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Treatment of waste effluent water in Studsvik

Thermodynamic modelling on the distribution of organic ligands between the liquid and solid phases

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Oktober 2000

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

ABSTRACT

This preliminary study based on theoretical chemical equilibrium calculations has been carried out in order to analyse the effects of complexing reagents such as EDTA, NTA and oxalate on the treatment of waste effluent water in Studsvik.

The necessary stability constants have been selected and added into the database in MEDUSA software for thermodynamic modelling. The modelling has been performed for a synthetic system of various components: Al^{3+} - Am^{3+} - Ca^{2+} - Co^{2+} - Cu^{2+} - Fe^{3+} - K^{+} - Mg^{2+} - Na^{+} - UO_2^{2+} - Zn^{2+} - SO_4^{2-} - Cl^{-} , in the absence and presence of one of the complexing ligands, EDTA, NTA and $\text{C}_2\text{O}_4^{2-}$ (oxalate). The concentration conditions for the modelling are based on the data supplied in the previous reports on the waste effluent water in Studsvik.

The calculated results are represented in graphic diagrams, compared and discussed. It is generally concluded:

- No solid phase of the complexing reagents concerned, except for calcium oxalate, may form according to the present modelling. It means that the distribution of EDTA and NTA between the slurry and the clean solution is mainly dependent upon the volume ratio of the liquid phase. Oxalate, however, may mostly precipitate as calcium oxalate in the slurry.
- The major eventual problem with the presence of the complexing reagents in the slurry is the probable re-dissolution of the radioactive components such as $\text{Am}(\text{OH})_3$ CaUO_4 . Therefore, it is necessary to study the solid formation of those radioactive compounds in the slurry, their stability in the presence of the complexing reagents and the respective conditions to avoid their re-dissolution.
- Sorption of organic ligands into the Fe(III)-hydroxides has not been included in the model, but available literature data suggest that sorption is improbable under the conditions used (at $\text{pH} \geq 8$).

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1 INTRODUCTION

The wastewater from the laundry at Studsvik Radwaste AB is subjected to a precipitation process in a small wastewater treatment plant before it is analysed for residual radioactivity and, if safe, released to the Tvären semi-lake in the Baltic coast. A schematic flowchart of the process involved is shown in Figure 1.

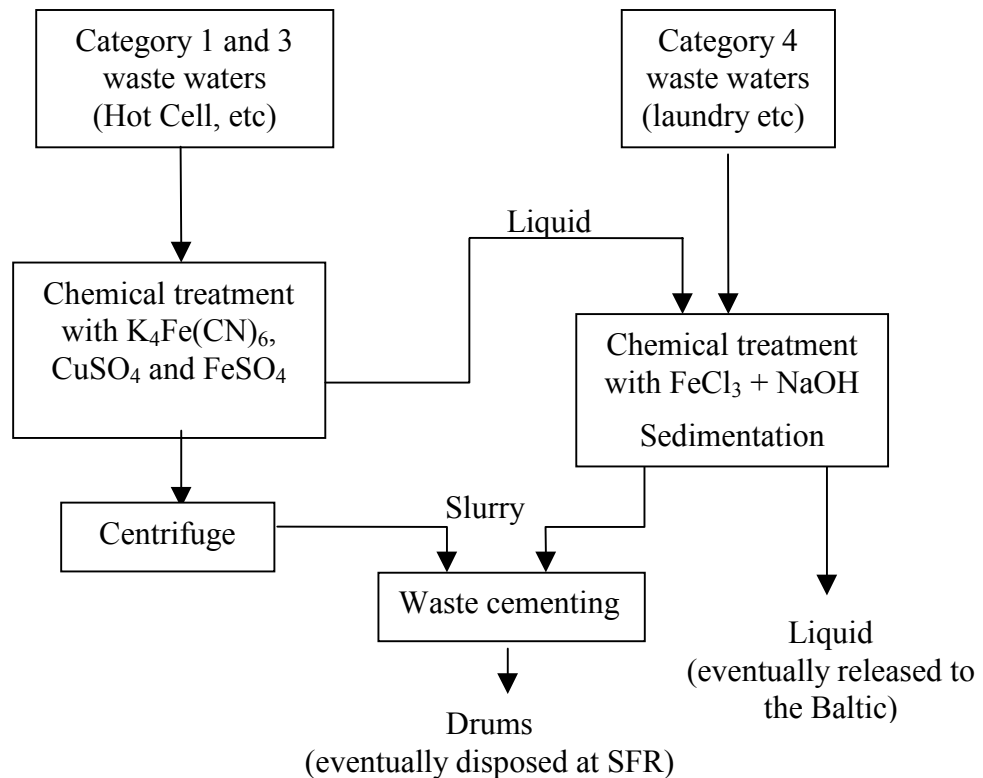
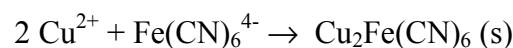
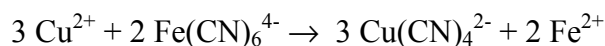


Figure 1. Schematic flowchart of the effluent cleaning process at Studsvik.

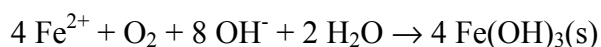
In this process, the wastewater effluents (Categories 1 and 3) are first chemically treated with $\text{K}_4\text{Fe}(\text{CN})_6$, CuSO_4 and FeSO_4 . The acidity of the wastewater is adjusted with NaOH and maintained at $\text{pH} \approx 6.5$. The addition of $\text{K}_4\text{Fe}(\text{CN})_6$ and CuSO_4 cause the precipitation



Radioactive Cs and Sr co-precipitate with $\text{Cu}_2\text{Fe}(\text{CN})_6(\text{s})$. The addition of FeSO_4 , to a concentration of 150 ppm, is to enhance the stability of $\text{Cu}_2\text{Fe}(\text{CN})_6(\text{s})$, by suppressing side reactions such as



On the other hand, the oxidation of Fe^{2+} results in another dominant precipitation as follows,

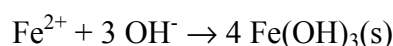


Essentially all other radioactivity components are expected to co-precipitate with $\text{Fe}(\text{OH})_3(\text{s})$.

The co-precipitates are centrifuged, mixed together with the $\text{Fe}(\text{OH})_3$ slurry coming from the chemical treatment of Category 4 waste waters, and then cemented for deposition. The centrifuged liquid solution is mixed with other wastewater effluents including the laundry (Category 4), and subjected to chemical treatment with FeCl_3 and NaOH .

The washing powders and chemicals used in the laundry contain ligands to form soluble complexes with the hardness components of the laundry water (Ca^{2+} and Mg^{2+} ions), avoiding the formation of insoluble Ca- and Mg-salts with the detergent, and increasing the efficiency of the washing powder. Normally phosphates are used for this task. In order to decrease the phosphorous pollution of the Baltic sea, washing powders containing alternative organic ligands like EDTA are used at Studsvik.

Thus, in Figure 1 organic ligands such as EDTA are introduced in the “Category 4” wastewater and then it is mixed with the pre-treated “Categories 1 and 3” effluents. When being treated with FeCl_3 , the pH is adjusted to ≈ 8.5 with NaOH and the precipitation of $\text{Fe}(\text{OH})_3(\text{s})$ occurs



Some of other components in the solution co-precipitate to different extents. The presence of EDTA and other complexing ligands may greatly affect these precipitation processes. The resultant suspension is settled for sedimentation. The clear liquid solution is eventually released to the Baltic Sea.

However, part of the liquid, (95% of the $\text{Fe}(\text{OH})_3$ slurry is water) finds its way to the cemented waste forms, and with it, some of the EDTA and other ligands included in the washing chemicals from the laundry. These ligands are of concern to the performance of the radioactive repository where they eventually will be disposed, because they may enhance the mobility of radionuclides.

1.1 OBJECTIVES

The present study aims at clarifying the following questions

- 1) How much of the organic complexing ligands are associated with the precipitates in the slurry?
- 2) A subordinate aspect is to find out how the complexing ligands (EDTA, etc.) affect the concentrations of the radioactive/toxic metals remaining in the cleaned water after the precipitation/sedimentation treatment.

This preliminary study is based on theoretical chemical equilibrium calculations, which will guide eventual experimental determinations in the future. The chemical equilibrium calculations were performed to reach the following objectives:

- 1) To establish a thermodynamic model for the description of the solution chemistry of the wastewater treatment system including all of the chemical components (metal ions and ligands) of interest.
- 2) To specify the complex formation between different components under various conditions (pH, concentrations of different components, etc.).
- 3) To calculate the chemical distributions of the components based on the modelling of the system under the given conditions (data of analyses).

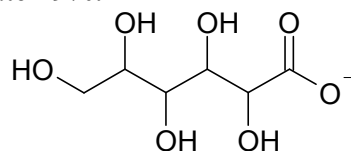
1.2 THE ORGANIC LIGANDS

The organic ligands present in the *washing powder* are (Chyssler, 1999):

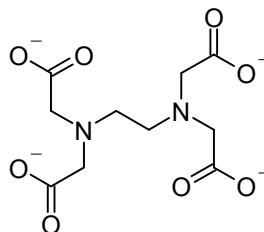
- polyacrylate 2.6%. This is a product of the polymerisation of acrylic acid: $\text{CH}_2=\text{CHCO}_2\text{H}$.

and the ligands present in the *conditioner* are:

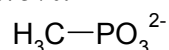
- gluconate 19%:



- EDTA 23%:



- Methylenefosfonate 1.75%:



2 RESULTS AND DISCUSSIONS

2.1 DATA SELECTION AND EVALUATION

Literature survey and data selections have been carried out on the stability constants of following reaction systems: **M-L-H₂O**,

M = one of metal ions, Al³⁺, Am³⁺, Ca²⁺, Co²⁺, Cu²⁺, Fe²⁺, Fe³⁺, K⁺, Mg²⁺, Na⁺, Np⁴⁺, NpO₂⁺, Pu³⁺, PuO₂⁺, U⁴⁺, UO₂²⁺ and Zn²⁺;

L = one of complexing ligands, EDTA, NTA and C₂O₄²⁻(oxalate).

The search was concentrated on electronic data bases (Martell et al., 1997; Pettit and Powell, 1997).

The selected values have been added into the database in MEDUSA software for thermodynamic modeling (Puigdomenech, 1983).

2.2 CHEMICAL EQUILIBRIUM MODELLING

Chemical equilibrium calculations have been carried out on several sets of synthetic systems: **(M)-L-H₂O**

(M) = 13 ions, Al³⁺-Am³⁺-Ca²⁺- Co²⁺-Cu²⁺-Fe³⁺-K⁺-Mg²⁺-Na⁺-UO₂²⁺-Zn²⁺-SO₄²⁻-Cl⁻, with various defined compositions, the lowest limits of which were based on the analysis data of the waste effluent water in Studsvik;

L = one of complexing ligands, EDTA, NTA and C₂O₄²⁻(oxalate), with a defined concentration based on the data supplied in the previous reports on the waste effluent water in Studsvik.

The calculated results are represented in graphic diagrams, mainly in a form of the fraction of a component, a metal ion such as Fe³⁺ or a complexing ligand such as EDTA⁴⁻, as a function of pH.

2.3 DISCUSSIONS AND REMARKS OF THE RESULTS

2.3.1 Effects of complexing reagents on the distributions of metal ions

Each metal ion in the system has got for comparison four different diagrams, one with no complexing ligand and three with one of EDTA, NTA and oxalate, respectively. The results of the major metal ions concerned are discussed.

1) Al³⁺

Solid aluminium compound is found to be KAl₃(SO₄)₂(OH)₆(c), as shown in Fig. A1. With no complexing ligand, KAl₃(SO₄)₂(OH)₆(c) is expected to precipitate between pH = 4-8, with 100% around pH = 6 (Fig. A1a). The complexation with EDTA or NTA is found to suppress the precipitation

completely (Figs. A1b and A1c). The oxalate has a similar but less remarkable effect so that the precipitation is limited within pH = 7-8 (Fig. A1d).

2) Am³⁺

Solid americium compound is Am(OH)₃(c), as shown in Fig. A2. With no complexing ligand, Am(OH)₃(c) is expected to precipitate at pH > 7.5, with 100% at pH > 9.5 (Fig. A2a). The complexation with EDTA is to suppress the precipitation significantly so that Am(OH)₃(c) appears instead at pH > 11 (Fig. A2b). Such an effect is more significant with NTA (Fig. A2c), but much less with oxalate (Fig. A2d). Am(OH)₃(c) precipitates at pH > 12 and pH > 8, respectively.

3) Ca²⁺

Solid calcium compounds are Ca(OH)₂(c) and/or CaC₂O₄(c), as shown in Fig. A3. With no complexing ligand, Ca(OH)₂(c) is to precipitate at pH > 13 (Fig. A3a). The complexation with EDTA or NTA suppresses the precipitation completely (Figs. A3b and A3c). In the presence of oxalate, CaC₂O₄(c) is expected to precipitate between pH = 3-14 (Fig. A3d).

4) Co²⁺

Solid cobalt compound is Co(OH)₂(c), as shown in Fig. A4. With no complexing ligand, Co(OH)₂(c), is to precipitate between 9.3-13.3 (Fig. A4a). The complexation with EDTA or NTA suppresses the precipitation completely (Figs. A4b and A4c). The oxalate has much less remarkable effect so that the precipitation of Cu(OH)₂(c) still occur between pH = 10-12.3 (Fig. A4d)

5) Cu²⁺

Two solid copper compounds are found to be CuCl₂:3Cu(OH)₂(c) and Cu(OH)₂(c), as shown in Fig. A5. With no complexing ligand, the precipitation of CuCl₂:3Cu(OH)₂(c) and Cu(OH)₂(c), is expected between 7-12.5 (Fig. A5a). The complexation with EDTA or NTA suppresses the precipitation completely (Figs. A5b and A5c). The oxalate has a similar but less remarkable effect so that the precipitation of Cu(OH)₂(c) still occur between pH = 8.7-12.5 (Fig. A5d).

6) Fe³⁺

Solid iron compound is found to be Fe(OH)_{2.7}Cl_{0.3}(c), or FeCl₃:9Fe(OH)₃(c), as shown in Fig. A6. With no complexing ligand, Fe(OH)_{2.7}Cl_{0.3}(c), is to precipitate at pH > 0.7 (Fig. A6a). The complexation with EDTA is to suppress the precipitation significantly so that Fe(OH)_{2.7}Cl_{0.3}(c) appears instead at pH > 7.5 (Fig. A6b). The effect of NTA or oxalate is much less remarkable, up to pH = 3.5 or 4, respectively (Figs. A6c and A6d). However, the precipitation operation of Fe(OH)_{2.7}Cl_{0.3}(c) can be kept under control at pH > 8.5 with the addition of excess Fe³⁺ as used in the existing process.

7) Mg²⁺

Solid magnesium compound is mainly Mg(OH)₂(c), as shown in Fig. A7. With no complexing ligand, Mg(OH)₂(c) is to precipitate at pH > 10

(Fig. A7a). The complexation with EDTA limits the precipitation to be at $\text{pH} > 12$ (Fig. A7b). The effect of NTA and oxalate is very little (Figs. A7c and A7d).

8) UO_2^{2+}

Solid UO_2^{2+} compounds are found to be $\text{CaUO}_4(\text{c})$ and $\text{Na}_2\text{U}_2\text{O}_7(\text{c})$, as shown in Fig. A8. With no complexing ligand, $\text{CaUO}_4(\text{c})$ is to precipitate at $\text{pH} > 7.5$, with 100% at $\text{pH} > 8.5$ (Fig. A8a). The addition of EDTA suppresses the precipitation almost completely so that $\text{CaUO}_4(\text{c})$ appears only at $\text{pH} > 13.4$ but $\text{Na}_2\text{U}_2\text{O}_7(\text{c})$ between $\text{pH} = 9-13.6$ (Fig. A8b). The effect of NTA or oxalate is much less remarkable, up to $\text{pH} = 8.2$ or 8, respectively (Figs. A8c and A8d). It is important to note the suppression of $\text{CaUO}_4(\text{c})$ precipitation is not mainly due to the complexation between UO_2^{2+} and a complexing reagent as the soluble species of UO_2^{2+} at equilibrium with $\text{CaUO}_4(\text{c})$ are just hydroxides. As a matter of fact, it is the more stable complexation of Ca^{2+} with the complexing reagent, as shown in Figs. A3b-A3d, that plays a key role in this case. Therefore, it has indicated the importance of adding excess Ca^{2+} in the slurry to avoid the dissolution of $\text{CaUO}_4(\text{c})$ due to the complexation of Ca^{2+} with the complexing reagents.

9) Zn^{2+}

Solid phase of the zinc compound is $\text{ZnO}(\text{c})$, as shown in Fig. A9. With no complexing ligand, $\text{Zn}(\text{OH})_2(\text{c})$ is to precipitate between $\text{pH} = 8.3-10.8$ (Fig. A9a). The complexation with EDTA or NTA is found to suppress the precipitation completely (Figs. A9b and A9c). The oxalate has a similar but much less remarkable effect. The oxalate has a similar but much less remarkable effect (Fig. A9d).

2.3.2 Distributions of complexing reagents

The distribution of each complexing ligand in the system is given in respective diagram.

1) EDTA

EDTA forms stable metal complexes mostly between $\text{pH} = 4-12$, as shown in Fig. A10. The most stable EDTA complex is $\text{Ca}(\text{EDTA})^{2-}$, followed by $\text{Mg}(\text{EDTA})^{2-}$. EDTA complexation with Na^+ and Fe^{3+} is less significant. No solid phase of EDTA compound is found.

2) NTA

The distribution of NTA is similar to that of EDTA though its complexation with metal ions is less significant, as shown in Fig. A11. No solid phase of NTA compound is found, either.

3) Oxalate

The distribution of oxalate is also similar, with an exception of the appearance of Al-complexes due to the higher ratio of oxalate to Al^{3+} , as shown in Fig. A12. However, it is important to note that the solid phase of CaC_2O_4 is expected to be dominant with a wide range of $\text{pH} = 3-14$

2.3.3 Ligand Adsorption

Ion-exchange, surface complexation and co-precipitation processes have not been modeled in this study. They are believed to be responsible for the separation of (radioactive) heavy metal cations by the gelatinous iron or aluminum hydroxides used in wastewater treatment plants.

The capacity of metal oxides and hydroxides for sorption is known to be pH-dependent. Sorption sites in these solids participate in acid-base reactions. At low pH values they become protonated, and the surface is positively charged, attracting soluble anionic species. At high pH values the sorption sites are de-protonated, and the surface is negatively charged, attracting cationic species. At the pH of zero charge, sorption capacity is at a minimum value.

The possibility of organic ligand sorption on iron hydroxides has been considered as a possible phenomenon introducing an uncertainty to the conclusions of this study. However the sorption processes for organic ligands are quite complicated. Dissociated (negatively charged) organic molecules may be sorbed on positively charged Fe(III) hydroxides at low pH values (Evanko and Dzombak, 1998). In the case of EDTA and other ligands the sorption of metal complexes is also possible (Nowack et al., 1996). In real systems several processes take place simultaneously (Burnett et al., 1998): Sorption of both free EDTA molecules and of metal-EDTA complexes, and competition with acid-base and complex formation in the aqueous phase.

The available data indicates however (Nowack et al., 1996) that sorption of free EDTA molecules and of metal-EDTA complexes on hydrous ferric oxide takes place at $\text{pH} \leq 8$, while at the Fe(III) precipitation process at Studsvik Radwaste AB more alkaline conditions are used ($\text{pH} \approx 8.5$) In summary, although the possibility for sorption of organic ligands introduces an uncertainty in the conclusions, at the pH conditions used sorption of organic matter is improbable.

2.3.4 EDTA Distribution after the Treatments

The annual amounts involved are (Chyssler, 1999; Larsson and et al., 2000):

- ≈ 980 kg washing powder
- ≈ 800 kg conditioner
- ≈ 6000 m³ wastewater
- ≈ 4 m³ of slurry, containing $\approx 95\%$ of water. Cemented as 40 m³ of solid waste

Mass-balance calculations for EDTA show that under these conditions, 184 kg of EDTA are released per year, corresponding to a concentration of 0.03 g/L in the wastewater.

Based on the above results and discussions, the distribution of EDTA between the slurry and liquid deposits is mainly dependent on the liquid volume fraction.

As shown schematically in Figure 2, about 3600 L of wastewater follow with the 4 m³ slurry. If 0.1 m³ of slurry are cemented in each waste drum (Chyssler, 1999), about 2.8 g of EDTA are encapsulated in each drum.

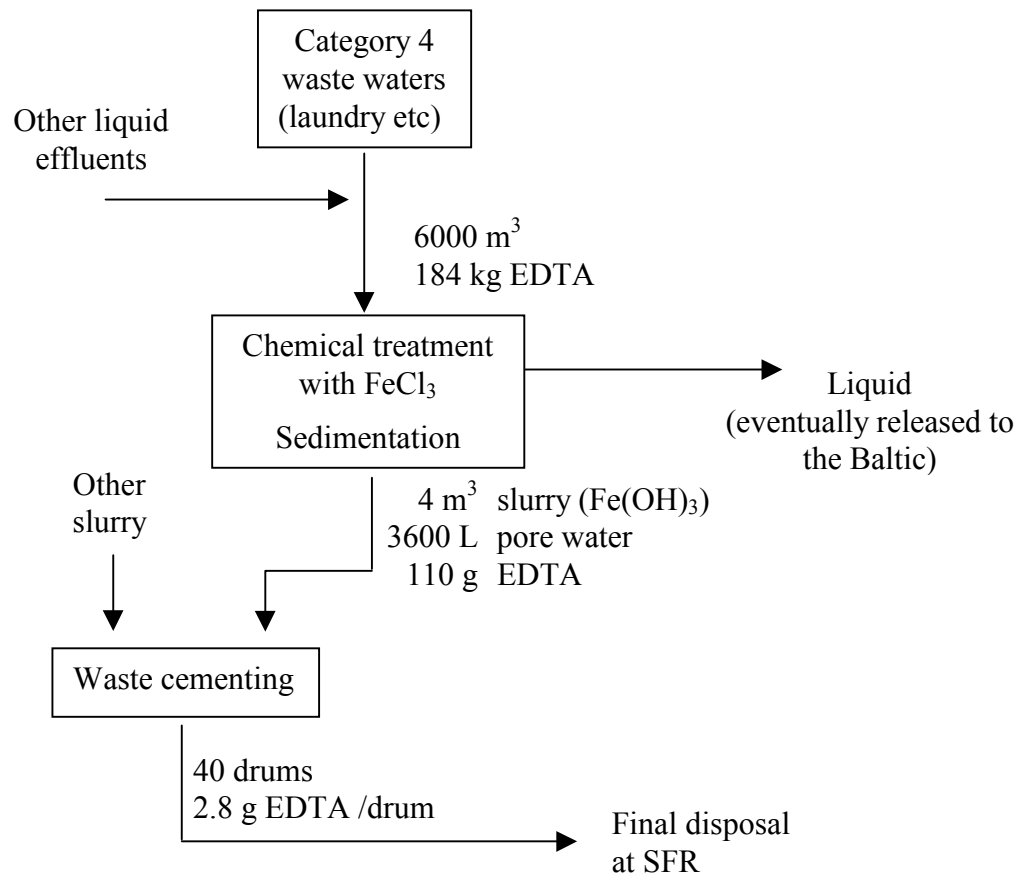


Figure 2. Annual amounts and flows of waste, with emphasis on fate of EDTA.

3 CONCLUSIONS

- The presence of complexing reagents may greatly suppress the precipitation of all of the major metal ions concerned.
- No solid phase of EDTA and NTA may form according to the present modelling. It means that the distribution of these two complexing reagents between the slurry and the clean solution is mainly dependent upon the volume ratio of the liquid phase.

- Oxalate is expected to precipitate dominantly as CaC_2O_4 , so that it is reasonable to suggest that all of the oxalate can go with the slurry deposit.
- The major eventual problem with the presence of the complexing reagents in the slurry is the probable re-dissolution of the radioactive components such as $\text{Am}(\text{OH})_3$ and CaUO_4 . Therefore, it is necessary to study the solid formation of those radioactive compounds in the slurry, their stability in the presence of the complexing reagents and the respective conditions to avoid their re-dissolution.
- Sorption of organic ligands into the Fe(III)-hydroxides has not been included in the model, but available literature data suggest that sorption is improbable under the conditions used (at $\text{pH} \geq 8$).
- An experimental determination of *e.g.* EDTA in typical slurry samples should be undertaken if the calculated amounts of organic ligands contained in the slurry-porewater are considered to threaten the performance of radioactive repositories.

4 ACKNOWLEDGEMENTS

This work has been supported by SKB. The helpful comments and discussions by Claes Johansson, Per Ryggare, Fred Karlsson and Kastriot Spahiu are gratefully acknowledged. Personnel at Studsvik Radwaste AB have kindly helped us with a site visit and diverse kinds of information.

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6 APPENDIX

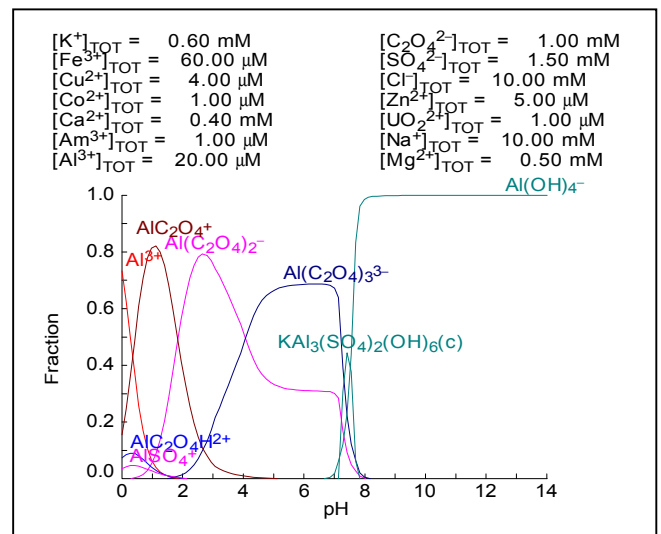
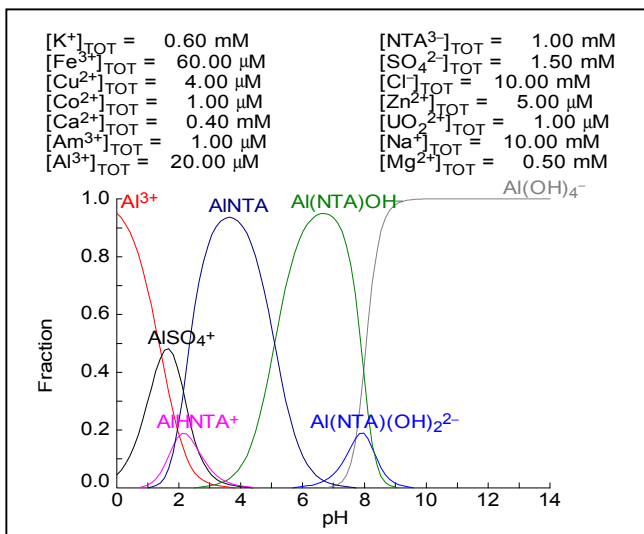
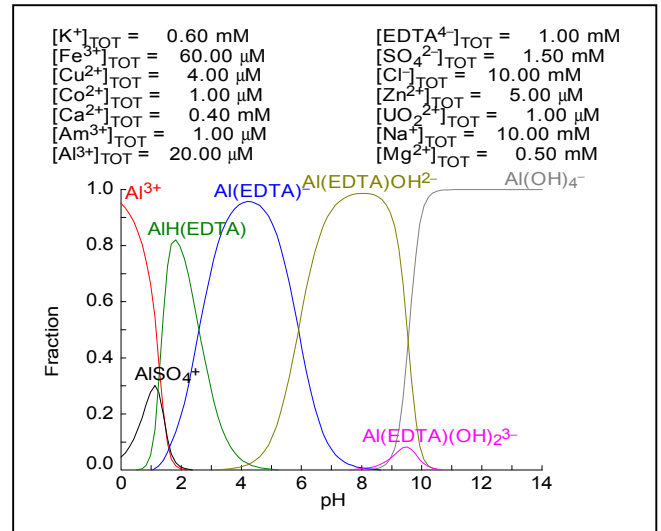
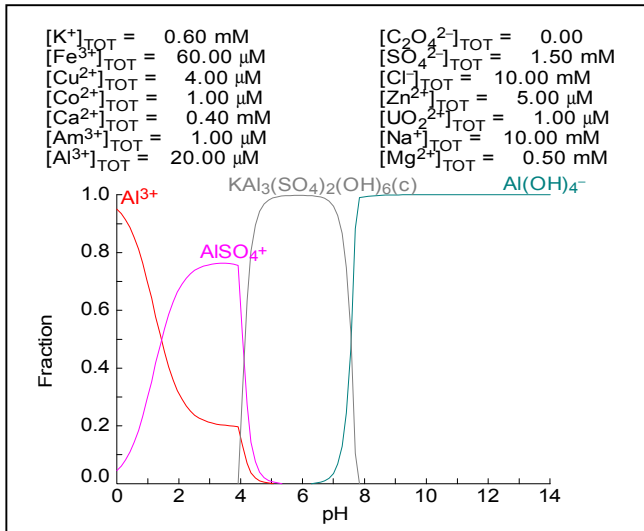


Figure A1. Al speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

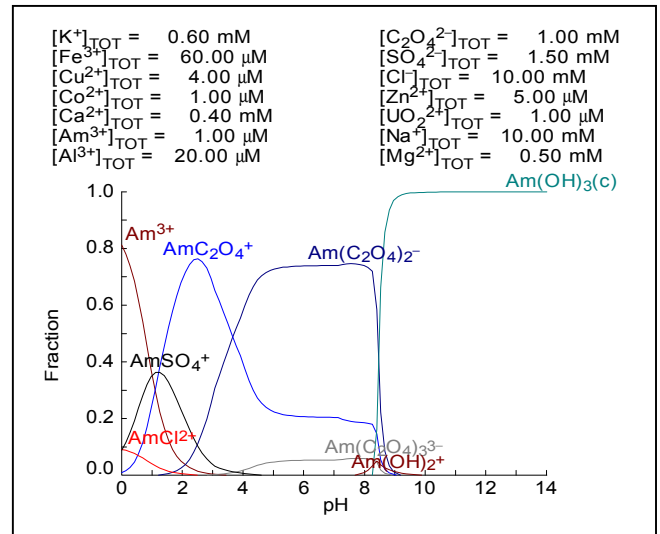
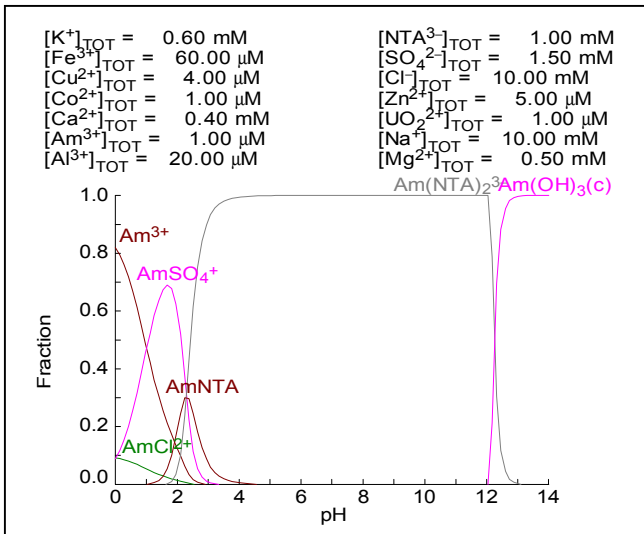
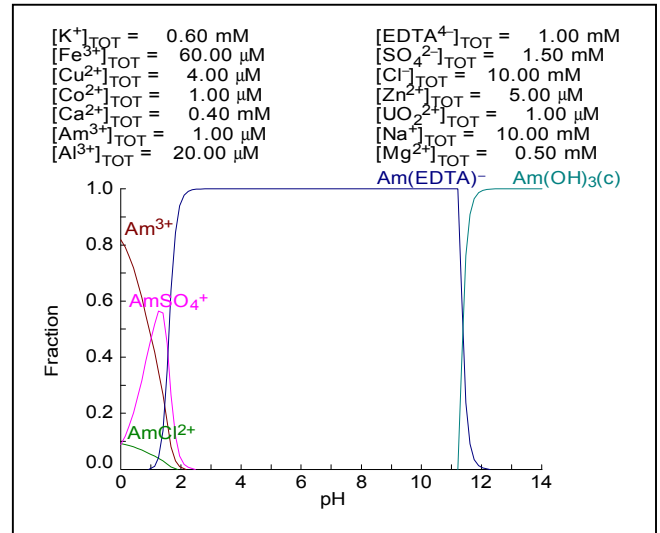
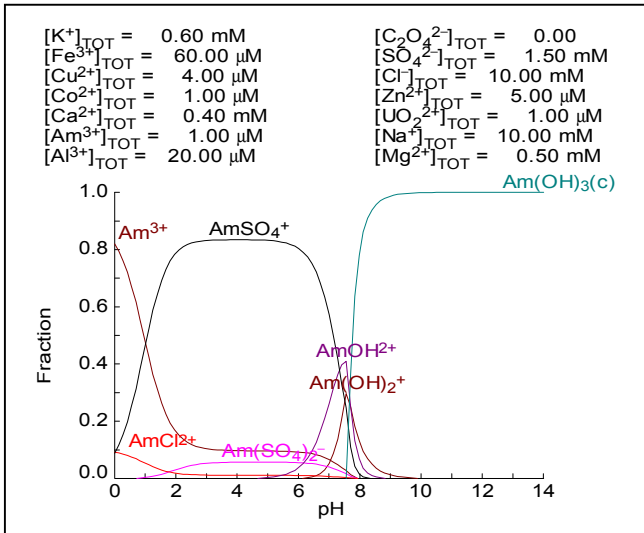


Figure A2. Am speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

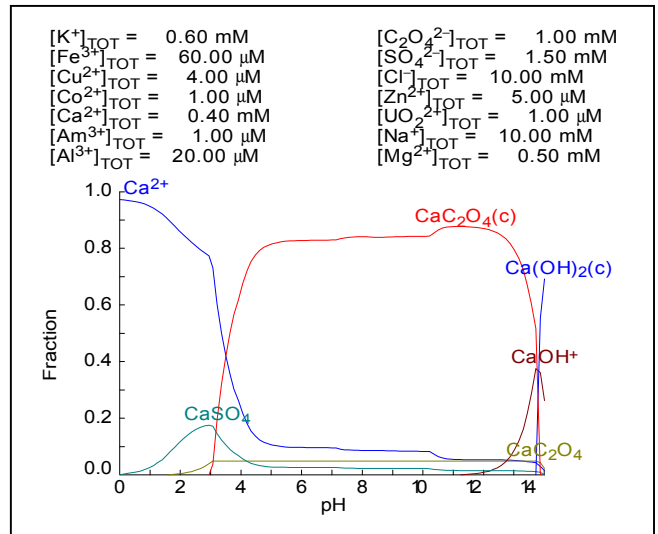
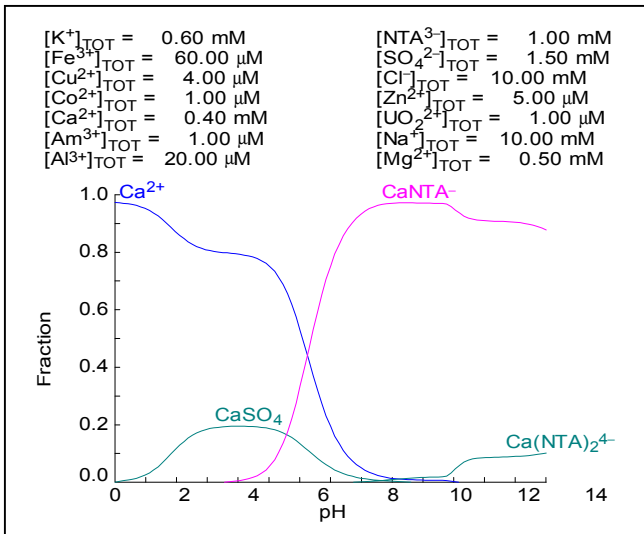
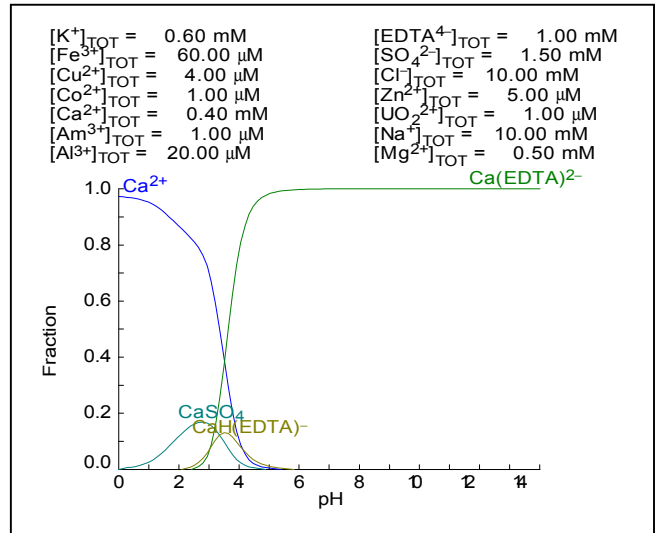
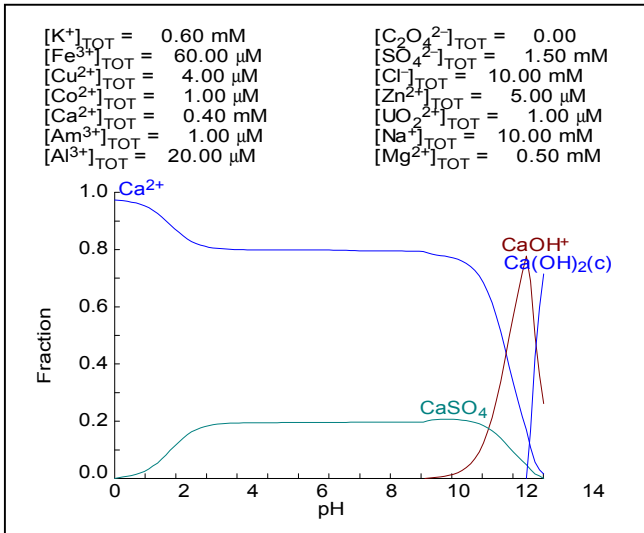


Figure A3. Ca speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

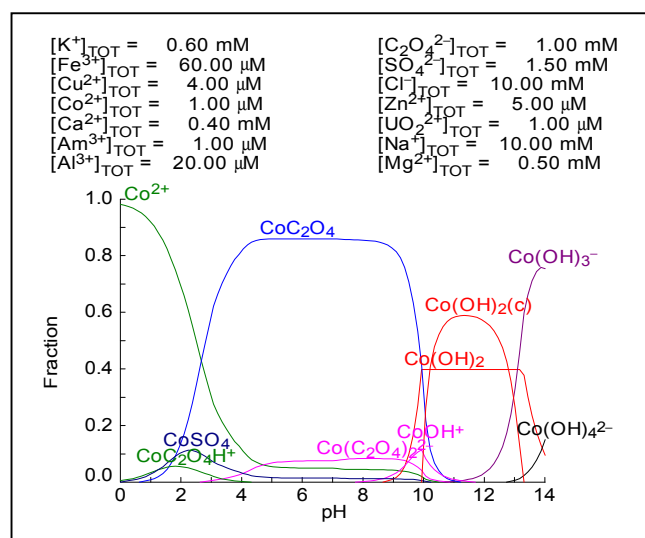
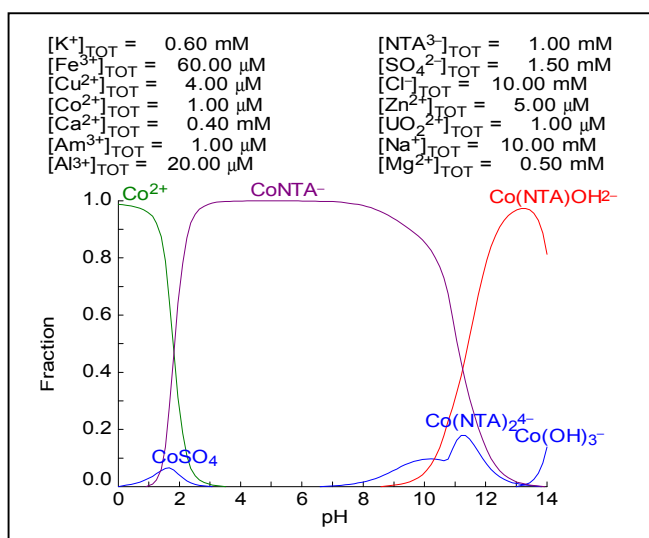
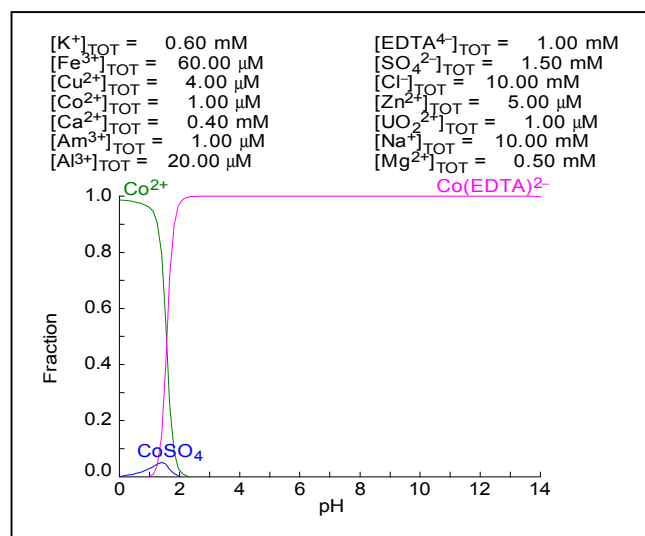
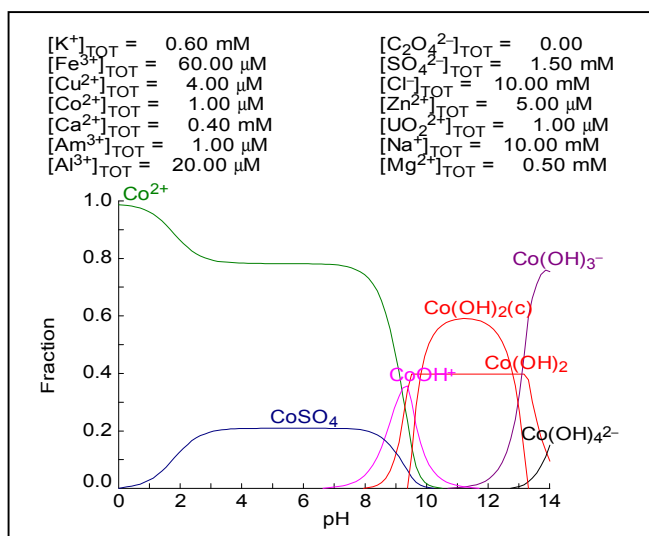


Figure A4. Co speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

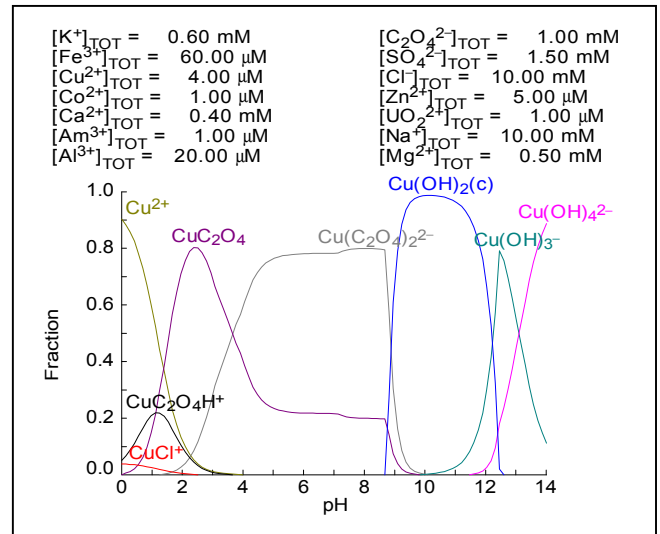
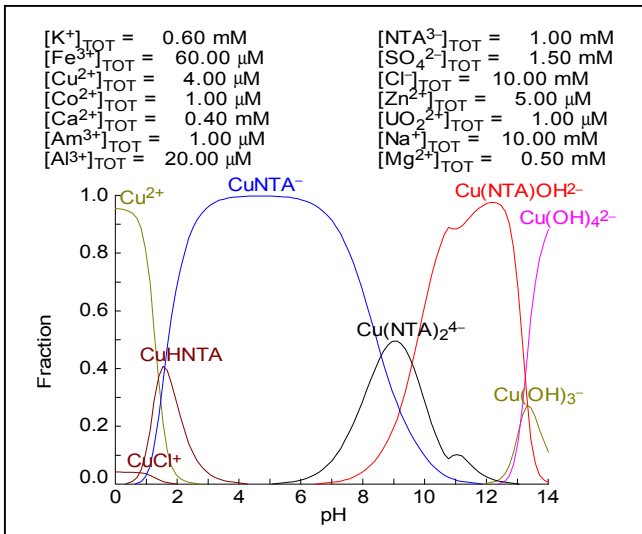
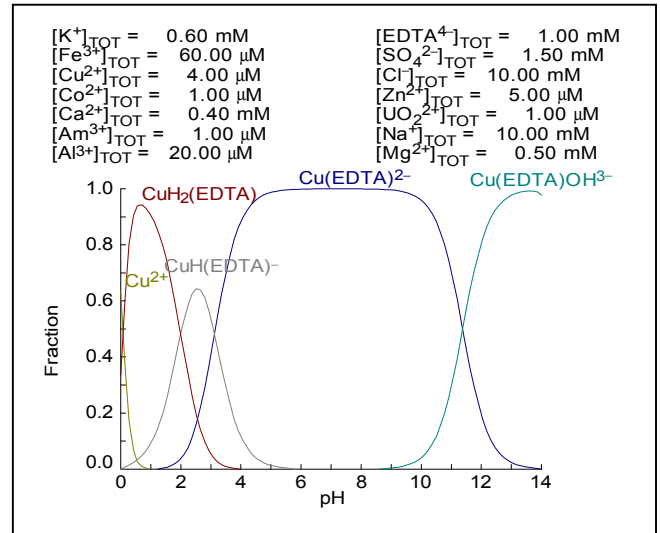
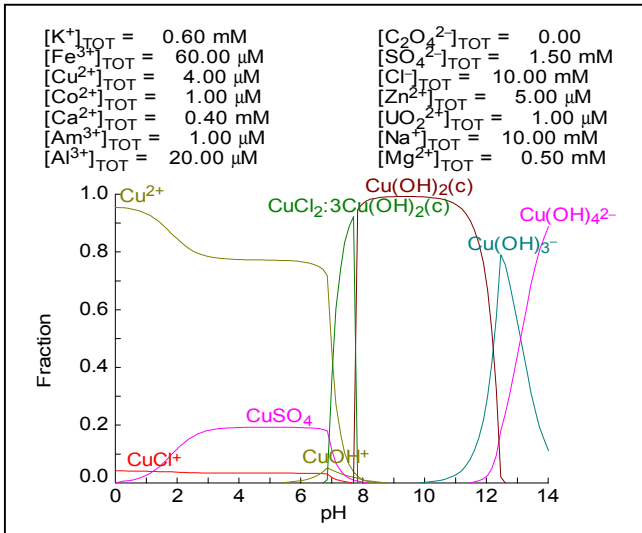


Figure A5. Cu speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

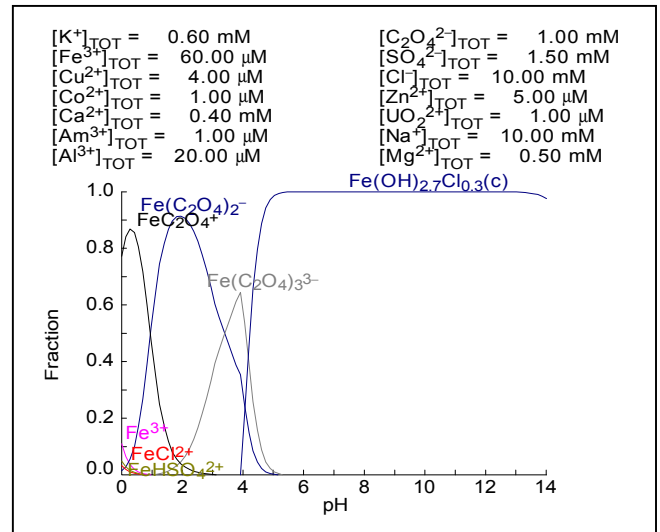
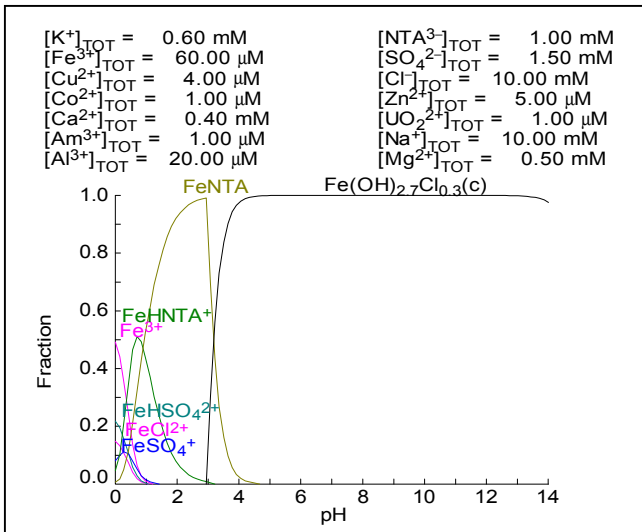
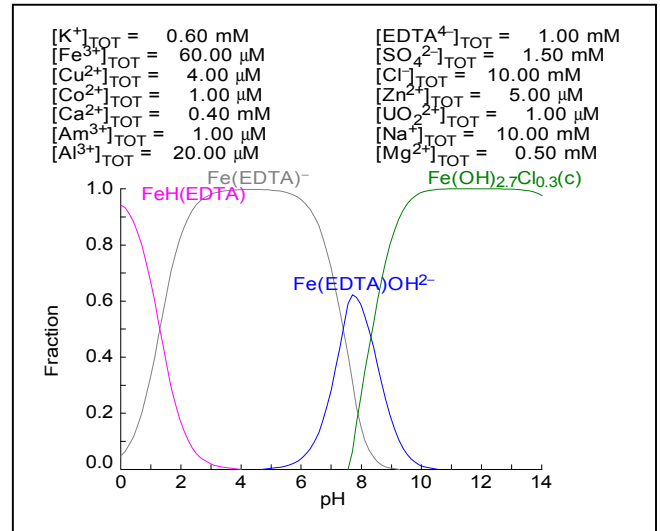
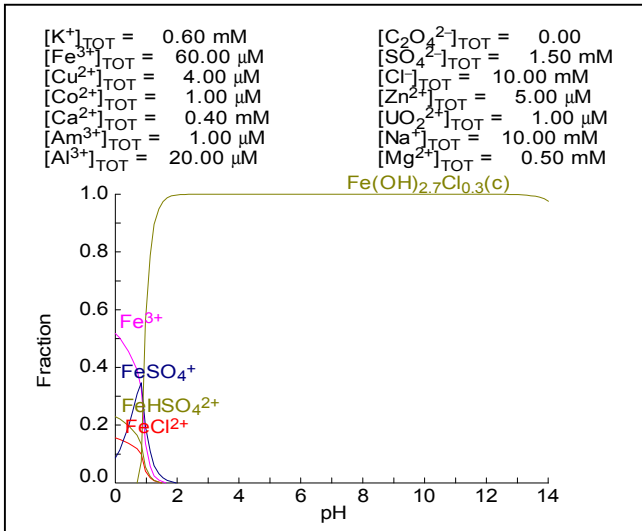


Figure A6. Fe speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

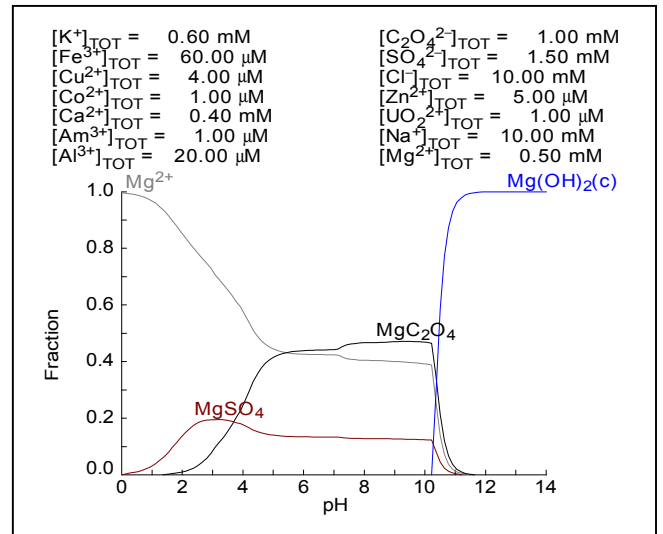
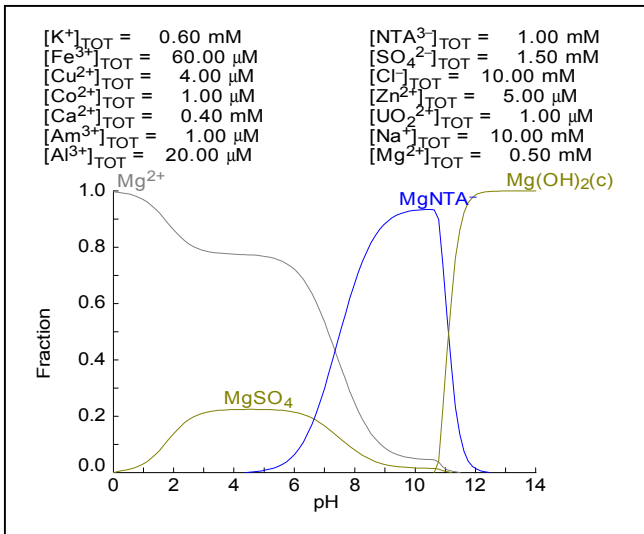
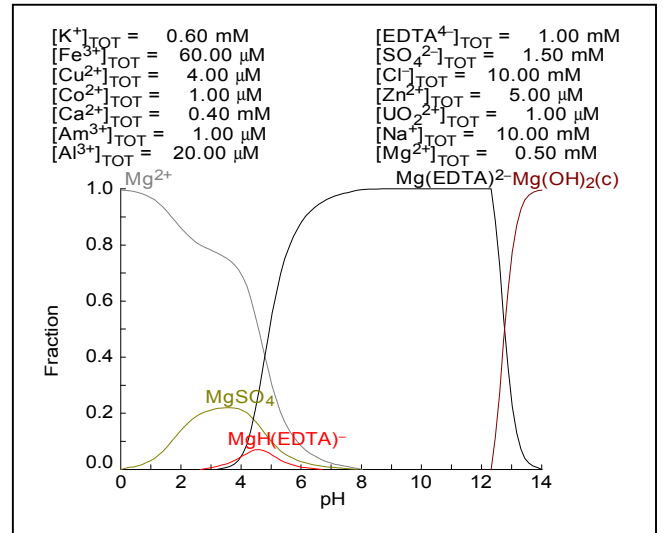
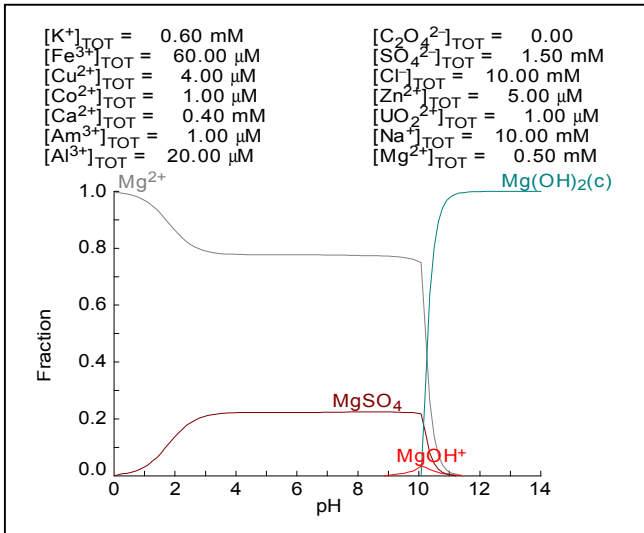


Figure A7. Mg speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

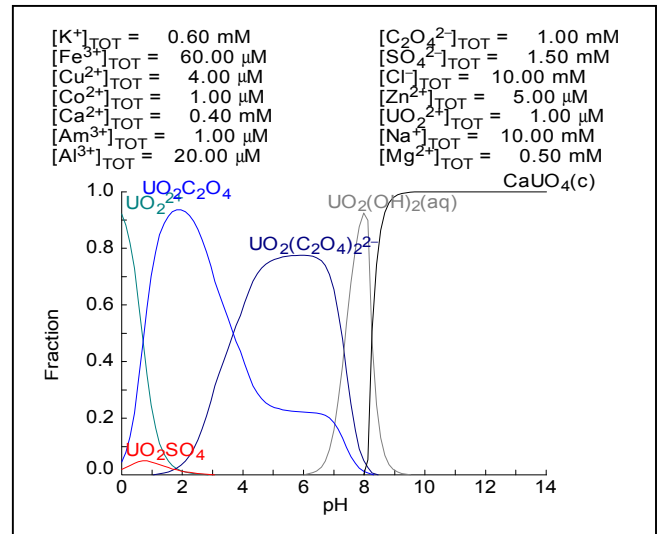
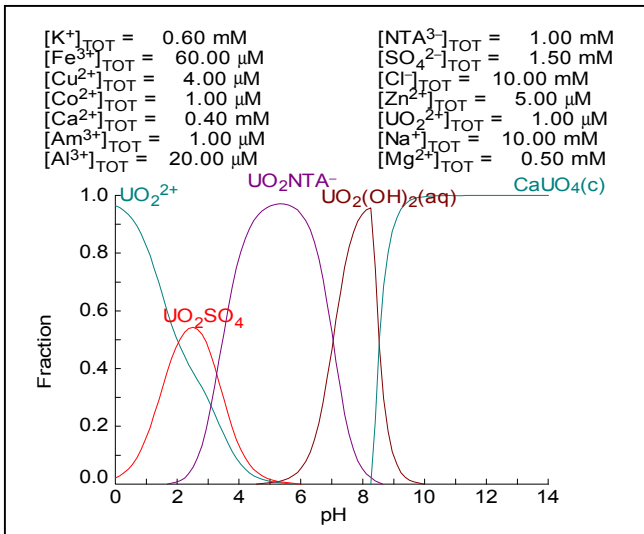
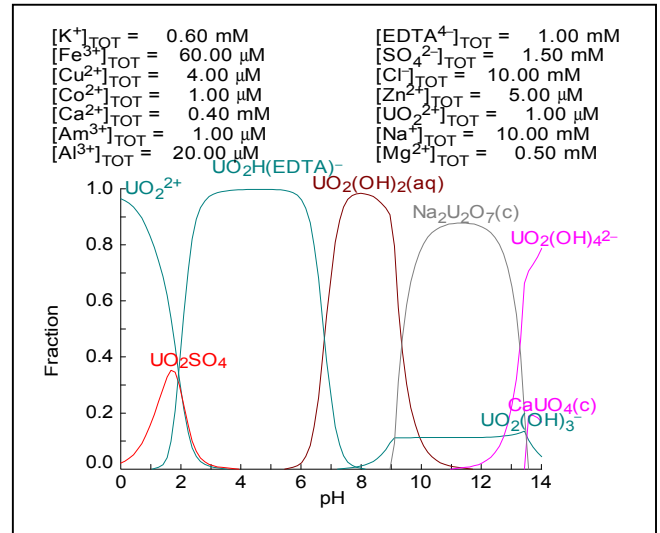
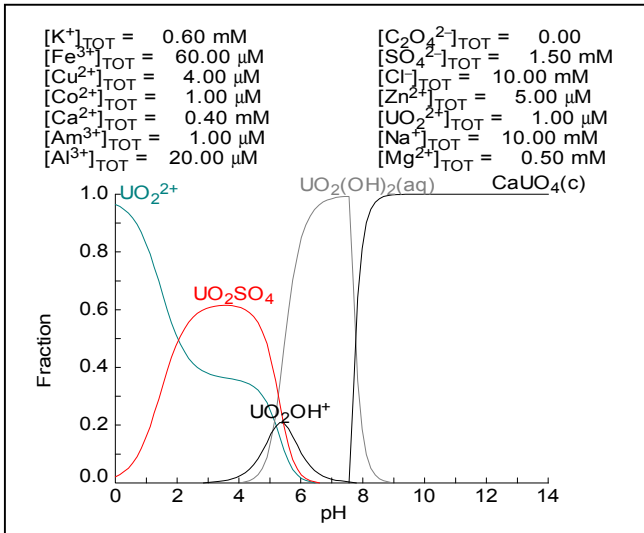


Figure A8. UO_2^{2+} speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

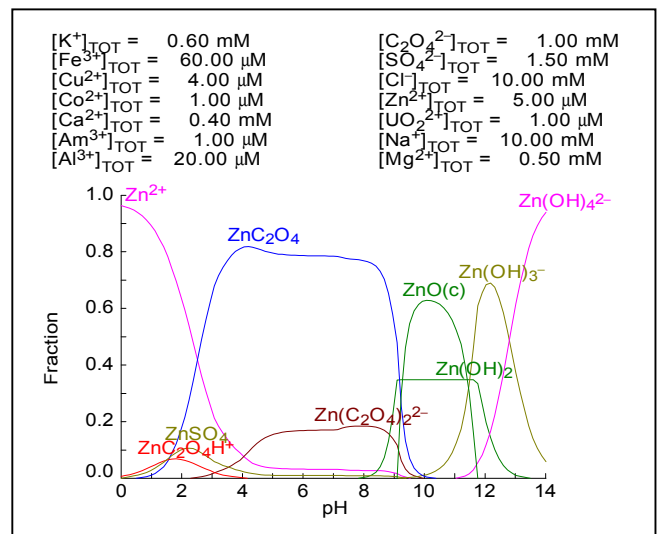
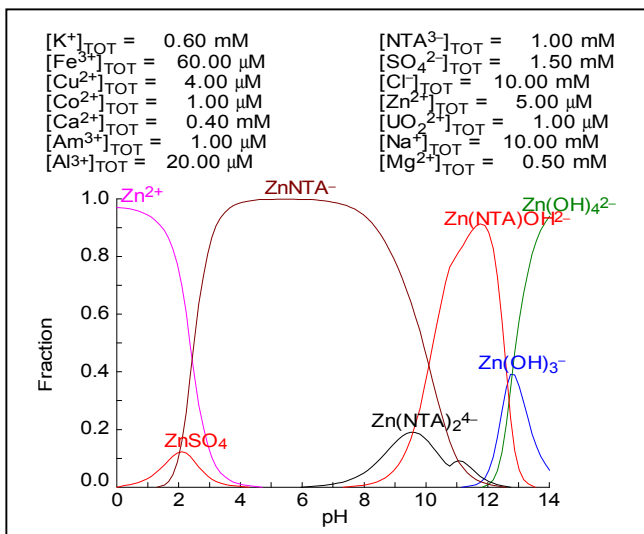
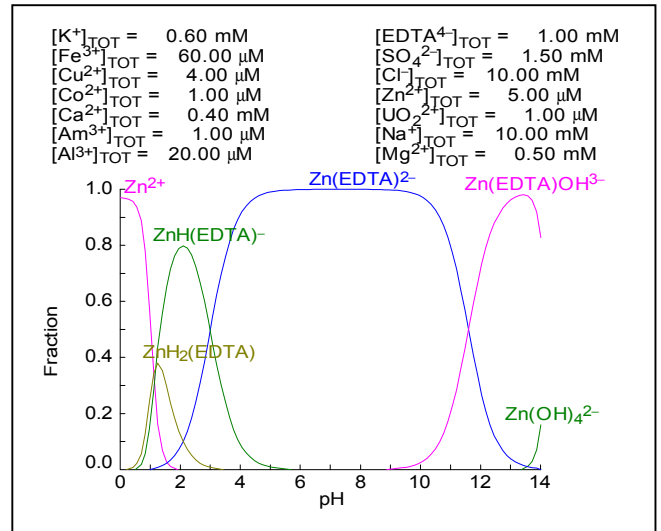
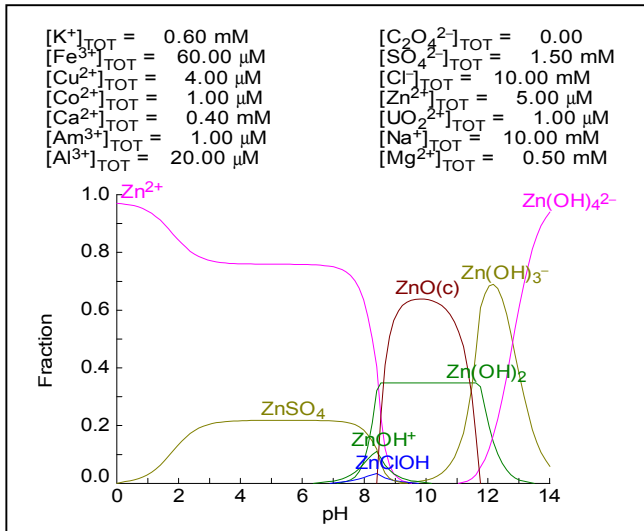


Figure A9. Zn speciation in the absence of ligands (upper left (a)) and in the presence of EDTA, NTA and oxalate (upper right (b), lower left(c) and lower right (d), respectively).

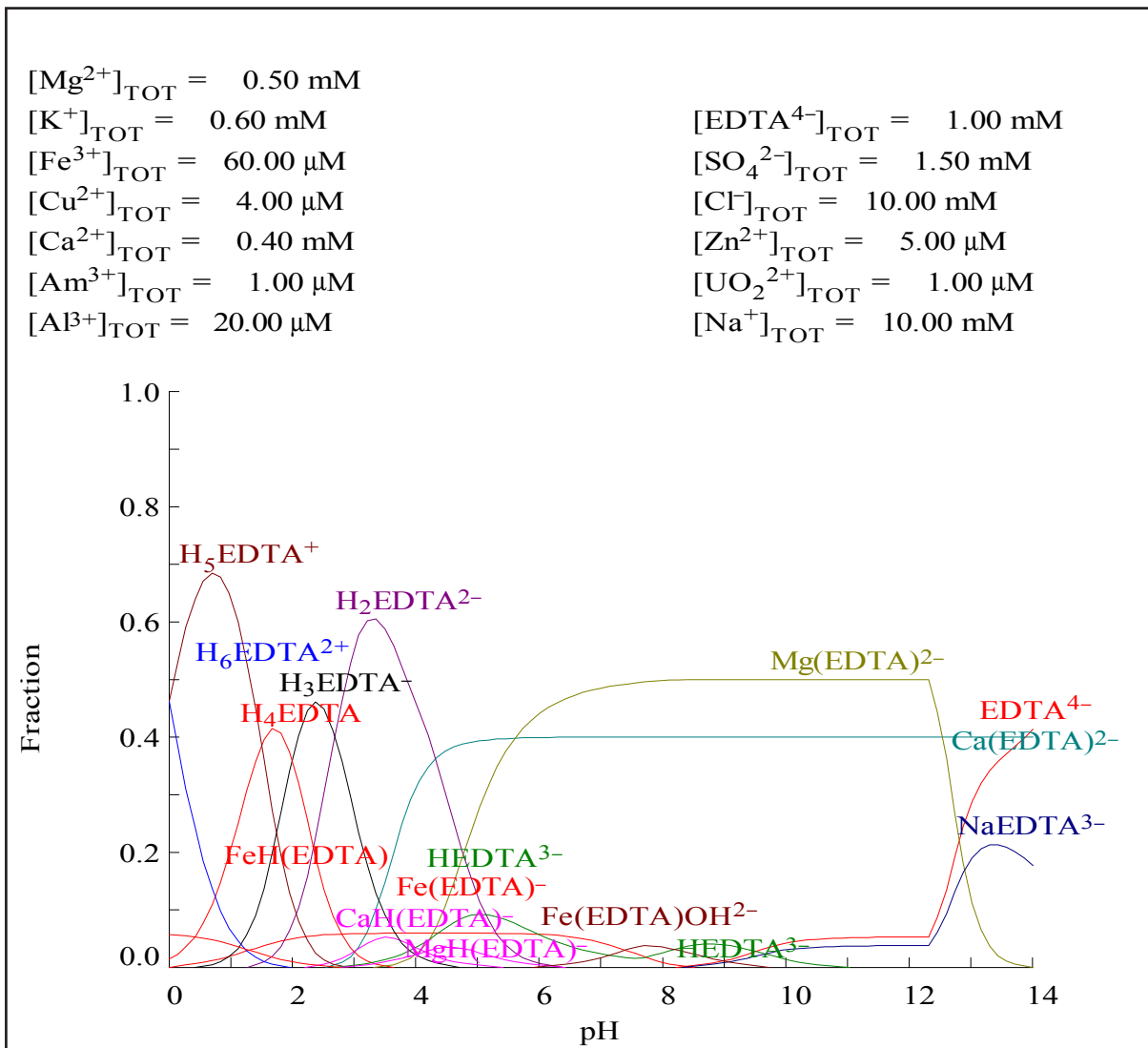


Figure 10. EDTA speciation and distribution vs. pH

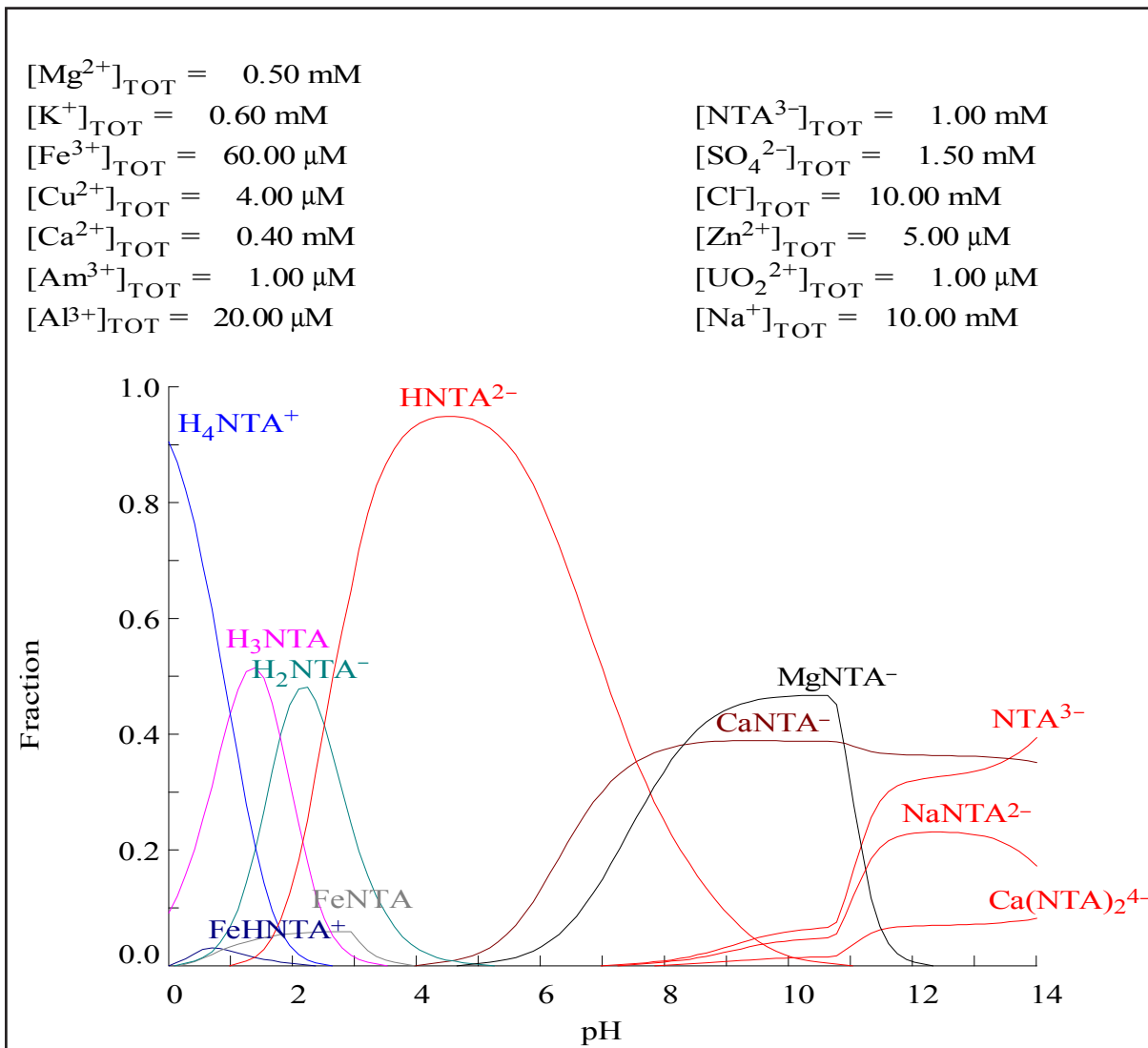


Figure 11. NTA speciation and distribution vs. pH

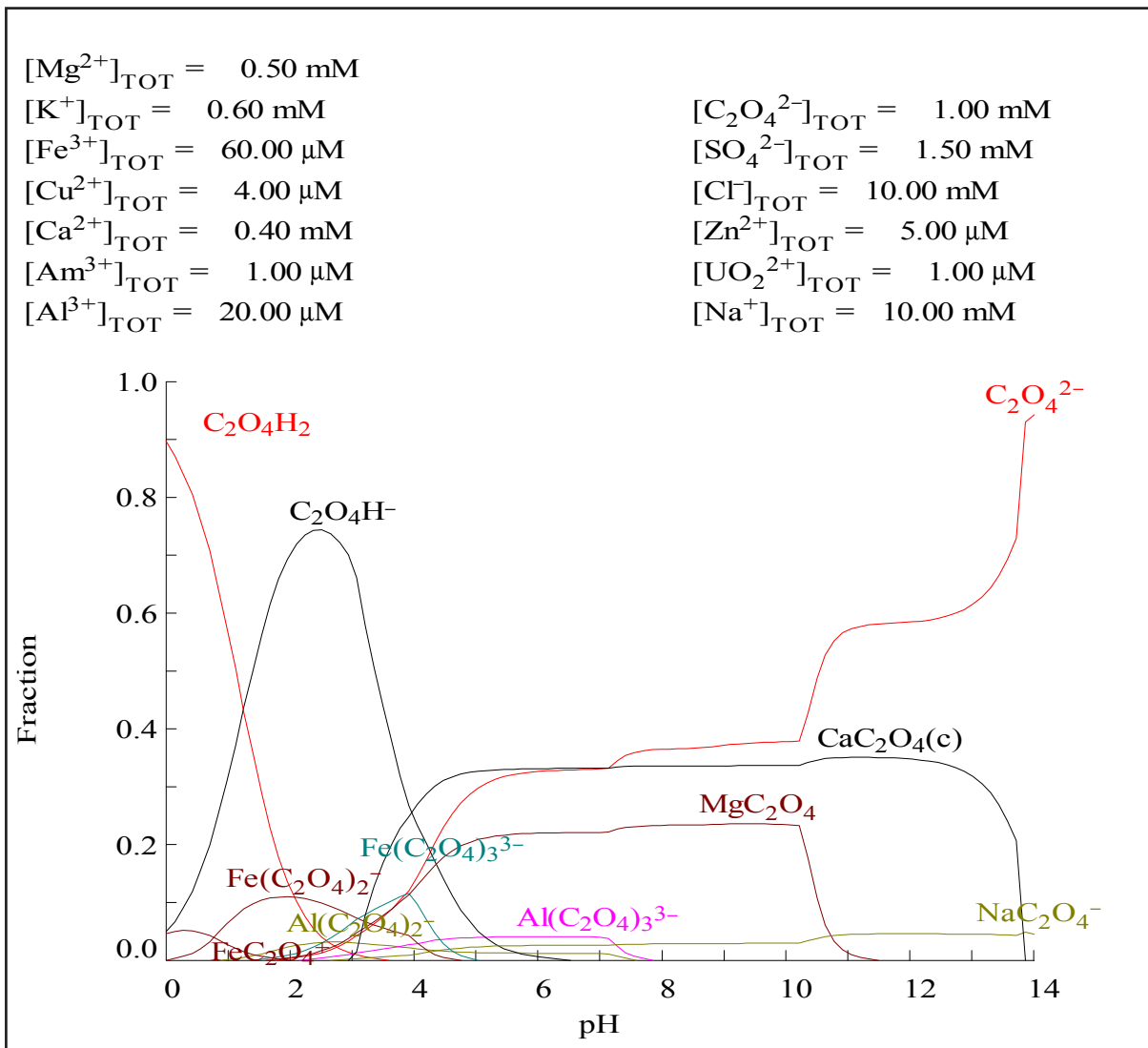


Figure 12. Oxalate speciation and distribution vs. pH