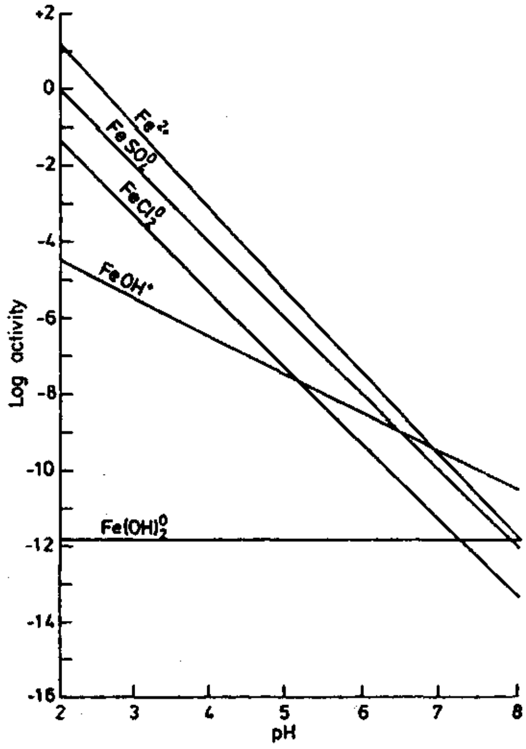

Fig. 9. Fe^{2+} sulfate, chloride and hydroxyl complexes in equilibrium with goetite (FeOOH) at pe + pH = 11.53 and the influence of acidity on their actual concentrations

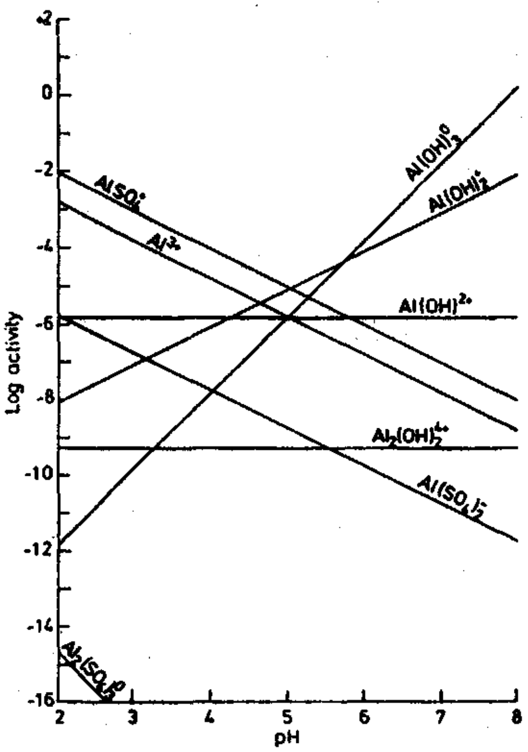

Fig. 10. Sulfate and hydroxyl complexes in equilibrium with jurbanite ($AlOHSO_4$) and the influence of acidity on their actual concentrations

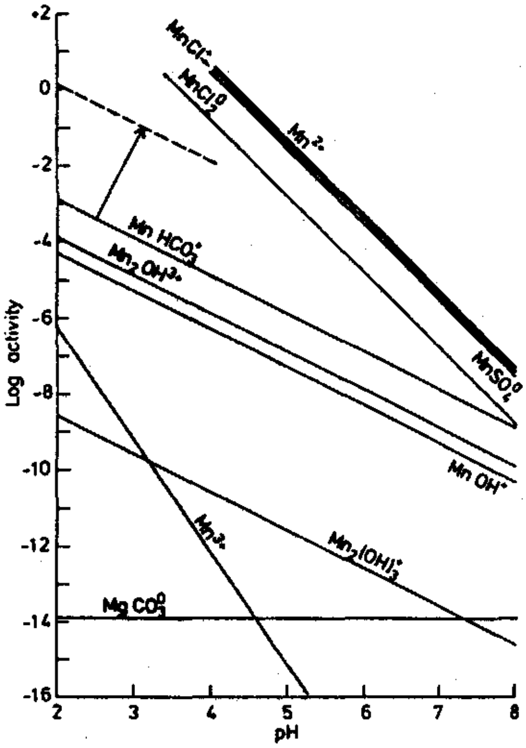

Fig. 11. Chloride, sulfate, bicarbonate and hydroxyl complexes in equilibrium with pyrolusite (MnO_2) at pe + pH = 16.62 and the influence of acidity and CO_2 pressure on their actual concentrations. Combined solid and broken lines correspond respectively with a P_{CO_2} of $10^{-3.52}$ and $10^{-0.52}$ atm

Only a few remarks have to be made to make an easily interpretation of the figures possible. First of all relatively important changes in pe, P_{CO_2} and pH in solutions of acid sulfate soils are usually caused by changes in the oxidation/reduction state of the soil as a result of irrigation (submergence) or drainage.

The redoxpotential, expressed as pe, controls the concentration ratio of Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+}. For example under fully oxidised circumstances Fe^{2+} and Mn^{2+} are present in minor amounts and can be neglected, while under strongly reduced circumstances this is the case for Fe^{3+} and Mn^{3+}. Changes in the partial CO_2 pressure and pH, as a result of irrigation or drainage practises, are interrelated to each other. It can be said that the partial CO_2 pressure only affects the actual concentrations of the bicarbonate complexes directly (see figures). Changes in concentrations of these complexes (and the influence of these changes on the pH) indirectly can cause changes in the concentrations of the other ions and ion-pairs. However it must be noted that the absolute changes in the pH of solutions of acid sulfate soils mainly can be controlled by the redoxreactions taking place after submergence or the oxidation reactions (for instance of pyrite) taking place after drainage.

5. CONCLUSIONS

- Ions and ion-pairs which can be present in relatively important amounts in solutions of acid sulfate soils are:

Na^+, $NaCl^o$, $NaCO_3^-$, $NaHCO_3^o$, $NaSO_4^-$
K^+, KCl^o, KSO_4^-
Ca^{2+}, $CaCl^+$, $CaCl_2^o$, $CaCO_3^o$, $CaHCO_3^+$, $CaSO_4^o$
Mg^{2+}, $MgCl_2^o$, $MgCO_3^o$, $MgHCO_3^+$, $MgSO_4^o$
Fe^{3+}, $FeCL^{2+}$, $FeCl_2^+$, $FeCl_3^o$, $FeSO_4^+$, $Fe(SO_4)_2^-$, $FeOH^{2+}$, $Fe(OH)_2^+$
Fe^{2+}, $FeCl_2^o$, $FeSO_4^o$, $FeOH^+$
Al^{3+}, $AlSO_4^+$, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3^o$
Mn^{2+}, $MnCl^+$, $MnCl_2^o$, $MnSO_4^o$, $MnHCO_3^+$
Mn^{3+}, $MnOH^{2+}$
H^+, e^-, Cl^-, HCO_3^-, SO_4^{2-}, OH^-, CO_3^{2-}, $H_2CO_3^o$

These ions and ion-pairs have to be incorporated in COMPLEX to achieve a complete and accurate computerprogram for solving chemical equilibria in solutions of acid sulfate soils.

- The total Al^{3+}, Fe^{3+} and/or Mn^{2+} concentrations in soil solutions of acid sulfate soils can be controlled mainly by respectively the minerals $AlOHSO_4$ (jurbanite), α-FeOOH (goetite) and MnO_2 (pyrolusite).
- The electron activity controls the concentration ratio between Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+}. Low electron activity corresponds with highly oxidised circumstances, high electron activity with reduced. Under oxidised circumstances Fe^{2+} and Mn^{2+} can be neglected under strongly reduced circumstances Fe^{3+} and Mn^{3+}.
- High partial CO_2 pressure, as been found in submerged soils, do result in an increase in concentration of bicarbonate complexes.
- Changes in partial CO_2 pressure (in)directly influence the soil solution pH. However observed absolute changes in pH of solutions of acid sulfate soils mainly can be controlled by redoxreactions taking place after submergence, or oxidation reactions (for instance of pyrite) taking place after drainage. Especially concentrations of bicarbonate and hydroxyl ion-pairs are sensitive for pH changes.

LITERATURE

ABDEL KHALIK, M.A. and F. BLÖMER (1984). Complex, a computer program for solving chemical equilibria on the basis of activities. Report 2: Reuse of drainage water project. Institute for Land and Water Management Research, Wageningen, The Netherlands.

BAAS BECKING, L.G.N., I.R. KAPLAN and D. MOORE (1960). Limits of the natural environment in terms of pH and oxidation-reduction potentials. In: J. Geology, vol. 68, 243-284.

BREEMEN, N. VAN (1973). Dissolved aluminium in acid sulfate soils and in acid mine waters. In: Soil Sci. Soc. Amer. Proc., vol. 37, 694-697.

——— (1976). Genesis and solution chemistry of acid sulfate soils in Thailand, p. 263.

CHO, D.J. and F.N. PONNAMPERUMA (1971). Influence of soil temperature on the chemical kinetics of flooded soils and the growth of rice. In: Soil Science, vol. 112, no. 3, 184-194.

INTERNATIONAL RICE RESEARCH INSTITUTE (1964). Annual Report.

KOWALIK, P.J. (1985). Influence of land improvement on soil oxidation. Swedish University of Agricultural Sciences. Report 42, p. 145.

LANGMUIR, D. (1971). Particle size effect on the reaction goetite = hematite + water. In: American Journal of Science, vol. 271, 147-156.

LINDSAY, W.L. (1979). Chemical equilibria in soils, p. 449.

MENSVOORT, M.E.F. VAN, H.W. DENECKE and N. VAN BREEMEN (1986). Report of a mission to Vietnam, october 3 - november 1, 1985. Agricultural University Wageningen, p. 44.

NICOL, W.E. and R.C. TURNER (1957). The pH of non-calcareous near-neutral soils. In: Canadian Journal of Soil Science, vol. 37, 96-101.

PONNAMPERUMA, F.N., E.M. TIANCO and T.A. LOY (1966). Ionic strengths of the solutions of flooded soils and other natural aqueous solutions from specific conductance. In: Soil Science, vol. 102, 408-413.

——— (1972). The chemistry of submerged soils. In: Advances in Agronomy, vol. 24, 29-96.

RITSEMA, C.J. and F. BLÖMER (1986). Formulas for activity coefficients of individual ions. Nota 1732. Institute for Land and Water Management Research, Wageningen, The Netherlands.

——— (1986). The development and behaviour of (potential) acid sulfate soils - a literature review - . Nota 1739. Institute for Land and Water Management Research, Wageningen, The Netherlands.

APPENDIX 1

Calculation of relations used for constructing the stability diagram of pyrite, goetite, hematite, ferric hydroxide and jarosite at 25°C.

Equilibrium reactions and solubility products used:

$$FeS_2 \text{ (pyrite)} + 2e^- \rightleftharpoons Fe^{2+} + 2S^{2-} \qquad K_1 = 10^{-45.52} \tag{1}$$

$$FeOOH \text{ (goetite)} + H_2O \rightleftharpoons Fe^{3+} + 3OH^- \qquad K_2 = 10^{-44.00} \tag{2}$$

$$F_2O_3 \text{ (hematite)} + 3/2H_2O \rightleftharpoons Fe^{3+} + 3OH^- \qquad K_3 = 10^{-42.50} \tag{3}$$

$$Fe(OH)_3 \text{ (ferric hydroxide)} + 3H^+ \rightleftharpoons Fe^{3+} + 3H_2O \qquad K_4 = 10^{2.70} \tag{4}$$

$$KFe_3(SO_4)_2(OH)_6 \text{ (jarosite) } 6H^+ \rightleftharpoons K^+ + 3Fe^{3+} + 2SO_4{}^{2-} + 6H_2O \qquad K_5 = 10^{-12.51} \tag{5}$$

$$SO_4{}^{2-} + 8e^- + 8H^+ \rightleftharpoons S^{2-} + 4H_2O \qquad K_6 = 10^{20.74} \tag{6}$$

$$H_2O \rightleftharpoons OH^- + H^+ \qquad K_7 = 10^{-14.00} \tag{7}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad K_8 = 10^{13.02} \tag{8}$$

Concentrations used:

1. $K^+ = 10^{-2.5}$ mol.l^{-1}

2. $SO_4{}^{2-} = 10^{-2.4}$ mol.l^{-1}

3. $Fe^{2+} = 10^{-3.3}$ mol.l^{-1}

Calculation of relations

1. According to equilibrium reaction 1 it follows that:

$$\frac{(Fe^{2+})(S^{2-})^2}{(e^-)^2} = K_1 \qquad (9)$$

According to equilibrium reaction 6 it follows that:

$$\frac{(S^{2-})}{(SO_4{}^{2-})(e^-)^8(H+)^8} = K_6 \qquad (10)$$

Substituting relation 10 into 9 (i.e. eliminating S^{2-}) and using the mentioned concentrations results for pyrite in:

$$(e^-)^{14} \ . \ (H^+)^{16} = 10^{-75.90} \qquad (11)$$

2. According to equilibrium reaction 2 it follows that:

$$(Fe^{3+}) \ . \ (OH^-)^3 = K_2 \qquad (12)$$

Substituting relation 7 and 8 into 12 (i.e. by eliminating OH^- and $Fe^{3\ +}$) and using the mentioned concentration data results for goetite in:

$$(e^-)(H^+)^3 = 10^{-14.32} \qquad (13)$$

3. According to equilibrium reaction 3 it follows that:

$$(Fe^{3+})(OH^-)^3 = K_3 \qquad (14)$$

Following the same procedures as been carried out in the case of goetite results for hematite in:

$$(e^-) \ . \ (H^+)^3 = 10^{-15.82} \qquad (15)$$

4. According to equilibrium reaction 4 it follows that:

$$(Fe^{3=}) = (H^{+})^{3} \; . \; K_{4} \tag{16}$$

Substituting relation 8 into 16 (i.e. by eliminating Fe^{3+}) results for ferric hydroxide in:

$$(e^{-}) \; . \; (H^{+})^{3} = 10^{-19.02} \tag{17}$$

5. According to equilibrium reaction 5 it follows that:

$$(K^{+}) \; . \; (Fe^{3+})^{3} \; . \; (SO_{4}{}^{2-})^{2} = (H^{+})^{6} \; . \; K_{5} \tag{18}$$

Substituting relation 8 into 18 (by eliminating Fe^{3+}) and using the known ionic concentrations results for jarosite in:

$$(e^{-})^{3} \; . \; (H^{+})^{6} = 10^{-43.75} \tag{19}$$

Relations 11, 13, 15, 17 and 19 have been used in constructing figure 1.

APPENDIX 2

Calculation of sulfate, chloride and hydroxyl Fe^{2+} complexes. Iron concentrations are controlled by the mineral goetite (α-FeOOH).

Equilibrium reactions and solubility and dissociation products used:

FeOOH (goetite) + $3H^3 \rightleftarrows Fe^{3+} + 2H_2O$	$K_1=10^{-0.02}$	(1)
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	$K_2=10^{13.04}$	(2)
$Fe^{2+} + H_2O \rightleftarrows FeOH^+ + H^+$	$K_3=10^{-6.74}$	(3)
$Fe^{2+} + 2Cl^- \rightleftarrows FeCl_2{}^o$	$K_4=10^{-0.07}$	(4)
$Fe^{2+} + SO_4{}^{2-} \rightleftarrows FeSO_4{}^o$	$K_5=10^{2.20}$	(5)

Assumptions

1. pe + pH = 11.53 pe + pH can be used as a measure of the oxidation/ reductions state of aqueous systems (see figure 2, chapter 2)

2. $Cl^- = 10^{-0.73}$ mol.l^{-1}

3. $SO_4{}^{2-} = 10^{-2.43}$ mol.l^{-1}

Calculations of relations

1. According to equilibrium reaction 1 it follows that:

$$Fe^{3+} = K_1 \cdot (H^+)^3 \tag{6}$$

According to equilibrium reaction 2 it follows that:

$$Fe^{2+} = Fe^{3+} \cdot (e^-) \cdot K_2 \tag{7}$$

Substituting relation 7 into 6 (by eliminating Fe^{3+}) results in:

$$Fe^{2+} = 10^{13.02} \cdot (H^+)^3 \cdot (e^-) \qquad (8)$$

or:

$$\begin{aligned} \log Fe^{2+} &= 13.02 + 3 \log H^+ + \log e^- \\ &= 13.02 - (pH+pe) - 2pH \qquad (9) \end{aligned}$$

Using the assumptions that pH + pe = 11.53 results in:

$$\log Fe^{2+} = 1.49 - 2\ pH \qquad (10)$$

or:

$$Fe^{2+} = 10^{1.49} \cdot (H^+)^2 \qquad (11)$$

2. According to equilibrium reaction 3 it follows that:

$$(FeOH^+) \cdot (H^+) = (Fe^{2+}) \cdot K_3 \qquad (12)$$

Substituting relation 11 into 12 results in :

$$FeOH^+ = 10^{-5.25} \cdot (H^+) \qquad (13)$$

3. According to equilibrium reaction 4 it follows that:

$$FeCl_2{}^o = (Fe^{2+}) \cdot K_4 \cdot (Cl^-)^2 \qquad (14)$$

Substituting relation 11 into 14 and using chloride concentration as assumed results in:

$$FeCl_2{}^o = 10^{-0.04} \cdot (H^+)^2 \qquad (15)$$

4. According to equilibrium reaction 5 it follows that:

$$FeSO_4^{o} = (Fe^{2+}) \ . \ K_5 \ . \ (SO_4^{2-}) \qquad (16)$$

Substituting relation 11 into 16 and using the presumed sulfate concentration results in:

$$FeSO_4^{o} = 10^{1.26} \ . \ (H^{+})^2 \qquad (17)$$

Relations 11, 13, 15 and 17 have been used in constructing figure 9.