Waste Isolation Pilot Plant

Compliance Certification Application

Reference 90

Bruno, J., and A. Sandino. 1987.
Radionuclide Co-precipitation, SKB Technical Report. no. 87-23. The Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm. 19pp. NTIS No.:DE88754187

Submitted in accordance with 40 CFR §194.13, Submission of Reference Materials.

87-23

Radionuclide co-precipitation

Jordi Bruno and Amaia Sandino

The Royal Institute of Technology
Department of Inorganic Chemistry
Stockholm

December 1987

SKB-TR--87-23

RADIONUCLIDE CO-PRECIPITATION

Jordi Bruno and Amaia Sandino

The Royal Institute of Technology
Department of Inorganic Chemistry

Stockholm December 1987

RADIONUCLIDE CO-PRECIPITATION

Jordi Bruno and Amaia Sandino

The Royal Institute of Technology
Department of Inorganic Chemistry
Stockholm

December 1987

CONTENT

SUMMARY

The thermodynamic and kinetic behaviour of the minor components of the spent fuel matrix has been theoretically and experimentally investigated. Two different situations have been studied: Part I, the near field scenario, where the release and migration of the minor components is dependent on the solubility behaviour of UO_2(s); Part II, the far field, where the solubility and transport of the radionuclides is related to the major geochemical processes occurring.

KEYWORDS: Co-precipitation/co-dissolution, spent nuclear fuel, radionuclide solubility.

PART I: RADIONUCLIDE CO-PRECIPITATION IN THE NEAR FIELD

1 Introduction

A first estimate of the release and transport of radionuclides from spent nuclear fuel in contact with groundwater is generally made by using thermodynamic models. The collection and critical evaluation of the necessary thermodynamic data requires much work. Solubility limits are often used as radionuclide source terms in the general security analysis and most of the solubility data used in these exercises relates to pure solid phases.

Spent nuclear fuel can be considered as a multicomponent solid solution of varying homogeneity, depending on the considered radionuclide. It is now well established that the release of uranium, the major component of UO_2 spent fuel, is solubility limited [1]. It is reasonable to expect that the dissolution of the minor components will be influenced by the release and dissolution of uranium. Consequently, the thermodynamic and kinetic behaviour of these components cannot be modelled only by using the data for the pure individual phases.

The solubility behaviour of $UO_2(s)$ depends on the redox potential of the aqueous medium in contact with the fuel. Hence, two different situations should be studied. In the first case a preliminary solubilization of the spent nuclear fuel caused by oxidation in the near field, (e.g. due to radiolysis), is followed by a reprecipitation in the far field when reducing conditions are restored. In the second case, co-dissolution of the minor component radionuclides may occur in relation to the dissolution of UO_2 under reducing conditions. In both cases, the solubility of these radionuclides will be effected by the behaviour of UO_2. The system is no longer dependent only on the thermodynamic and kinetic properties of the various individual phases for the different radionuclides, but on the distribution of the components in the solid phase, e.g. the formation of solid solutions.

The attachment of a certain metal ion to a host solid phase may occur in several forms, from adsorption of the ion at the surface of the solid to true ideal solid solutions, where the foreign

metal ion is regularly placed in the host lattice. There is a sequential transition from surface co-precipitation to ideal solid solution formation through these three processes:

a) Surface co-precipitation
b) Lattice diffusion
c) Solid solution

At room temperature, diffusion in a solid matrix is generally very slow and the first process, surface co-precipitation, is the one expected to occur. In this case, there is no major structural arrangement and the radionuclide distribution equilibria is established between the solid surface and the solution. However, the initial source (UO_2 spent fuel), may be considered as an ideal solid solution for most of its components.

All these phenomena can be included under the term co-precipitation. Co-precipitation has been defined as "the contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation [2]". This concept is limited since there are some cases which cannot be explained by this definition. Therefore, Gordon [3] redefined co-precipitation as "the precipitation of a compound in conjunction with one or more components". We will use the concept co-precipitation in this sense. Four types of co-precipitation have been characterized:

a) Isomorphous mixed crystal formation
b) Anomalous mixed crystal formation
c) Adsorption
d) Occlusion

where the first two cases are different degrees of solid solutions [3].

The constituents of isomorphous mixed crystals have similar chemical and crystallographic properties. In the case of anomalous mixed crystal formation, the characteristics are the same as in the former case, but their formation cannot be explained on the same basis. Adsorption can be considered to some extent, as anomalous mixed crystal formation at the surface of the precipitate. The term occlusion is usually applied for the case where adsorbed species on crystal planes are subsequently covered with other crystal layers.

Co-precipitation is a well known chemical phenomenon. It has been extensively applied in analytical chemistry for the separation of trace elements [3,4]. Also in radioanalytical applications, particularly in enrichment processes [5,6], and for mixed oxide fuel production [7,8,9]. In the field of geochemistry, there are many processes which should be explained by means of co-precipitation, for instance the anomalous behaviour of the Sr-Ca carbonate system [10], or the Ba^{2+}, Sr^{2+} system in calcite [11].

In a previous work [12] we have studied the co-precipitation behaviour of the $La(OH)_3$-UO_2 system at room temperature. In this communication we present some recent results on the thermodynamics of co-precipitation at room temperature of some radionuclides. The effect of hydrothermal aging on the co-precipitation/co-dissolution distribution is also studied, by using Th^{4+}, La^{3+} and Ba^{2+} as radionuclide analogues.

2 Choice of Analogues

The investigation of the basic processes related to radionuclide co-dissolution/co-precipitation, requires well controlled experimental conditions. The study of the actual radionuclides has experimental difficulties due to their radioactive nature. Because of this, proper analogues have to be chosen. One of the aims of this research program has been to investigate the dependence of the degree of co-precipitation/co-dissolution with the charge of the radionuclide ion. Consequently Th^{4+}, La^{3+} and Ba^{2+} have been selected as analogue ions for this purpose.

The co-precipitation and co-dissolution phenomena are controlled by many different variables: temperature, the concentration of the minor components, the rate of the process, the ionic radius and the ionic charge [3]. The two main factors are the ionic charge and size, since the formation of isomorphous mixed crystals is dependent on similarities in both the chemical properties and the size of the substituting ions. The probability that co-precipitation/co-dissolution occurs is larger when these parameters are similar for both the host and the minor component. In Table I-1 we have summarized the ionic radii for various ions of interest.

Table 1-1. Effective ionic radii [13] of some ions of interest.

Ion	Å	Coordination number
U^{6+}	1.00	8
U^{4+}	1.14	8
Th^{4+}	1.19	8
Pu^{4+}	1.10	8
Pu^{3+}	1.14	6
Ln^{3+}	1.00-1.21	6
Ra^{2+}	1.62	8
Ba^{2+}	1.56	8

In the case of Pu^{4+} and Th^{4+} an isomorphous substitution of U^{4+} in the UO_2 lattice is obviously possible since both charge and size are very similar.

For Pu^{3+} and the lanthanide ions (here symbolized by Ln^{3+}) the ionic radii are in a range of values which indicates the possibility of isomorphous substitution of U^{4+}, although this would imply a readjustment of the charge. We found it would be interesting to test to which extent a larger ion like Ba^{2+} (analogue to Ra^{2+}), would behave in the co-precipitation system.

3 Thermodynamics of Radionuclide Co-precipitation

The equilibrium distribution of the components A, B of a solid solution between the solid and the aqueous phases can be described in two different ways.

If equilibrium is attained between the bulk of the solid solution and the aqueous phase the system follows the Berthelot-Nernst homogeneous distribution law [14]. This can be expressed as:

$$\frac{[A]_{(aq)}}{[B]_{(aq)}} = D \frac{[A]_{(s)}}{[B]_{(s)}} \qquad (1)$$

When equilibrium is only reached between the surface of the solid and the aqueous solution, the distribution of the components between the solid and the aqueous phases follows the Doerner-Hoskins logarithmic law [15]. This is formulated as:

$$\log \frac{[A]_{(aq)}}{[B]_{(aq)}} = k \log \frac{[A]_{(s)}}{[B]_{(s)}} \qquad (2)$$

The co-precipitation equilibria in the system La(III)/U(IV). [12] and Ba(II)/U(IV) have been studied under well controlled conditions at 25°C. The experimental details have been previously described [12].

From these experimental data we conclude that the distribution of the different ions involved between the aqueous phase and the solid solution follows the logarithmic law. From these data it is possible to calculate conditional solubility products [12] of $La(OH)_3(s)$ and $Ba(OH)_2(s)$, in the presence of $UO_2(s)$. From a few data obtained [16], in the Pu(III)/U(IV) system, we have also estimated a conditional solubility product for $Pu(OH)_3(s)$ in the presence of $UO_2(s)$. In Table I-2 we make a comparison between these conditional solubility products and the values for the individual phases.

Table I-2. A comparison between conditional (K^*_{so}) and individual solubility products for the equilibria:

$$M^{n+} + n\,H_2O \rightleftarrows M(OH)_n(s) + n\,H^+$$

M^{n+}	log K^*_{so}	log K_{so}
Pu^{3+}	- 2.4	-19.3
La^{3+}	-12.5	-20.5
Ba^{2+}	- 9.1	-24.4

From these data it is possible to conclude that:

- The solubility of the minor components is strongly reduced by the presence of $UO_2(s)$.
- At low temperature the co-precipitation equilibrium obeys the Doerner-Hoskins distribution law. This indicates that equilibrium is only attained between the surface of the solid and the aqueous phase.

4 The Effect of Aging on Co-precipitation

Because of the long-term predictions necessary for the safety and performance assessment of nuclear waste repositories, it is important to consider the effect of aging of the co-precipitate on the distribution equilibria.

In order to study this, a solution initially containing

$[U(VI)] = 1.00\ 10^{-2}$ mol dm^{-3}
$[Th(IV)] = 1.00\ 10^{-4}$ mol dm^{-3}
$[La(III)] = 5.00\ 10^{-5}$ mol dm^{-3}
$[Ba(II)] = 5.00\ 10^{-5}$ mol dm^{-3}

in 0.5 mol dm^{-3} $NaClO_4$ was reduced with H_2/Pd(g) at pH = 3 by using the same experimental approach as previously described [12]. A black precipitate was formed which was characterized by X-ray powder diffraction (XPD), (see Figure I-1). The broad lines observed, showed the presence of a microcrystalline solid. This solid was kept in contact with the mother solution for six months, at T = 110 to 120°C under N_2 (g) atmosphere. After this time the solution and the solid phase were analyzed. In Table I-3 we summarize the percentages of the different components both in the aqueous and the solid phases.

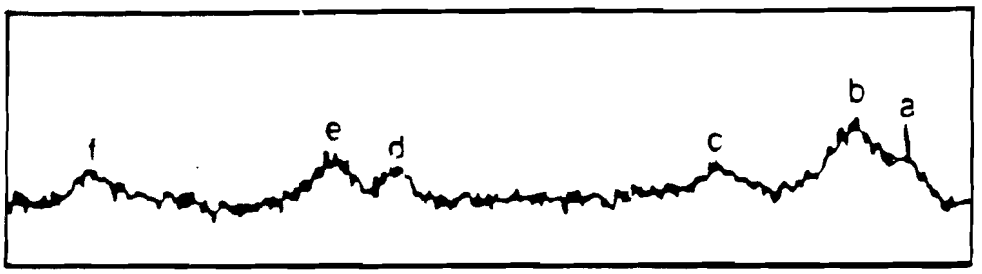

Figure I-1. XPD pattern of the solid used in our experiments where the theoretical assigned distances [19], are in (Å):

a: 3.234 (ThO_2)
b: 3.157 $(U,Th)O_2$
c: 2.73 $(U,Th)O_2$
d: 1.98 (ThO_2)
e: 1.93 (UO_2)
f: 1.65 $(U,Th)O_2$

Table I-3. Relative composition of the aqueous phase and the co-precipitate after aging.

Metal ion	% in solution	% in solid
U(IV)	98.0	97.5
Th(IV)	1.0	1.7
La(III)	0.5	0.4
Ba(II)	0.5	0.4

The results in Table I-3, indicate a congruent co-precipitation of La(III) and Ba(II) and an enrichment of Th(IV) in the solid.

5 Kinetics of Co-dissolution

A portion of this solid phase was put in contact with a 0.5 mol dm^{-3} $NaClO_4$ solution at pH = 4.5 under $N_2(g)$ atmosphere. The time dependence and the equilibrium distribution between the solid and the aqueous phase were studied. Several samples were taken at different times, and we analyzed the uranium, lanthanum, thorium and barium contents in the initial solid and in the liquid samples by induced coupled plasma spectrophotometry, (IC). These analysis were performed by using a Perkin Elmer ICP/5500 spectrophotometer.

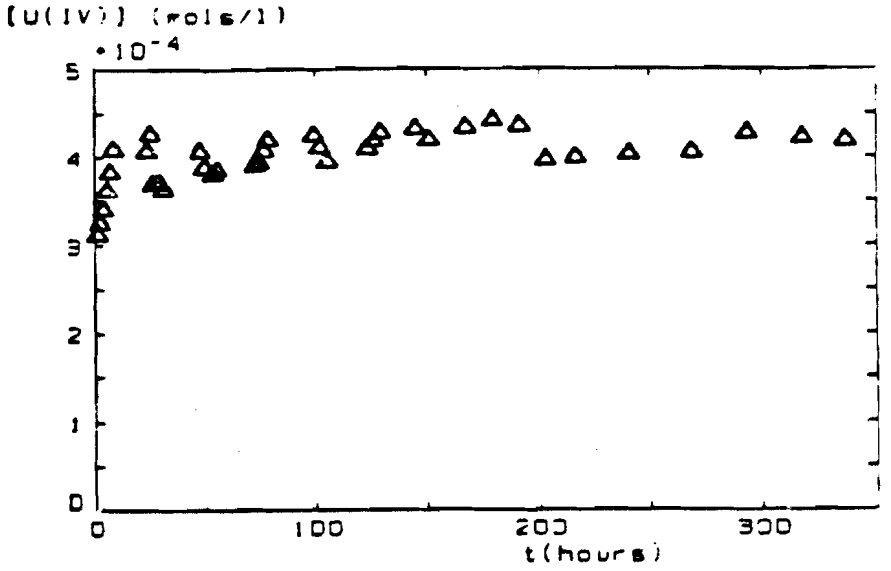

Figure I-2a. Values of uranium concentration vs time.

The results are summarized in Figure I-2. The plot of [U(IV)] vs. contact time, (Figure I-2a) shows that steady state concentrations are reached after 50 hours. The average steady state concentrations of U(IV), is of the same magnitude as the expected [U(IV)] in equilibrium with amorphous UO_2(s) (3.0 10^{-4} mol dm^{-3}), [17].

The plots of the normalized concentrations of the minor components with respect to the uranium concentration in solution vs. time (Figure I-2b-c-d), indicate that the release of these minor components from the solid matrix is totally controlled by the uranium dissolution, e.g., congruent release. This behaviour is largely time independent (see Figure I-2b-d). Finally, a calculation of the distribution factors D according to the Berthelot-Nernst distribution law (Eq. 1):

$$\frac{[M]_{(s)}}{[U(IV)]_{(s)}} = D \frac{[M]_{(aq)}}{[U(IV)]_{(aq)}} \qquad (3)$$

gives $D_{Th}4+ = D_{La}3+ = 1$, while $D_{Ba}2+ = 2$. This strongly suggests that hydrothermal aging of the co-precipitate has caused the initial logarithmic distribution to shift to a normal type of distribution.

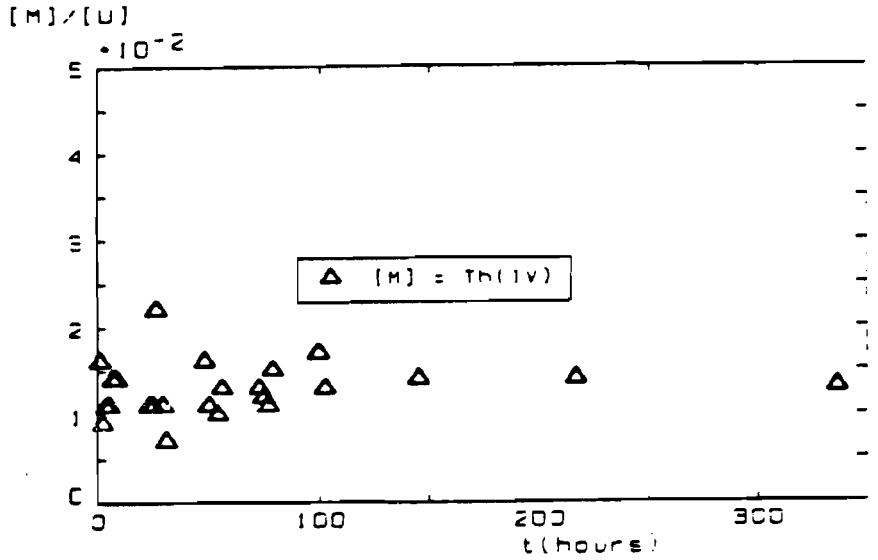

Figure I-2b. Plot of the normalized concentration of [Th(IV)] vs [U(IV)].

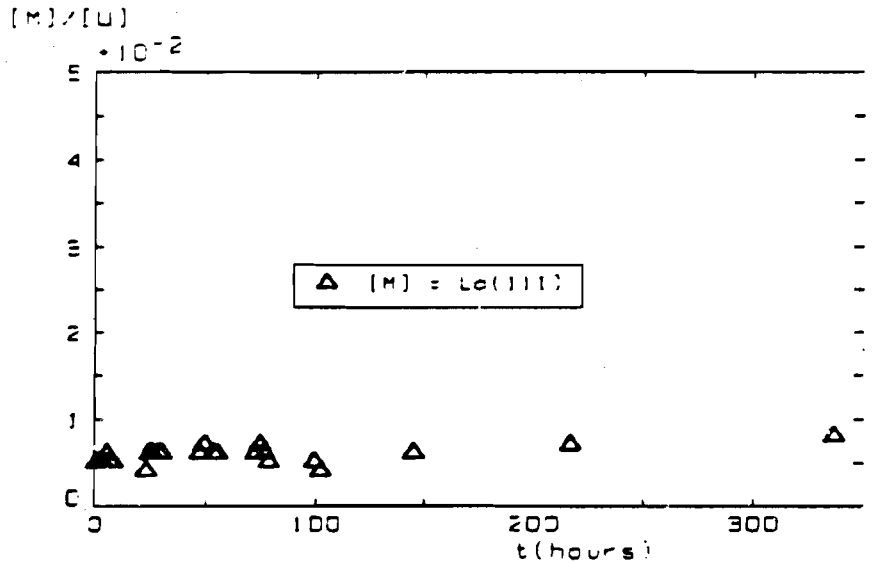

Figure I-2c. Plot of the normalized concentration of [La(III)] vs [U(IV)].

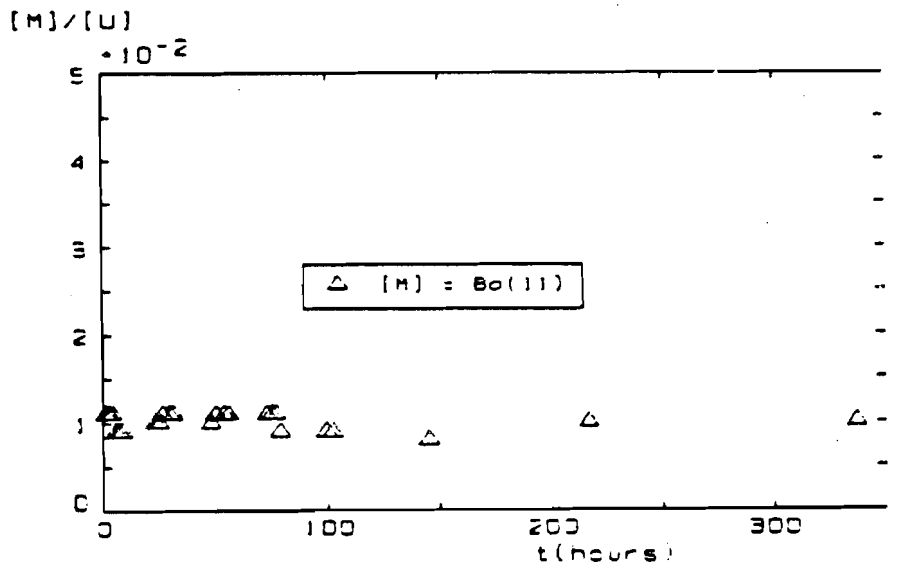

Figure I-2d. Plot of the normalized concentration of [Ba(II)] vs [U(IV)].

6 Conclusions

In this work we have attempted a general study of the solubility behaviour of the minor components of the nuclear waste matrix in relation to the major component UO_2.

As we have shown in this and previous studies [12,16], the solubility of the minor components cannot be only predicted on basis of the individual solid phases. Co-precipitation occurs, and at low temperatures the distribution of the components between the solid and the aqueous phases follows the logarithmic distribution law. Hydrothermal aging causes the co-precipitation system to shift from the logarithmic (Doerner-Hoskins) to a normal (Berthelot-Nernst) distribution. This is in agreement with previous observations in other co-precipitation systems [3].

At the same time, we have also shown that the dissolution of the minor components from a $U(Th,La,Ba)O_2$ solid solution is kinetically and thermodynamically controlled by the behaviour of the major component, uranium dioxide.

In this work we have only studied the co-precipitation/co-dissolution systems in connection with a near field situation, where uranium can be the major component in case of oxidation and container failure. In the far field, the co-precipitation/co-dissolution systems have to be related to the major geochemical processes occurring in granitic groundwaters. Possible systems

affecting the "individual solubility" of radionuclides are the precipitation/dissolution of calcite, Fe(III)-hydroxide, MnO_2 and feldspars modification [18]. Future work will be focused to an understanding of these processes.

7 Acknowledgements

This investigation was financially supported by SKB (Swedish Nuclear Fuel and Waste Management Co.). Prof. I. Grenthe is thanked for valuable criticism. Dr. Inga-Kari Björner is gratefully acknowledged for carrying out the ICP measurements.

8 References

1. FORSYTH, R., WERME, L.O., BRUNO, J.: J. Nucl. Mat. 138, 1 (1986).

2. KOLTHOFF, I.M., SANDELL, E.B.: Textbook of quantitative inorganic analysis, 3rd ed, Mac Millan, New York 1952.

3. GORDON, L., SALUTSKY, M.L., WILLARD, H.H.: Precipitation from homogeneous solution, John Wiley and Sons, Inc., New York 1959.

4. KIMURA, T., KOBAYASHI, Y., ANATSU, K.: Radiochim. Acta 39, 179 (1986).

5. SALUTSKY, M.L., STITES, J.G., MARTIN, A.W.: Anal. Chem. 25, 1677 (1953).

6. HERMANN, J.A.: U.S. Atomic Energy Commision, AECD-3637, (1954).

7. SCHNEIDER, V.W., HERMANN, F., DRUCKENBRODT, W.G.: Trans. Am. Nucl. Soc. 176 (1979).

8. RADFORD, K.C., BRATTON, R.S.: J. Nucl. Mat. 57, 28 (1975).

9. D'ANNUCCI, F., SARI, C., SCHUMACHER, G.: Nucl. Technol. 35, 80 (1977).

10. KINSMAN, D.J., HOLLAND, H.D.: Geochim. Cosmochim. Acta 33 (1969).

11. PINGITORE, N.E.: Geochemical Processes at Mineral Surfaces, ACS, Symp. Ser. 323, Washington D.C., 1986.

12. BRUNO, J., GRENTHE, I., MUÑOZ, M.: Mat. Res. Soc. Symp. Proc. 50, 717 (1985).

13. SHANON, R.D.: Acta Cryst. A32, 751 (1976).

14. HENDERSON, L.M., KRACEK, F.C.: J. Am. Chem. Soc. 49, 738 (1927).

15. DOERNER, H.A., HOSKINS, W.M.: J. Am. Chem. Soc. 47, 662 (1925).

16. GRENTHE, I., PUIGDOMENECH, I., BRUNO, J.: KBS-Technical Report 83-02. SKB/KBS, Stockholm (1983).

17. BRUNO, J., CASAS, I., LAGERMAN, B., MUÑOZ, M.: Mat. Res. Soc. Symp. Proc. 84, 153 (1987).

18. STUMM, W., MORGAN, J.J.: Aquatic Chemistry, 2nd ed., John Wiley and Sons, New York 1981, p. 536.

19. J.C.P.D.S. Diffraction Data Cards No. 4-0556, 5-0550, 5-0549.

PART II: RADIONUCLIDE CO-PRECIPITATION IN THE FAR FIELD

1 Introduction

As we have already pointed out in the previous section, the co-precipitation/co-dissolution behaviour of the radionuclides in the far-field will be related to the major hydrogeochemical changes in the groundwater.

According to Eriksson [1] and Stumm and Morgan [2], the major geochemical changes occurring as water percolates from the surface towards deep areas can be schematized by Figure II-1.

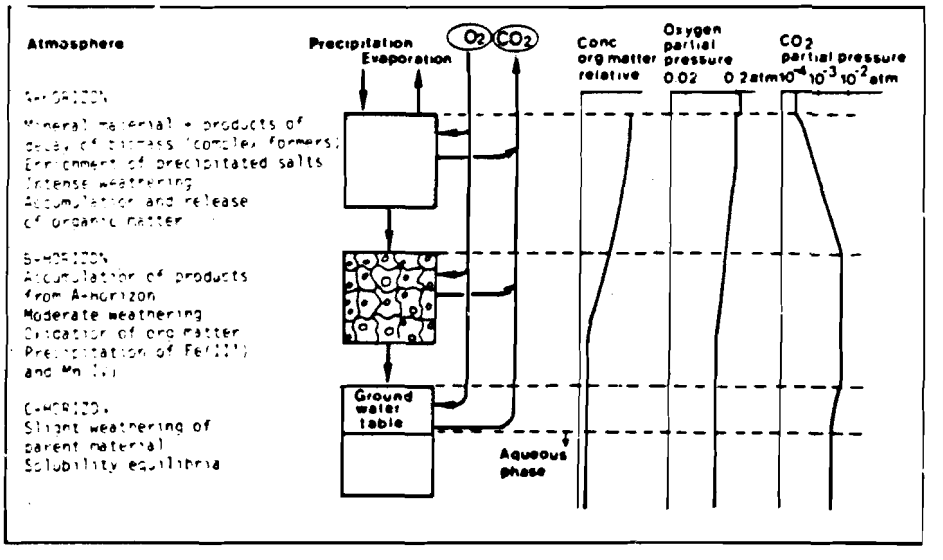

Figure II-1. Acquisition of solutes during infiltration.

It is now well established [3] that groundwater flows preferentially through fissures. It is logical to expect that the major chemical processes will occur in these fissures and at the interface with the fracture filling minerals. Independently of the flow pattern, the geochemical changes will be related to the weathering of the bedrock. Hence, it is necessary to identify which are the possible fracture filling minerals and weathering products in granitic bedrock and the geochemical processes related with them. Muller [4] has made a compilation of the different types of minerals present in granite. In Table II-1, we show the fracture-filling and secondary minerals for granite.

During the SKB site characterization program, investigations of low temperature fracture fillings have been performed [5a-b]. Calcite, iron-oxides and clay minerals have been found to correspond to the latest geological event. It has also been observed that calcite is found in areas of recharge and discharge [3]. The dissolution-precipitation reactions of calcite and iron-oxides are known to proceed fast, even at low temperatures. The mean life of a calcite surface (monolayer) in seawater has been experimentally demonstrated to be one day [6,7]. Consequently, calcite and iron-oxides mobilization will play an important role in the geochemical cycle of radionuclides in the granite environment. There is a great deal of information about co-precipitation systems related to calcite dissolution-precipitation. Much less has been done respect to iron hydroxides. In the case of goethite and limonite much emphasis has been put in studying the adsorption properties of different ions on the iron hydroxide surface.

J. Morse [8] has done an excellent overview on the surface chemistry of calcium carbonate minerals. According to his work and the experimental findings of different investigators it is possible to find that there is a related sequence from adsorption to co-precipitation through surface precipitation. Adsorption and surface precipitation require the existence of a contiguous solid phase. However, in most of the cases the mechanisms of these three, processes are closely related.

Hence, in our literature survey we have devoted our attention not only to radionuclide co-precipitation with calcite and iron hydroxide, but also to the investigations of radionuclide adsorption on these solid phases where emphasis has been put in the surface coordination aspects.

2 Radionuclide Co-precipitation with Calcite

As pointed out by Pingitore [9] the incorporation of trace elements in calcite has an extensive impact in several areas of environmental chemistry and geochemistry. The experimental information collected in these areas can be summarized as follows.

Table II-1. Minerals found in granites.

Mineral Group	Species	Type	Specific Formula
Sulphides	Pyrite	Fract. fill.	FeS_2
	Pyrrhotite	Fract. fill.	FeS(pyrr), Fe_7S_8
Oxides	Pyrolusite	Second. min.	MnO_2
Hydroxides	Goethite	Second. min.	FeOOH
	Diaspore	Second. min.	AlOOH
	Bohemite	Second. min.	AlOOH
	Gibbsite	Second. min.	$Al(OH)_3$
	Limonite	Second. min. Fract. fill.	FeOOH nH_2O
Halides	Fluorite	Second. min.	CaF_2
Carbonates	Calcite	Fract. fill.	$CaCO_3$
Sulphates	Alunite	Second. min.	$KAl_3(SO_4)_2(OH)_6$
	Jarosite	Second. min.	$KFe_3(SO_4)_2(OH)_6$
	Anhydrite	Second. min.	$CaSO_4$
	Gypsum	Second. min. Fract. fill.	$CaSO_4 \cdot 2H_2O$
Sorosilicates	Zoisite	Fract. fill.	$Ca_2Al_3(SiO_4)_3OH$
	Clinozoisite	Fract. fill.	$Ca_2Al_3(SiO_4)_3OH$
	Epidote	Second. min. Fract. fill.	$Ca_2FeAl_2(SiO_4)_3OH$
	Piemontite	Fract. fill.	$Ca_2(Al,Mn,Fe)_3(SiO_4)_3OH$
Phyllosilicates	Kaolinite	Second. min. Fract. fill.	$Al_2Si_2O_5(OH)_4$
	Smectite	Second. min.	$CaAl_{14}Si_{22}O_{60}(OH)_{12}$
	Clinochlore	Second. min. Fract. fill.	$Mg_{40}Al_{16}Si_{24}O_{80}(OH)_{64}$
	Illite	Second. min.	$K_2Al_{10}Si_{14}O_{40}(OH)_{80}$
	Sericite	Second. min.	$KAl_2(AlSi_3O_{10})(OH,F)_2$
Tectosilicates	Chalcedony	Fract. fill.	SiO_2(chal)
	Opal	Fract. fill.	$SiO_2 \cdot 0.5H_2O$(am)

Doubled charged ions with ionic radii less than calcium (e.g. Mn^{2+}, Zn^{2+}, Fe^{2+}, Cd^{2+} and Co^{2+}) can be extensively incorporated into calcite precipitated at groundwater conditions. Spectroscopic techniques, X-Ray diffraction and EPR measurements, have demonstrated that these trace cations substitute Ca^{2+} in the lattice. The calcium ion may occur in the $CaCO_3$ lattice as hexacoordinated (calcite), or ninefold-coordinated (aragonite). Cations larger than Ca^{2+}, like Sr^{2+}, Ba^{2+}, Pb^{2+} and Ra^{2+} substitute also Ca^{2+} in the rombohedral calcite, even if their pure carbonates, like strontianite or barite, bild up orthoromboedral structures. A great number of studies have been carried out on the adsorption/co-precipitation of Mg^{2+} with calcite [10,11,12,13]. Bancroft et al., [10] studied the uptake of Ba^{2+} by calcite. Also the sorption of Mn^{2+} on calcite has been investigated by several authors [11,12,13]. McBride carried out an spectroscopic investigation of the Mn^{2+} surface concentrations by ESR [13]. He observed the formation of a new $MnCO_3$ phase at high Mn^{2+} surface concentrations. Also the uptake of Cu(II) by calcite has been investigated [14]. In this case the surface precipitated phase seem to correspond to malachite $Cu_2(OH)_2CO_3$. The interaction of Cd(II) with calcite surfaces has also been investigated by McBride [15]. The uptake patterns are very similar to those of Mn^{2+}. Kornicker et al. [16] studied the adsorption of CO^{2+} on carbonate mineral surfaces, no evidence for the formation of a differentiated $CoCO_3$ phase was observed. Finally, Morse and coworkers have dedicated much effort to the study of the interaction of actinides with calcite surfaces. Am(III) [17], Th(IV) [18], NpO_2^+ [19], PuO_2^+ [20] and UO_2^{2+} [21] adsorb significantly on calcite. Nevertheless, there is a competition from carbonate complexation in the aqueous phase, particularly for U(VI). From all these data a general mechanistic pattern can be found for the transition from adsorption to co-precipitation. This is schematized in Figure II-2.

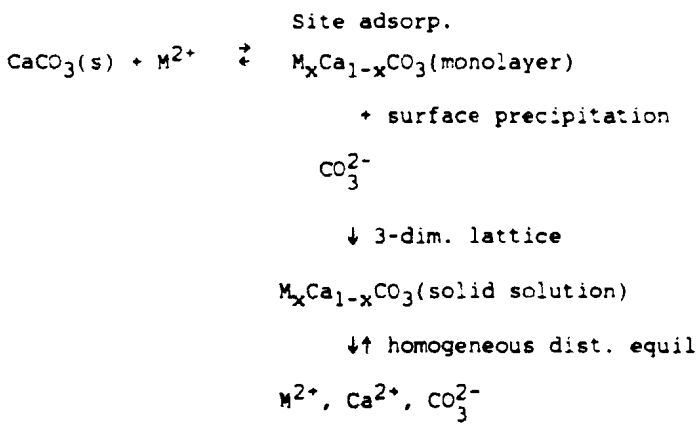

Figure II-2. A tentative mechanism for ion-adsorption/co-precipitation transition in calcite.

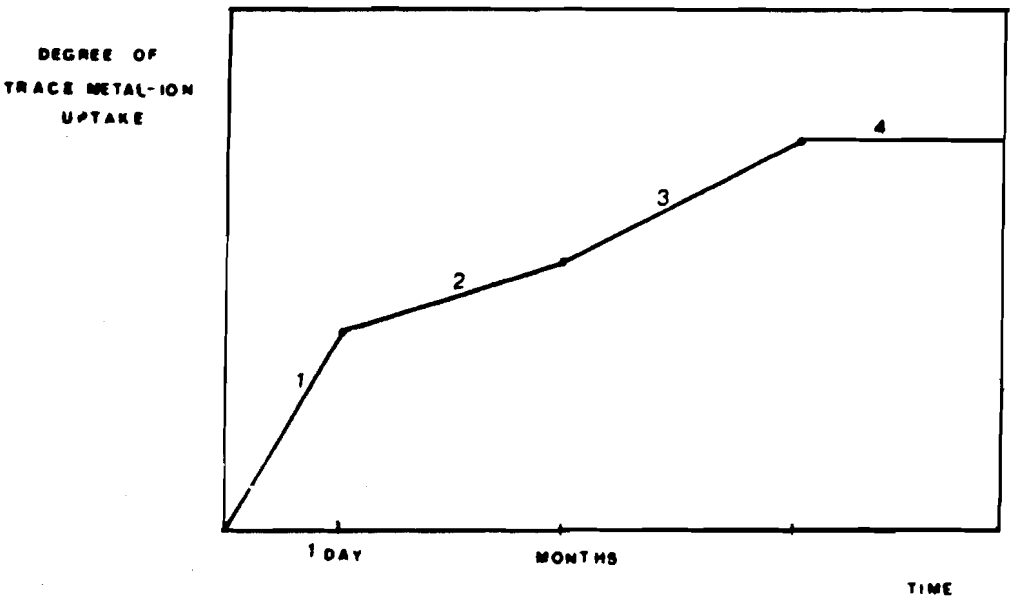

Figure II-3. Schematic time-dependence of radionuclide uptake by calcite. (1) Langmuir type adsorption = surface complexation; (2) Freundlich type adsorption = surface precipitation; (3) Co-Precipitation; (4) Equilibrium.

According to this model the kinetics of radionuclide uptake by calcite could be visualized as in Figure II-3.

3 Radionuclide Co-precipitation with Iron-Oxides

There is practically no information available about co-precipitation of trace metals with iron-hydroxides/oxides. Much experimental and theoretical work has been devoted to the study of the metal adsorption on goethite-hematite surfaces. Nevertheless, Benjamin and Leckie [22], studied in a very comprehensive work the adsorption of trace metals (Cd, Cu, Zn and Pb) on amorphous goethite. They observed that at low adsorption density the data could be described by a Langmuir isotherm. At larger adsorption density, the metal uptake fitted to a Freundlich behaviour (see Figure II-3). During their kinetic experiments they also observed that the initial adsorption was fast, followed by a much slower uptake. This last step was related by the authors to a possible solid-state diffusion. This behaviour is perfectly in concordance with the previously proposed kinetic model for trace metal uptake by calcite.

The adsorption of actinides on different ferric oxy/hydroxides has been extensively studied. There is quantitative information for UO_2^{2+} [23], Pu^{4+} and PuO_2^+ [24] and Np(V) [25]. In all these studies

the triple layer model (TLM) [26,27,28] for surface site bonding has been applied and intrinsic surface binding constants for different actinide species have been obtained.

4 Conclusions

This study on the large literature available on trace metal uptake by calcite and iron indicates that:

- Trace metal and radionuclide uptake by naturally occurring minerals is extensive. The solubility of trace metals in natural waters cannot be only modelled from their individual thermodynamic properties. Also the redox properties of radionuclides are drastically affected by their interaction with naturally occurring solid surfaces [20].

- There is a sequential transition, ADSORPTION → SURFACE PRECIPITATION → CO-PRECIPITATION. This has been demonstrated by spectroscopic methods in the case of calcite and adsorption data indicate a similar behaviour for iron hydro/oxides.

- There is a need for theororetical and experimental development in order to include and quantify the water-particle interface processes in the general radionuclide speciation model. Empirical scavenging parameters like K_d are of very limited validity. Intrinsic surface binding constants are by definition non-conditional and consequently the only ones applicable to the modelling of radionuclide mobility in groundwater environments. This approach has been successfully tested by Balistrieri, Murray and coworkers [29] in order to model trace metal speciation in sea water.

5 References

1. ERIKSON, E., in "Principles and applications of hydrochemistry", ed. Chapman and Hall, London 1985.

2. STUMM, W., MORGAN, J., in "Aquatic Chemistry", John Wiley and Sons, New York 1981.

3. SMELLIE, J., LARSSON, N., WIKBERG, P., CARLSSON, L., "Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Experience from the SKB test-sites in Sweden", SKBF/KBS, Technical Report TR 85-11, November 1985.

4. MULLER, A.B., NEA Compilation of Chemical Thermodynamic Data for Minerals Associated with Granite, RWM-5, OECD, Nuclear Energy Agency, Paris.

5a. TULLBORG, E-L., LARSSON, S-Å., "Fissure fillings from Finnsjön and Studsvik, Sweden. Identification, chemistry and dating". SKBF/KBS Technical Report TR 82-20, Stockholm 1982.

5b. TULLBORG, E-L., LARSSON, S-Å., "Fissure fillings from Gideå, Central Sweden", SKBF/KBS, Technical Report TR 83-74, Stockholm 1983.

6. BERNER, R., MORSE, J.: Am. J. Sci., 274, 108 (1974).

7. MUCCI, A., MORSE, W.: Geochim. Cosmochim. Acta, 48, 815 (1984).

8. MORSE, J.: Mar. Chem., 20, 91 (1986).

9. PINGITORE, N., in "Geochemical Processes at Mineral Surfaces", ed. Hayes and Davis, ACS Symp. Ser. 323, Am. Chem. Soc., Washington DC, 1986.

10. BANCROFT, M., BROWN, J., FYFE, W.: Chem. Geol. 19, 13[illegible] (1977).

11. BOISCHOT, P., DURROUX, M., SYLVESTRE, G.: Ann. Inst. Natl. Recherche Argon., Ann. Argon. A., 1, 307 (1950).

12. LEEPER, G.W.: Ann. Rev. Plant. Physiol., 3, 1 (1952).

13. McBRIDE, M.: Soil Sci. Soc. Am. J., 43, 693 (1979).

14. FRANKLIN, M.L., MORSE, J.W.: Ocean. Sci. Engn., 7, 147 (1982).

15. McBRIDE, M.: Soil Sci. Soc. Am. J., 44, 26 (1980).

16. KORNICKER, W.A., MORSE, J.W., DAMASCENO, R.N.: Chem. Geol., 53, 229 (1985).

17. SHANBAG, P.M., MORSE, J.W.: Geochim. Cosmochim. Acta 46, 241 (1982).

18. SHANBAG, P.M., MORSE, J.W.: unpublished data.

19. KEENEY-KENNICUTT, W.L., MORSE, J.W.: Mar. Chem., 15, 133 (1984).

20. KEENEY-KENNICUTT, W.L., MORSE, J.W.: Geochim. Cosmochim. Acta 49, 2577 (1985).

21. MORSE, J.W., SHANBAG, P.M., SAITO, A., CHOPPIN, G.R.: Chem. Geol., 42, 85 (1984).

22. BENJAMIN, M., LECKIE, J.: J. Coll. Inter. Sc., 79(1), 209 (1981).

23. HSI, C., LANGMUIR, D.: Geochim. Cosmochim. Acta 49, 1931 (1985).

24. SANCHEZ, A., MURRAY, J., SIBLEY, T.: Geochim. Cosmochim. Acta 49, 2297 (1985).

25. GIRVIN, D.C., AMES, L.L., McGARRAH, J.E.: Pacific Northwest Laboratory: Richland W.A., November 1984, PNL-SAAA-11229.

26. DAVIS, J., JAMES, R., LECKIE, J.: J. Coll. Inte. Sc., 63(3), 480 (1978).

27. DAVIS, J., LECKIE, J.: J. Coll. Int. Sci., 67(1), 90 (1978).

28. DAVIS, J., LECKIE, J.: J. Coll. Int. Sci., 74(1), 32 (1980).

29. BALISTRIERI, L.S., MURRAY, J.: Am. J. Sci., 281, 788 (1981).

List of SKB reports

Annual Reports

1977–78
TR 121
KBS Technical Reports 1 – 120.
Summaries. Stockholm, May 1979

1979
TR 79–28
The KBS Annual Report 1979.
KBS Technical Reports 79-01 – 79-27.
Summaries. Stockholm, March 1980.

1980
TR 80–26
The KBS Annual Report 1980.
KBS Technical Reports 80-01 – 80-25
Summaries. Stockholm, March 1981

1981
TR 81–17
The KBS Annual Report 1981.
KBS Technical Reports 81-01 – 81-16
Summaries. Stockholm, April 1982.

1982
TR 82–28
The KBS Annual Report 1982.
KBS Technical Reports 82-01 – 82-27
Summaries. Stockholm, July 1983.

1983
TR 83–77
The KBS Annual Report 1983.
KBS Technical Reports 83-01 – 83-76
Summaries. Stockholm, June 1984.

1984
TR 85–01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01– 84-19)
Stockholm June 1985.

1985
TR 85-20
Annual Research and Development Report 1985
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01-85-19)
Stockholm May 1986.

1986
TR86-31
SKB Annual Report 1986
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

Technical Reports

1987

TR 87-01
Radar measurements performed at the Klipperås study site
Seje Carlsten, Olle Olsson, Stefan Sehlstedt, Leif Stenberg
Swedish Geological Co, Uppsala/Luleå
February 1987

TR 87-02
Fuel rod D07/B15 from Ringhals 2 PWR: Source material for corrosion/leach tests in groundwater
Fuel rod/pellet characterization program part one
Roy Forsyth, Editor
Studsvik Energiteknik AB, Nyköping
March 1987

TR 87-03
Calculations on HYDROCOIN level 1 using the GWHRT flow model
Case 1 Transient flow of water from a borehole penetrating a confined aquifer
Case 3 Saturated-unsaturated flow through a layered sequence of sedimentary rocks
Case 4 Transient thermal convection in a saturated medium
Roger Thunvik, Royal Institute of Technology, Stockholm
March 1987

TR 87-04
Calculations on HYDROCOIN level 2, case 1 using the GWHRT flow model
Thermal convection and conduction around a field heat transfer experiment
Roger Thunvik
Royal Institute of Technology, Stockholm
March 1987

TR 87-05
Applications of stochastic models to solute transport in fractured rocks
Lynn W Gelhar
Massachusetts Institute of Technology
January 1987

TR 87-06
Some properties of a channeling model of fracture flow
Y W Tsang, C F Tsang, I Neretnieks
Royal Institute of Technology, Stockholm
December 1986

TR 87-07
Deep groundwater chemistry
Peter Wikberg, Karin Axelsen, Folke Fredlund
Royal Institute of Technology, Stockholm
June 1987

TR 87-08
An approach for evaluating the general and localized corrosion of carbon steel containers for nuclear waste disposal
GP March, KJ Taylor, SM Sharland, PW Tasker
Harwell Laboratory, Oxfordshire
June 1987

TR 87-09
Piping and erosion phenomena in soft clay gels
Roland Pusch, Mikael Erlstrom,
Lennart Borgesson
Swedish Geological Co, Lund
May 1987

TR 87-10
Outline of models of water and gas flow through smectite clay buffers
Roland Pusch, Harald Hokmark,
Lennart Borgesson
Swedish Geological Co, Lund
June 1987

TR 87-11
Modelling of crustal rock mechanics for radioactive waste storage in Fennoscandia—Problem definition
Ove Stephansson
University of Luleå
May 1987

TR 87-12
Study of groundwater colloids and their ability to transport radionuclides
Kåre Tjus* and Peter Wikberg**
*Institute for Surface Chemistry, Stockholm
**Royal Institute of Technology, Inorganic Chemistry Stockholm
March 1987

TR 87-13
Shallow reflection seismic investigation of fracture zones in the Finnsjö area method evaluation
Trine Dahl-Jensen
Jonas Lindgren
University of Uppsala, Department of Geophysics
June 1987

TR 87-14
Combined interpretation of geophysical, geological, hydrological and radar investigations in the boreholes ST1 and ST2 at the Saltsjötunnel
Jan-Erik Andersson
Per Andersson
Seje Carlsten
Lars Falk
Olle Olsson
Allan Stråhle
Swedish Geological Co, Uppsala
1987-06-30

TR 87-15
Geochemical interpretation of groundwaters from Finnsjön, Sweden
Ignasi Puigdomenech[1]
Kirk Nordstrom[2]
[1]Royal Institute of Technology Stockholm
[2]U S Geological Survey, Menlo Park, California
August 23, 1987

TR 87-16
Corrosion tests on spent PWR fuel in synthetic groundwater
R S Forsyth[1] and L O Werme[2]
[1]Studsvik Energiteknik AB, Nyköping Sweden
[2]The Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm, Sweden
Stockholm, September 1987

TR 87-17
The July – September 1986 Skövde aftershock sequence
Conny Holmqvist
Rutger Wahlstrom
Seismological Department, Uppsala University
August 1987

TR 87-18
Calculation of gas migration in fractured rock
Roger Thunvik[1] and Carol Braester[2]
[1]Royal Institute of Technology
Stockholm, Sweden
[2]Israel Institute of Technology
Haifa, Israel
September 1987

TR 87-19

Calculation of gas migration in fractured rock – a continuum approach

Carol Braester[1] and Roger Thunvik[2]
[1]Israel Institute of Technology
Haifa, Israel
[2]Royal Institute of Technology
Stockholm, Sweden
September 1987

TR 87-20

Stability fields of smectites and illites as a function of temperature and chemical composition

Y Tardy, J Duplay and B Fritz
Centre de Sédimentologie et de Géochimie de la Surface (CNRS)
Institut de Géologie Université Louis Pasteur (ULP)
1 rue Blessig, F-67084 Strasbourg, France
April 1987

TR 87-21

Hydrochemical investigations in crystalline bedrock in relation to exesting hydraulic conditions: Klipperås test-site, Småland, Southern Sweden

John Smellie[1]
Nils-Åke Larsson[1]
Peter Wikberg[3]
Ignasi Puigdomenech[4]
Eva-Lena Tullborg[2]
[1]Swedisch Geological Company, Uppsala
[2]Swedisch Geological Company, Goteborg
[3]Royal Institute of Technology, Stockholm
[4]Studsvik Energiteknik AB, Nykoping
September 1987

TR 87-22

Radionuclide sorption on granitic drill core material

Trygve E Eriksen and Birgitta Locklund
The Royal Institute of Technology
Department of Nuclear Chemistry
Stockholm November 1987


G-426
88.09.15
AD.89.12