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Groundwater Chemistry of a Nuclear-Waste Repository in Granite Bedrock

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PREFACE

The importance of understanding groundwater chemistry in predicting the long-term behavior of nuclear waste deposited in granite bedrock percolated by groundwater became obvious to me and my colleagues at the Department of Nuclear Chemistry, Chalmers University of Technology in Gothenburg, Sweden, in 1977, from which time our work in this area has been supported by generous grants from the Swedish Natural Science Research Council, the Research Council for Radioactive Waste and the Swedish Nuclear Fuel Safety Project (KBS).

Groundwater chemistry is much more complex than the educated layman would believe, as is already obvious at a glance in any of the excellent textbooks in the field, foremost of which, in my opinion, is W. Stumm and J. J. Morgan's *Aquatic Chemistry*. A simple description of groundwater is therefore needed for people dealing with the nuclear waste issue. The main text of this report is an attempt to meet this need. In order to make available the tools for exact calculations as well, I have included a number of appendices. In these I have also pointed out the difficulty caused by the fact that renowned reference texts use different notations. In many parts of the main text and of the appendices I have been forced to simplify things, for brevity; this is particularly true in the appendix on actinide hydrolysis. Nevertheless I hope this report provides a better understanding of the complex chemistry of an underground nuclear waste repository and the need for extensive research in that area.

I have drawn extensively on previously published materials. I am indebted to the KBS project for Figures 13c and 14. I thank Pergamon Press for permission to use material from Pourbaix' book *Atlas of Electrochemical Equilibria in Aqueous Solutions* (Figures 6-11, 13-17 and Table C), John Wiley and Sons for permission to use Figure 5 from the 1970 edition of Stumm and Morgan's textbook, and Prentice-Hall for the material in Table 2 (R. A. Freeze and J. A. Cherry, *Groundwater*, © 1979). Some material is also taken from other books which I co-authored with G. Choppin (*Nuclear Chemistry*, Pergamon Press, 1980) and S. Aldrich and I. O. Ibbenzin (*The Chemistry of the Actinides*, Pergamon Press, 1972).

The inspiration to write this report was provided by Dr. R. Williams of the Electric Power Research Institute. The report was written during my stay at the Lawrence Livermore National Laboratory in 1980 during a sabbatical leave of absence from the Chalmers University of Technology, and revised in the subsequent year.

I wish to thank particularly Drs. Chris Gatroutsis of Lawrence Livermore National Laboratory and Bob Williams of The Electric Power Research Institute, in addition to the organizations mentioned above, for supporting me in this endeavor.

Groundwater Chemistry of a Nuclear Waste Repository in Granite Bedrock

ABSTRACT

This report concerns the prediction of the maximum dissolution rate for nuclear waste stored in the ground. That information is essential in judging the safety of a nuclear waste repository.

With a limited groundwater flow, the maximum dissolution rate coincides with the maximum solubility. After considering the formation and composition of deep granite bedrock groundwater, the report discusses the maximum solubility in such groundwater of canister materials (iron, copper, lead, titanium and alumina), matrix materials (uranium dioxide and glass) and waste elements (fission products and actinides). The parameters considered are pH, Eh and complex formation. The use of potential-pH (Pourbaix) diagrams is stressed; several appendixes are included to help in analyzing such diagrams. It is repeatedly found that desirable basic information on solution chemistry is lacking, and an international cooperative research effort is recommended. The report particularly stresses the lack of reliable data about complex formation and hydrolysis of the actinides.

The Swedish Nuclear Fuel Safety (KBS) study has been used as a reference model. Notwithstanding the lack of reliable chemical data, particularly for the actinides and some fission products, a number of essential conclusions can be drawn about the waste handling model chosen by KBS:

- (1) Copper seems to be highly resistant to groundwater corrosion. The canister wall thickness can probably be reduced from the 20 cm suggested by KBS to a few centimeters.
- (2) Lead and titanium are also very resistant to groundwater, but inferior to copper.
- (3) Iron is not a suitable canister material.
- (4) Alumina (Al_2O_3) is not a suitable canister material if groundwater pH goes up to or above 10. Alumina is superior to copper at pH < 9, if there is a risk of the groundwater becoming oxidizing.
- (5) The addition of vivianite (ferrous phosphate) to the clay backfill around the waste canisters improves the corrosion resistance of the metal canisters, and reduces the solubility of many important waste elements.

This report does not treat the migration of dissolved species through the rock.

INTRODUCTION

Harmful substances can be released from a waste repository in bedrock and reach man only through dissolution and transport by groundwater or by purposeful intrusion by man. In order to predict the amounts of harmful substances reaching man in the former case, it is necessary to know how groundwater interacts with the constituents of the repository: which water-soluble species are formed, and how they interact with rock surfaces when transported by groundwater through fractures to water recipients. In a nuclear waste repository the harmful substances are primarily the nuclear waste elements (about 30 different fission products and 10 different heavy elements), but the waste matrix and canning materials may also be harmful. In order to predict which water-soluble species are formed and their dissolution rates, it is necessary to have detailed information on groundwater chemistry. Although it is a huge task to make reliable predictions about the species formed in groundwater, nevertheless, in principle, this first step can be taken if analytical data and equilibrium constants are known.* The second step, to predict sorption coefficients, is more difficult because every species formed is characterized by a sorption coefficient which may be a sum of several types of interactions: specific to each mineral of the rock. Research to determine such coefficients has only recently begun.^{1,2}

Given all the required fundamental data, it will be possible to predict with assurance how soon a bedrock waste repository will deteriorate and what radioactive nuclides (taking radioactive decay into account) may reach man in the distant future. This prediction also requires that the water transport conditions are known, but these can be established through hydrogeological studies at the actual site.

Our confidence in our predictions is based on the simple fact that the elementary physical chemistry principles exactly demonstrated in the laboratory also apply to nature for the same system. To be sure, laboratory deductions may overlook some species formed in nature, especially if the kinetics are slow. Problems may arise from missing complex species as well as from the difficulty in identifying the only essential ones. There is much to be said in favor of having reliable predictions: they warn against insufficiently designed or poorly located repositories, or indicate overly safe designs; they provide insight into hydrogeological processes, also offering a potential means to discover new ore resources; they provide reassurance that man can protect future generations against the present-day production of harmful wastes. The studies may also be used as a basis for disposing of non-radioactive hazardous wastes.

It should be pointed out that some answers to the question of what may leak out from a nuclear waste repository are already available without the complicated approach indicated above. These answers are obtained from geological findings (e.g., for actinides and fission products at the prehistoric natural reactor at Oklo^{3,4} Gabon), and for meteoric or volcanic glasses^{5,6} and archeological studies (e.g., findings of copper, lead and other metal objects at historical sites^{7,8}). Such information also serves as a check for the more theoretical approach. However, these empirical findings are always site-specific and not general.

*Compare the seawater models by Sillen⁹ and others.

1. CHOOSING A MODEL SYSTEM

The following paragraphs deal with some of the chemical problems of the theoretical approach. Due to the size and complexity of the whole system, as indicated in Fig. 1, many of the problems can only be touched upon here.

The Swedish Nuclear Fuel Safety Project (KBS) system is used as a model ^{8,9}. The KBS system contains most of the components suggested for a waste repository. The system has been studied at great depth, and critically reviewed by an international body of experts (geologists, hydrologists, chemists, corrosion specialists, etc.). In addition to this model system, two more canning materials (iron and corundum) will be considered, because of their lower costs and value compared to the copper and lead suggested as canning metals by KBS.

Bedrock Granite: ~ 10 essential minerals Salt domes: salt elements rock minerals Clay: varying composition	Groundwater Cations: Na^+ , Ca^{2+} , K^+ , Mg^{2+} , Fe^{2+} , ... Anions: Cl^- , SO_4^{2-} , CO_3^{2-} , F^- , ... pH Redox potential
Waste matrix Glass: SiO_2 , Na_2O , B_2O_3 , ... Canning: Fe, Ti, Zr, Pb, Cu, ... Spent fuel elements: UO_2	Waste nuclides^a Pu(23%), Rare Earths(22%), Mo - Tc(9%), Zr(8%), Ru - Rh + Pd(8%), Rb - Cs(6%), I(0.6%), and about 20 more elements ^a About 46 kg actinides (excluding uranium) and fission products in 1 tonne spent reactor fuel.

Fig. 1. Chemical systems in waste repositories.

2. SIMPLIFYING THE SYSTEM

In addition to choosing the KBS design as a model, a number of further simplifications are made. These simplifications should be considered temporary, pending the availability of better data and models.

a. It is assumed that the input composition of the groundwater now entering the repository will be unchanged in the future. It is also assumed that the groundwater's composition will change only due to reactions with the waste and its man-made barriers. The chemical composition of water leaving the repository will change only due to rock sorption mechanisms and to the addition of more groundwater (flowing in from the sides).

b. It is assumed that pressure changes have no effect on the chemical equilibria. The water pressure difference between the surface and an open mine at 500 m depth is negligible. When the mine is closed the water pressure increases to about 50 atm (5 MPa). This water pressure changes non-gaseous equilibria (change in equilibrium constant K) by $\sim 20\%$. Since pressure changes occur only *into* the repository has been closed against the atmosphere (gas system), the pressure effect can be neglected.

c. A temperature change of 50 °C (from ambient at 25 °C to a maximum of 75 °C in the repository) has a considerable effect on most equilibrium reactions (dissolution, precipitation, complex formation, etc.) and may force the equilibrium towards higher vapor pressure, lower or higher solubility, increased dissociation, increased solubility, etc. In order to predict the changes, the chemical potential of the species must be known at different temperatures, or changes in enthalpy (ΔH) and entropy (ΔS), using the $\Delta G = \Delta H - T\Delta S$ relation. In general, it is found that $\log K$ may change up to 15% in either direction (positive or negative sign). For example, pK_a of water changes from 11.93 to 13.20 when the temperature goes from 0 to 50 °C. Since hydrolysis constants may be of the order of 10^{-12} , a $\pm 10\%$ change in $\log K$ (10^{-13} to 10^{-11}) represents a considerable shift in equilibrium constant.

Unfortunately, necessary thermodynamic data are often missing, so that in the following we must neglect temperature effects. However, since the canisters will not dissolve until ~ 1000 years after deposition, by which time the temperature of the depository will have returned almost to the ambient temperature (around 25 °C), temperature effects are only important when considering canister dissolution.

d. Radiation decomposition of the groundwater can be neglected, because the long cooling time presently assumed for temporary ground level storage (50–100 years) and waste shielding reduce to very low levels the total radiation dose to the water outside the canisters.^{11,12} Because radiation effects are much smaller on solid materials than on water, all radiation effects outside the canisters can be neglected.

e. Geologic reactions occur over millennia. However, when considering only water reactions, we have to rely on equilibrium data from laboratory experiments. From the chemical potentials for the reacting species we can deduce whether an equilibrium has been reached. The equilibrium values represent the final conditions which are being approached. In view of the long life of the repository, it is reasonable to neglect kinetic effects in groundwater composition and use equilibrium data.¹³

f. The groundwater of Swedish granite repositories will contain ~ 1 g dissolved species per liter, i.e., have an ionic strength of $\sim 10^{-2}$ M. In exact equilibrium calculations, the activity factors must be considered, particularly for multivalent species. On the average, the activity factors for monovalent species are ~ 0.9 , for divalent ~ 0.7 , and for trivalent species ~ 0.4 at $\mu = 0.01$ M. However, these corrections are left out in the equilibria discussed later, because taking them specifically into account would unnecessarily complicate the principal discussion.

These simplifications make more manageable the problem of interaction between groundwater and the components of the repository. First, interaction between rainwater and rock is considered to produce a specific groundwater. This groundwater is then considered to interact with (1) canister material (Cu, Pb, Ti, Fe and Al_2O_3), (2) waste matrix (glass and UO_2), and (3) waste elements (fission products and actinides). For each system we analyze dissolution, hydrolysis and complex formation at expected pH and redox potential, and attempt to identify the most probable stable soluble species.

3. SURFACE WATER COMPOSITION

Rainwater is saturated with respect to atmospheric gases. It also washes out particulates from the atmospheric layer close to the ground. These dissolved substances have a profound effect on the interaction of groundwater with the surface soil layers.

Of the dissolved gases, O_2 and CO_2 are most important. The O_2 determines the oxidation power (Eh) and the CO_2 determines the acidity (pH) of the surface water. Important atmospheric impurities are SO_2 , NO_2 , and NH_3 . SO_2 and NO_2 come from burning fossil fuels, and in the atmosphere they are already transformed into H_2SO_4 and HNO_3 ; these species increase acidity of rainwater. Ammonia (NH_3) may appear in agricultural areas. Close to coastal areas, rain also contains seawater salts, mainly NaCl. A more detailed look reveals the following:

3.1. OXYGEN

The equilibrium constant for dissolution of oxygen in water

is $\log K_{O_2} = -2.8$ at 15–20 °C. Since partial pressure of O_2 in the atmosphere is $p_{O_2} = 0.21$ atm, the oxygen concentration in rain, $O_2(l)$, is

$$K_{O_2} = p_{O_2} = 0.21 = 10^{-2.8} \\ 0.33 \times 10^{-3} = 10^{-4.8}$$

For molecular weight = 32, one gets the concentration = $0.33 \times 10^{-3} \times 32$ g/liter
 $= 10.6$ mg/liter = 10.6 ppm

K is given in $M \cdot atm^{-1}$. At lower temperature, the concentration of O_2 in water increases somewhat. Oxygen is the most important oxidant in groundwater. The oxidation reaction in acidic solution (neglecting Reaction (1) for simplicity) can be written

The equilibrium constant for this reaction is $\log K = 83.3$. The Nernst equation (see Appendix B) becomes

$$Eh = Eh^\circ + \frac{0.059}{4} \log p_{O_2} (H^+)^4 \quad (3)$$

From Eq. (B7) one gets $Eh^\circ = 1.228 V^{12-13}$. Since for surface waters p_{O_2} is constant at 0.21 atm $\frac{0.059}{4} \log 0.21 = -0.010$, the redox potential, Eh, becomes pH-dependent according to

$$Eh = 1.22 - 0.059pH \quad (4)$$

¹² for liquid or dissolved state; ¹³ for gaseous state; ¹⁴ for solid state; ¹⁵ for aqueous state

At $pH < 7$, which holds for most surface waters, $E_h > 0.81$. That is, the groundwater still has considerable oxidizing power, sufficient to oxidize all the canister metals (Fe to the +3 state) as well as numerous organic compounds. We shall say more about this later.

Water can also be reducing, as in the well known reaction

which occurs, for example, in 1 M HCl. The half-reaction for water acting as a reductant is

for which the Nernst equation becomes

$$E_h = 1h^+ + \frac{0.059}{2} \log p_{H_2} / [H^+]^2. \quad (16)$$

Since Reaction (15) is used as the standard reference couple for all electrochemical reactions, $E_h^\circ = 0$ (the h in $1h^+$ indicates that hydrogen is the reference couple). Thus

$$E_h = 0.059pH - \frac{0.059}{2} \log p_{H_2}. \quad (17)$$

If $p_{H_2} = 1$ atm, which is the partial pressure necessary for hydrogen to evolve at surface atmospheric conditions, then

$$E_h = 0.059pH. \quad (18)$$

In Fig. 2, the lines of Eqs. (18) and (14) are drawn, indicated respectively by (a) and (b). ($E = E_h$, $rH = \log p_{H_2}$, $rO = \log p_{O_2}$). The redox potentials of some canister materials and for the half-reaction of the Zn^{2+}/Zn couple are also indicated.

Any reducing substance with its E_h° value below line (a) (like Zn) liberates H_2 until the redox potential of the solution has increased to a value above line (a) (consuming, e.g., practically all $Zn(s)$). The water has then reached a thermodynamically stable condition. Analogously, any oxidizing agent with an E_h° value above line (b) liberates O_2 from the water until the oxidant has been consumed (or water used up), and the E_h value of the solution has fallen below line (b). The region between lines (a) and (b) represents thermodynamically stable water at 1 atm pressure.

In any pair of redox couples, the one with the higher E_h° value (using IUPAC rule, i.e., Appendix B) will act as an oxidizing agent on the other couple, while itself being transformed into the reduced state. For example, if the couple and redox-potentials are

and $E_h^\circ_1 > E_h^\circ_2$, then the reaction proceeds according to

The couple $Ox_1 = H^+$ and $Zn = Red_2$ satisfies these conditions and the reaction proceeds according to (9c).

Thus, in principle, Fig. 2 indicates that oxygen dissolved in groundwater is capable of oxidizing all canister materials. We shall discuss this more later on.

FIG. 2. Domain of thermodynamically stable groundwater (shaded area) and some water-canister redox couples at $[H^+] = 1 \text{ M}$.

3.2. CARBON DIOXIDE

When CO_2 dissolves in water, carbonic acid (H_2CO_3^*) is formed. Since we cannot easily distinguish between $\text{CO}_2(\text{l})$ and $\text{H}_2\text{CO}_3(\text{l})$, it is common to use an asterisk to define $\text{H}_2\text{CO}_3^* (\text{l}) = \text{CO}_2(\text{l}) + \text{H}_2\text{CO}_3(\text{l})$. We will use H_2CO_3^* as identical to $\text{H}_2\text{CO}_3(\text{l})$. The equilibrium between $\text{CO}_2(\text{g})$ in the atmosphere and undissociated carbon dioxide in water will be written

for which $-\log K = 1.50$. K is given in M atm^{-1} . The atmosphere contains $0.032 = \text{CO}_2(\text{v}) = p_{\text{CO}_2}$ ($3.2 \times 10^{-4} \approx 10^{-3.5}$). Thus, the H_2CO_3^* concentration in rainwater is $10^{-1.50} \times 10^{-3.5} = 10^{-5.0} \text{ M}$, or 1 for $M = 14$ for CO_2 $44 \times 10^{-5} \text{ g}$, or 0.44 mg dissolved CO_2 liter

H_2CO_3^* is a weak acid:

For the first step, equal amounts of H^+ and HCO_3^- must be formed. Thus, $[\text{H}^+] = [\text{HCO}_3^-]$. Then, Reaction (11) gives $[\text{H}^+]^2 = 10^{-6.35 \times 5.0}$, or $[\text{H}^+] = 10^{-11.32} \approx 10^{-5.7}$. Thus, rainwater saturated with

atmospheric CO_2 only, should have a pH of 5.7. The total concentration of "free" carbonate is $[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] = 10^{-5.6} + 10^{-5.7} = 1.2 \cdot 10^{-5} \text{ M}$, or 0.53 mg (as CO_2) per liter.

3.3. SULPHURIC ACID

Acid rains of pH ~ 4 occur in and close to industrial countries, due to the presence of sulphuric acid formed from SO_2 polluted air. Reactions and equilibrium constants are

Thus, at pH 4, $[\text{H}^+] = 2 \cdot 10^{-4}$, from which $[\text{SO}_4^{2-}] = 0.5 \cdot 10^{-4}$, or (for $M = 96/98 = 0.5 \cdot 10^{-4} \text{ g/liter} = 0.5 \text{ mg/liter}$). Average SO_4^{2-} content in rain in Sweden in 1955-1966 was somewhat lower, 3.2 mg/liter. If 50% is added for dry precipitates, and the result is multiplied by 3 for concentration after precipitation, a surface groundwater may contain about 14 mg SO_4^{2-} /liter, or 14 ppm; values up to 20 ppm are commonly found.

3.4. SALT

Rain in Sweden contains on the average 0.6 mg Cl/liter. Through dry precipitation and through concentration by evaporation, surface groundwater may contain about 3 mg Cl, or 5 mg NaCl, per liter. Values up to 10 mg (or ppm) are often found.

In conclusion, before interacting with surface soil, surface water contains about 11 ppm O_2 , 0.5 ppm CO_2 , 20 ppm SO_4^{2-} and 5 ppm Cl, and has a pH between 4 and 5.7 and a redox potential of 0.9 V; the latter value is obtained from Eq. (4).

4. COMPOSITION OF GROUNDWATER CLOSE TO THE SURFACE

In this section we discuss some of the reactions which change the composition of rainwater to that found in groundwater close to the water table, i.e., waters found in most wells. We also discuss the range of existence for stable groundwater.

Because of the interaction of rainwater with soil and surface minerals, waters in lakes, rivers and shallow (<50 m) wells are quite different from rainwater. The composition varies with the environmental conditions, but Table 1 nevertheless gives a useful picture of how the composition of natural water changes in the sequence *rain > surface water > deep bedrock water* in a granitic environment. (See also Fig. 3.) The main changes are increase in pH and carbonate (coupled) decrease in O_2 and Eh (coupled) and increase in dissolved inorganic constituents and conductivity (coupled). Some of the geochemical processes causing these changes are indicated in Tables 2a, 2b and Fig. 4.

The most important reaction between surface water and soil is the oxidation of organic matter to dissolved oxygen. This may be indicated by the reaction, requiring microorganisms to surmount activation energy:

where formaldehyde (CH_4O) is used to designate any organic matter. As a consequence, the CO_2 partial pressure of the natural water may rise from that of rainwater, 0.00032 atm, to 0.1 atm. From Reaction (1), one gets $H_2CO_3 = 10^{-3.5} + 10^{-1} = 10^{-2.5}$, which, combined with Reaction (1), gives $H^+ = 10^{-5.5}$. That is, pH of the surface water decreases from 5.7 to 4.4.

When the carbon dioxide charged water infiltrates through the soil zone, it encounters minerals that are soluble under the influence of H_2CO_3 , particularly calcite:

Through this reaction, acidity is reduced (i.e., pH increases). However, reaction, leading to an increase in acidity (decrease in pH), may also occur, as in the oxidation of pyrite, catalyzed by microorganisms:

The sulphate ions may react with the calcium ions released in Fe:

precipitating gypsum. These examples are only used to indicate the interplay between the components of the surface water system, involving pH changes, and numerous oxidation-reduction and dissolution-precipitation reactions. Some of these reactions are collected in Tables 2a and 2b.

For simple systems with few components, the pH, Eh and chemical composition of the groundwater may be predicted from known equilibrium constants; see e.g., Stumm and Morgan.² For the many components usually encountered in nature, such predictions are not always feasible, or even useful, since equilibrium may not have been reached in young surface waters. However, there are some important generalities concerning pH and O_2 -consumption.

The pH is mainly influenced by the carbonate system. Figure 5 shows that the buffering capacity, β , of this system has maxima at pH 6 and 10, and a minimum around pH 8. Surface groundwater with a pH > 8 is therefore rather resistant to pH changes. Therefore, weak acids which do not reach high concentrations in normal groundwater will have little effect on the pH. Examples are boric acid ($B(OH)_3$; $pK_1 = 9$), orthosilic acid ($Si(OH)_4$; $pK_1 = 9.5$), and humic acids (assumed to have $pK_1 = 9$). The concentration in groundwater of boron is < 1 ppm and of $Si(O_2)_2$ 20 ppm.

TABLE 1. Composition of natural waters. (Data are mainly from Refs. 2, 8, 9, and 14.)

Analysis	Units	Rainwater	Surface water	Bedrock water	Ocean water
Depth	m	0	≤50	≤500	~surface
Age	years	0	10	100	0
pH		4-6	6-7	7-10	7.9
Eh	volts	0.9	0-0.3	-0.05	0.8
O ₂	mg/liter or ppm	~10	—	<0.1	≤9
COD _{Mn}	O ₂ ppm	~0	10-20	5-10	1.2-3
Conductivity	μS/cm	—	120-150	400-600	—
Ca ²⁺	mg/liter or ppm	~1	≤20	20-60	400
Mg ²⁺	mg/liter or μm	~0.5	≤8	15-30	1 272
Na ⁺	mg/liter or ppm	0.3-3	~5	10-100	10 561
K ⁺	mg/liter or ppm	0.1-0.5	≤2	1-5	380
Fe _{tot}	mg/liter or ppm	industrial contamination	0.1-0.3	5-30	<0.02
Fe ²⁺	mg liter or ppm	—	—	1-30 ^d	—
CO ₂	mg/liter or ppm	0.6 ^b	5-10	0-25	140 ^c
P _{CO₂}	atm	3 × 10 ⁻⁴	—	—	4 × 10 ⁻⁴
HCO ₃	mg liter or ppm	~1	50-60	50-400	~140 ^c
Cl ⁻	mg liter or ppm	5	5-20	~20 ^d	18 980
SO ₄ ²⁻	mg liter or ppm	~20(2)	10-20	1-15	2 650
NO ₃	mg liter or ppm	~2	0.5-2	<1	~0.7
PO ₄ ³⁻	mg liter or ppm	—	≤0.1	≤0.1	~0.1
F ⁻	mg liter or ppm	—	≤0.1	0.5-2	1.4
SiO ₂	mg liter or ppm	~1	3-15	5-30	0.01-7
HS ⁻	mg liter or ppm	—	0	~1	—
NH ₃	mg liter or ppm	0.5	~0.1	~0.5	0.05

^a 5 ppm will be selected as a typical and recommendable value (see main text).^b As free H₂CO₃ and HCO₃ at pH = 5.^c Mainly as carbonate complexes and free HCO₃.^d For relict water, the value may be 500-3000 ppm.

The most important O₂-consuming reactions are (15) and (17). Other reactions in surface waters are the oxidation of ammonia to nitrate (NH₃ to NO₃), and manganese to pyrolusite, Mn²⁺ to MnO₂. However, Fe²⁺, NO₃⁻ and MnO₂ are also capable of oxidizing organic matter, see Table 2a. Many of these reactions occur only by, or are accelerated through, microbiological activity. Consequently, the groundwater environment becomes more and more reduced with "age", that is, with time and movement down through the soil. It should also be observed that in all the oxidizing reactions in Table 2a, H⁺ ions are produced. Oxidation thus also acidifies the water.

Mineral weathering is the most intense at the aggressive surface conditions. Soil is composed of minerals, which have been weathered through physical processes and biological activity, and always contains organic matter. Weathering of granite minerals ultimately leads to some kind of clay mineral. This may schematically be illustrated by the sequence

FIG. 3. Geochemical variations of groundwater with depth (data from the Stripa mine).¹⁵

TABLE 2a-1. Important hydrogeochemical reactions: dissociation reactions, equilibrium constants, and solubilities of some minerals that dissolve congruently in water at 25°C and 1 atm.¹⁴

Mineral	Dissociation reaction	Equilibrium constant, K_{eq}	Solubility at pH 7 (mg/liter or g/m ³)
Gibbsite	$Al_2O_3 \cdot 2H_2O \rightarrow 2Al^{3+} + 6OH^-$	10^{-34}	0.001
Quartz	$SiO_2 \cdot 2H_2O \rightarrow Si(OH)_4$	$10^{-3.7}$	12
Hydroxylapatite	$Ca_5OH(PO_4)_3 \rightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$	$10^{-58.6}$	30
Amorphous silica	$SiO_2 \cdot 2H_2O \rightarrow Si(OH)_4$	$10^{-2.7}$	120
Fluorite	$CaF_2 \rightarrow Ca^{2+} + 2F^-$	$10^{-10.6}$	160
Dolomite	$CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	$10^{-17.0}$	90, ^a 480 ^b
Calcite	$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$	$10^{-8.4}$	100, ^a 500 ^b
Gypsum	$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	$10^{-4.5}$	2 100
Sylvite	$KCl \rightarrow K^+ + Cl^-$	$10^{-0.4}$	264 000
Epsomite	$MgSO_4 \cdot 7H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 7H_2O$	—	267 000
Mirabilite	$Na_2SO_4 \cdot 10H_2O \rightarrow 2Na^+ + SO_4^{2-} + 10H_2O$	$10^{-1.6}$	280 000
Halite	$NaCl \rightarrow Na^+ + Cl^-$	$10^{-1.6}$	360 000

^a Partial pressure of CO₂ = 10⁻³ bar.

^b Partial pressure of CO₂ = 10⁻¹ bar.

TABLE 2a-2. Important hydrogeochemical reactions: some inorganic oxidation processes that consume dissolved oxygen in groundwater.¹⁴

Process	Reaction
Sulfide oxidation	$O_2 + \frac{1}{2}HS^- \rightarrow \frac{1}{2}SO_4^{2-} + \frac{1}{2}H^+$
Iron oxidation	$\frac{1}{4}O_2 + Fe^{2+} + H^+ \rightarrow Fe^{3+} + \frac{1}{4}H_2O$
Nitrification	$O_2 + \frac{1}{2}NH_4^+ \rightarrow \frac{1}{2}NO_3^- + H^+ + \frac{1}{2}H_2O$
Manganese oxidation	$O_2 + 2Mn^{2+} + 2H_2O \rightarrow 2MnO_2(s) + 4H^+$
Iron sulfide oxidation ^a	$\frac{15}{4}O_2 + FeS_2(s) + \frac{7}{2}H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+$

^a Expressed as a combined reaction.

TABLE 2a-3. Important hydrogeochemical reactions: some redox processes that consume organic matter and reduce inorganic compounds in groundwater.¹⁴

Process	Equation
Denitrification ^a	$CH_2O + \frac{4}{3}NO_3^- \rightarrow \frac{2}{3}N_2(g) + HCO_3^- + \frac{4}{3}H^+ + \frac{2}{3}H_2O$
Manganese(IV) reduction	$CH_2O + 2MnO_2(s) + 3H^+ \rightarrow HCO_3^- + 2H_2O$
Iron(III) reduction	$CH_2O + 4Fe(OH)_3(s) + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$
Sulfate reduction ^b	$CH_2O + \frac{1}{2}SO_4^{2-} \rightarrow \frac{1}{2}HS^- + HCO_3^- + \frac{1}{2}H^+$
Methane fermentation	$CH_2O + \frac{3}{2}H_2O \rightarrow \frac{1}{2}CH_4 + \frac{1}{2}HCO_3^- + \frac{1}{2}H^+$

^a CH₂O represents organic matter; other organic compounds can also be oxidized.

^b HS⁻ exists as a dissolved species in the water: HS⁻ + H⁺ ⇌ H₂S. H₂S is the dominant species at pH > 7.

TABLE 2b. Some important hydrogeochemical reactions and associated changes in pH and ionic concentrations.

Reaction	Increase	Decrease	No effect
1. CaCO_3 (calcite) $\rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$	pH, DIC ^a , Cd^{2+}	-	
2. $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaMg}(\text{CO}_3)_2$ (dolomite)	-	pH, DIC, Ca^{2+} , Mg^{2+}	-
3. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite) $\rightarrow 5\text{H}_2\text{O} + 2\text{H}_4\text{SiO}_4$ $\rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$ (gibbsite)	SiO_2	-	pH
4. $\text{KAl}_2\text{Si}_2\text{O}_{10}(\text{OH})_2$ (muscovite) $\rightarrow \text{H}^+ + 3/2 \text{H}_2\text{O}$ $\rightarrow 3/2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{K}^+$	K^+	pH	
5. $\text{NaAlSi}_3\text{O}_8$ (albite) $\rightarrow \text{H}^+ + 9/2 \text{H}_2\text{O} + (1/2 \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ $\rightarrow \text{Na}^+ + 2\text{H}_4\text{SiO}_4$	Na^+ , SiO_2	pH	
6. $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) $\rightarrow 2\text{H}^+ + \text{H}_2\text{O}$ $\rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Ca}^{2+}$	Ca^{2+}	pH	
7. In soil: $\text{O}_2 + \text{CH}_2\text{O}$ (organic matter) $\rightarrow \text{CO}_2 + \text{H}_2\text{O}$	DIC	pH, O_2 , Eh	
8. In clay: $\text{Ca}^{2+} + 2\text{NaR} \rightarrow \text{CaR}_2 + 2\text{Na}^+$ (R is immobile ion-exchange radical)	Na^+	Ca^{2+}	
9. FeS_2 (pyrite) $\rightarrow 3\text{O}_2 + 2\text{H}_2\text{O} + \text{Fe}^{3+} + 2\text{H}^+ + \text{SO}_4^{2-}$	SO_4^{2-}	pH, O_2 , Eh	
10. SiO_2 (quartz) $\rightarrow 2\text{H}_2\text{O} + \text{H}_4\text{SiO}_4$ (or $\text{Si}(\text{OH})_4$) [log K = -3.7]	-		
11. $\text{H}_2\text{SiO}_4 \rightarrow \text{H}_4\text{SiO}_4 + \text{H}^+$ [log K = -9.46]		-	

^a DIC = dissolved inorganic carbon.

In the first transformation step, quartz and alkali are leached out through the effect of carbonic acid, leaving a layered framework of aluminum hydroxide and quartz, linked together by common oxygen atoms. Further weathering increases the number of OH groups, and since these are negatively charged, neutralization occurs by sorption of cations (K^+ , Mg^{2+} , Fe^{3+} , etc.). The cations are located between the aluminum hydroxy-silicate layers, and keep the layers together. These cations can be replaced by other cations, and the clay mineral therefore functions as an ion exchanger, as in the reaction

where R represents the inexchangeable clay radical. The sorption tendency for cations increases with their charge density (i.e., ionic charge/hydrated radius). Thus, sorption increases in the order $\text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{K}^+ > \text{Na}^+$. Many clay minerals, like the sodium bentonite used as a buffer in the KBS study, have been "loaded" with Na ions in prehistoric time. Therefore, Reaction (9) occurs when the sodium bentonite comes in contact with groundwater rich in Ca^{2+} . Typical ion-exchange capacity for clay is 0.05 meq/g clay. (Compare this figure with the few meq/g for synthetic ion-exchange resins.) Minerals that have been in contact with groundwater for a long time are often coated with weathering products that exhibit ion-exchange properties.

The third type of groundwater-mineral interaction involves dissolution-precipitation reactions. Since they are of especial significance for the conditions in the waste repository in deep bedrock, they are further treated in the next section. Table 2a contains a number of such reactions.

FIG. 4. Effect of atmosphere, aqueous phase and mineral phase on groundwater composition.¹⁶

FIG. 5. The aqueous carbonate system.²

5. WATER COMPOSITION IN DEEP GRANITIC BEDROCK

When the surface water percolates through fractures in the granite rock, it encounters many different minerals, with which it exchanges ions or which it partly dissolves. Table 3 gives the analytical elemental and main mineral composition of typical granites. Table 4 lists special chemical effects of some minerals on groundwater. Of especial importance is the presence of minerals with divalent ("reduced") iron (pyrite, ilmenite). Table 2b summarizes some of the more important hydrogeological reactions.

Because dissolution, particularly of silicates, is a slow process, it is reasonable to expect that the amount of dissolved species will increase with depth ("age") until saturation is reached. This is supported by data in Table 1 and Fig. 3. Although the solubility of quartz is only 6 mg/liter, granite groundwater typically contains around 20 mg/liter. This higher value is due to the presence of polymeric silicates identified as " SiO_2 ". The solubility of polymeric silica has been reported to be ~130 mg/liter groundwater at 25 °C (see Section 9.1). Groundwater therefore seems to be unsaturated with regard to silicates; this appears to hold also for granite groundwater many thousands of years old. Since it is uncertain whether this anomaly can be attributed to slow kinetics, it is worth further investigation.

Chebotairev¹ has concluded that groundwater tends to evolve chemically towards the composition of seawater. As water moves along the flow path ("ages"), the dominating anionic species follows the sequence

where minor components are in parentheses. Table 1 and Fig. 3 support this sequence, except for Fb and pH.

The main source of energy for bacteria is the oxidation of organic matter, which is concentrated in the upper soil zone. As the water moves through the upper part of the granite, which contains no organic matter, remaining organic matter in the water is gradually consumed. As the water becomes

TABLE 3. Typical chemical and mineral composition of granitic rock.^a

Chemical content	Composition (%)	Mineral constituent	Composition (%)
SiO_2	67-75	Quartz, SiO_2	22-29
TiO_2	0.2-1.0	Orthoclase, KAlSi_3O_8	18-32
Al_2O_3	13-16	Albite, $\text{NaAlSi}_3\text{O}_8$	26-33
Fe_2O_3	0.5-2.0	Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$	6-16
FeO	0.5-4.0	MgSiO_3	1.3-3.9
MnO	0.05-0.15	FeSiO_3	1.7-2.9
MgO	0.2-1.3	Magnetite Fe_3O_4	1.4-1.9
CaO	0.1-4	Ilmenite, FeTiO_3	0.8-1.1
Na_2O	2.5-4	Apatite, $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$	0.1-0.5
K_2O	3-5		
H_2O	0.5		
P_2O_5	0-0.2		
CO_2	0.01-0.1		
S	0-0.04		
Li	5-15 ^b		

^a Range of values of chemical content for Western U.S.¹⁷ and Sweden (KBS);^{8,9} values of mineral constituents from D. Isherwood.¹⁷

^b ppm.

TABLE 4. Chemical effect of main minerals of granite and some important accessory minerals and weathering products.¹⁸

Mineral or weathering product	Chemical effect
Main minerals:	
Quartz 25-30%	Source of colloid SiO ₂ ?
Feldspar 50-75%	
E.g., orthoclase KAlSi ₃ O ₈	Interstitial K, Na, Ca-exchangeable?
E.g., plagioclase (Na, Ca) (Al, Si) ₄ O ₈	Easily weathered
Amphiboles ~ 20%	
E.g., hornblende Ca ₂ Na(Mg, Fe) ₂ (Al, Fe, Ti) ₇ Si ₈ O ₂₂ (O, OH) ₂	
Micas ~ 20%	Cation exchangers?
E.g., biotite K(Fe, Mg) ₃ (AlSi ₃ O ₁₀ VOH) ₂	
Accessory minerals:	
Magnetite Fe ₃ O ₄	Eh-effect
Pyrite FeS ₂	Eh-effect; SO ₄ ²⁻ -source
Ilmenite FeTiO ₃	
Zircon ZrSiO ₄	Partially exchangeable M(IV)?
Fluorite CaF ₂	F ⁻ -source
Calcite CaCO ₃	CO ₃ ²⁻ -source
Apatite Ca ₅ (F, Cl, OH) (PO ₄) ₃	PO ₄ ³⁻ -source
Monazite (Ce, La, Th) PO ₄	Sorption of Ln and An?
Weathering products:	
Kaolinite Al ₂ (Si ₄ O ₁₀) (OH) ₂	From feldspars; cation exchanger
Chlorite (Mg, Fe, Al) ₂ (Si ₄ O ₁₀) (OH) ₂	From amphiboles and micas; cation exchanger

depleted in organic matter, microbiological activity declines; it is not recognizable in deep granite bedrock. For a while, though, bacteria may thrive on reducible minerals; see Table 2a.

Thus, free O₂ usually disappears below the analytically detectable level (about 0.01 mg O₂/liter), while the ratio Fe(II)/Fe(total) increases. From the relation

$$E_{h,32} = E_{h,32}^0 + 0.059 \log [Fe^{3+}] / [Fe^{2+}], \quad (20)$$

where $E_{h,32}^0 = 0.77$ V (the subscript 32 being used to symbolize the $+3 \rightarrow +2$ reduction), it is seen that Eh decreases as the ratio $[Fe^{3+}] / [Fe^{2+}]$ decreases. The redox potential of deep groundwater in granite is found to reach values down to -200 mV.^{9,10} A representative Swedish value at 500 m depth is -50 mV, and Eq. (20) then implies that the $[Fe^{3+}] / [Fe^{2+}]$ ratio becomes $10^{-13.9}$, i.e., $[Fe^{3+}] \ll [Fe^{2+}]$. It should be pointed out that determinations of Eh in groundwater must be carried out with great care; see Appendix D.

The increase in pH is due to Reaction (16), although the formation of insoluble dolomite opposes the pH increase:

Ion exchange of polyvalent ions in clay minerals also tends to increase pH, since these ions in themselves are acid. This can (in principle) be demonstrated by the reaction

Weathering also increases pH according to Reaction 6, Table 2b. Too many components are involved to allow a reliable prediction of pH in granite groundwater.

Weathering also leads to a general dissolution of cations Na^+ , K^+ , Mg^{2+} , and Ca^{2+} . The corresponding anion is mainly HCO_3^- , but may also be some Cl^- , F^- and SO_4^{2-} . While Ca^{2+} mainly comes from calcite (usually reaching saturation at ≥ 100 m depth), Na^+ and K^+ are released through ion exchange reactions like Reaction (19); see also Table 2b. Fluoride is present in the minerals fluorite (CaF_2), apatite and mica. From the solubility product of CaF_2 in Table 2a, one finds for 1 mM Ca^{2+} (i.e., 40 mg/liter) that the maximum F⁻ concentration is 8 mg/liter (0.4 mM). Granite does not contain many minerals with chloride. A high concentration of chloride is therefore interpreted as being due to relict seawater (i.e., water left from the time when seawater covered the rock). From knowledge of geologic history, areas with relict sea water can be avoided. A high concentration of sulphate is interpreted likewise.

Table 2b contains a number of important hydrogeochemical reactions. Many demonstrate the principle of "incongruent dissolution," i.e. a reaction involving solids on both sides of the equilibrium reaction. Reactions 3-6 in Table 2b are of this sort; in Reactions (4), (5) and (6), H^+ is consumed, alkalizing the groundwater. All reactions involve highly insoluble aluminosilicates.

Organic matter in deep groundwater is complicated to describe qualitatively as well as quantitatively, because of the difficulty of identifying the organic compounds (even in humic-rich surface waters). The compounds are assumed to be humic and fulvic acids, i.e., carboxylic acids of high molecular weight (in the range 10^3 to 10^4). In surface soil their concentration is ≥ 100 mg/liter. Granitic groundwater may contain some tens of milligrams of organic matter per liter. The clay buffer in the KBS concept has higher values — 200 mg of organic matter per kilogram of bentonite. Leaching may produce a water with 30-40 mg/liter. The complex-forming capacity is claimed to correspond to $\sim 10^{-2}$ equiv/g fulvic acid, but this is far too high for the assumed molecular weight. The complexing ability has long been assumed to be weak, but recent research indicates rather the opposite.²⁰ Unfortunately, our knowledge in this area is too limited to make any reliable predictions; more research is sorely needed.

Colloids (silica, organic matter, etc.) are another class of groundwater components of uncertain abundance. Two main types of colloids are expected — hydrated silicates and hydrated polyvalent metal ions. Filtration through micropore filters with successively finer pores also reduces the analytical amount of Al(III), Fe(III) and SiO_2 . Our knowledge of groundwater colloids is small and needs to be enlarged, although the presence of such colloids does not seem to increase the dissolution rate or solubility of waste products in the groundwater. (The formation of waste matrix and radioactive waste product colloids is discussed in Sections 9-10.)

The anions OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^- and PO_4^{3-} can form soluble complexes (in addition to precipitates) with the elements of the nuclear waste (anion and cation). Some complex formation (or ion-pairing) occurs with the cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ , which reduces the anion concentrations available for the waste elements. However, most of the groundwater anions are free (except perhaps for CO_3^{2-} and H^+ complexes) and their concentrations span a rather large range (Table 1). It is not meaningful to make corrections for the "internal complexation" of the groundwater. We will assume that the anion concentrations of Table 1 are all available for reaction with the nuclear waste. The appropriate equilibrium constants are presented in Table 5. Detailed accounts of groundwater composition are presented by Kitano²² and Jenne.²³ The groundwater composition of any selected repository site should be accounted for quantitatively from the known mineral composition of the rock, and there should be detailed calculations of all aqueous species (uncomplexed, complexed, polymeric, etc.). Such a detailed treatment, though difficult, should nevertheless be feasible today, and is essential to the credibility of predictions about the stability of the repository over a long period of time.

TABLE 5a. Logarithmic value ($\log \beta$) of first and second complexity constant ($\beta_1; \beta_2$, where $\beta_n = [ML_n]/[M][L]^n$) for important or typical waste, canning, and matrix elements with groundwater ions. (Data, from Ref. 21, refer to different ionic strengths.)

Metal ion	Groundwater anion								
	OH	HCO ₃	CO ₃ ²⁻	Cl	F ⁻	SO ₄ ²⁻	H ₂ PO ₄	HPO ₄ ²⁻	PO ₄ ³⁻
Mg ²⁺	2.6	0.95	2.9	-1.0	1.8	2.2	0.7	1.8	3.4
Ca ²⁺	1.3	1.0	3.2	—	1.1	2.3	1.4	2.7	6.5
Sr ²⁺	0.8	—	—	—	—	2.6	—	1.3	4.2 ^d
Fe ²⁺	4.5; 7.4 ^d	—	—	—	0.8	2.2	2.7	3.6	—
Fe ³⁺	11.8; 22.3	—	—	7.5; 2.1	6.9; 12	4.0; 5.4	3.5	8.3	—
Cu ⁺	—	—	—	2.7; 5.5	0.4	—	—	—	—
Cu ²⁺	6.3; 12.8	—	6.8; 9.9	0.4	—	2.4	1.3	3.3	—
Pb ²⁺	6.3; 10.9	—	8.2	1.6; 1.8	1.4; 2.5	2.8	1.5	3.1	—
Al ³⁺	9.0; 18.7 ^a	—	—	—	7.0; 12.6	—	—	—	—
Sm ³⁺	5.4	—	—	-0.1; -0.8	3.1	1.3	1.5	—	18
TiO ₂ ²⁺	—	—	—	—	—	2.5	—	—	—
Zr ⁴⁺	14.3	—	—	0.9; 1.3	9.8; 17.2	3.7	—	—	—
TcO ₄ ⁻	12.6; 24.2	—	—	—	—	—	—	—	—
UO ₂ ²⁺	^b	—	—	0.2	4.5; 8.0	1.8; 2.8	—	—	—
U ⁴⁺	^b	—	—	-0.1	9.0; 15.6	3.7; 6.1	4	—	—

^d Value uncertain.

^b See Appendix E.

TABLE 5b. Solubility products at 25°C for important (or typical) waste, canning and matrix elements with groundwater anions (data from Ref. 21). Each entry is $-\log$ (solubility product).

Metal ion	Groundwater anion					
	OH	CO ₃ ²⁻	Cl	F	SO ₄ ²⁻	PO ₄ ³⁻
Mg ²⁺	11.15	4.5-7.5	—	—	8.2	25.2
Ca ²⁺	5.19	8.35	—	—	10.4	6.6
Sr ²⁺	—	9.03	—	—	8.5	6.9
Fe ²⁺	15.1	10.7	—	—	—	36.0
Fe ³⁺	38.8	—	—	—	—	26.4
Cu ⁺	14.7	—	6.7	—	—	—
Cu ²⁺	19.3	9.63	—	—	—	—
Pb ²⁺	15.3	13.1	5.0	6.3	7.8	43.5
Al ³⁺	33.5	—	—	—	—	—
Sm ³⁺	25.4	32.5	—	—	—	22.5
TiO ₂ ²⁺	—	—	—	—	—	—
Zr ⁴⁺	54.1	—	—	—	—	—
TcO ₄ ⁻	—	—	—	—	—	—
UO ₂ ²⁺	—	—	—	—	—	49.7
U ⁴⁺	—	—	—	—	28	—

6. THE IRON-WATER SYSTEM

In Fig. 2 we have established the stable region for water (between lines (a) and (b) at 1 atm and 25°C), and for all surface and groundwater (pH 4-10). We now proceed one step further, taking into account that (almost) all granite minerals contain divalent iron, which in the groundwater produces reducing conditions. In order to strengthen these reducing conditions, it has been suggested that the mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, where iron is in the Fe(II) state), be included in the backfill around the waste canisters.^{8,9} Therefore, we now add the limitations imposed on the redox potential by the presence of Fe(II). In considering this complication, we shall make a number of simple assumptions about the iron system, which permit us to arrive at an approximately correct picture of this system. In the next section we shall elaborate it further, adding important details.

Since our pH scale spans the alkaline side, the formation of iron hydroxides must be considered. We shall assume that they are of the simple form $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. We then consider the iron species Fe^{2+} , Fe^{3+} , $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, and the relations between them given below (Reactions 22-26).

It is well known that Fe^{3+} easily hydrolyzes and may precipitate out at pH as low as 3, while Fe^{2+} does not precipitate until pH 7 is exceeded. This motivates the formulation of Reactions (22)-(24), even at neutral pH, where Fe^{2+} is stable and $\text{Fe}(\text{OH})_3$ has precipitated; we must have a redox equilibrium. This is also true in alkaline solutions, where most of both Fe(II) and Fe(III) has precipitated out; there are always dissolved species (even at unmeasurably low concentrations). Each of these reactions is governed by an equilibrium relation. We write out the corresponding relations, obtained according to the principles outlined in Appendixes A, B and C (numerical data from Pourbaix¹³):

$$\text{E} = 0.771 - 0.059 \log [\text{Fe}^{3+}] / [\text{Fe}^{2+}] \quad (22\text{b})$$

$$\log [\text{Fe}^{3+}] = 13.29 - 2\text{pH} \quad (23\text{b})$$

$$\log [\text{Fe}^{3+}] = 4.84 - 3\text{pH} \quad (24\text{b})$$

$$\text{E} = 1.057 - 0.177\text{pH} - 0.059 \log [\text{Fe}^{2+}] \quad (25\text{b})$$

$$\text{E} = 0.271 - 0.059\text{pH} \quad (26\text{b})$$

These equations allow us to construct the potential-pH diagram of Fig. 6a. We now describe the construction steps. We begin with the relations which must be valid at pH 0 and pH 14. From Eq. (22b), we can draw an iso-concentration line (i.e. $[\text{Fe}^{3+}] / [\text{Fe}^{2+}] = 1$) from pH 0 at $\text{E} = 0.771$; we draw a horizontal line to pH 3, and then a dashed line (we do not know yet when Fe(III) starts to precipitate). We also draw line (26b), beginning at pH 14, going up to pH -9, where we dash the line (we do not know yet when all Fe(III) hydroxide has dissolved). We then consider the solubility of the hydroxides; for this we must assume an iron concentration, and we choose 10^{-3}M (5 ppm). This gives the lines (23b) and (24b), which we draw from top and bottom till they hit lines (22b) and (26b). We can finally draw the line for Reaction (25), which meets the crossing points of lines (22b), (24b) and (23b), (26b), at pH 3 and pH 9.

FIG. 6a. The potential-pH diagram for iron-water.

The iron-water potential-pH diagram now contains 4 zones, one of which represents Fe^{2+} . If the groundwater contains ≥ 5 ppm Fe^{2+} , the redox conditions of all other dissolved species must be found within the Fe^{2+} zone. At lower concentrations, the Fe^{2+} zone is larger, as is shown, for example, by the dotted line for $[Fe(II)] \geq 10^{-6}$ M. In Fig. 6a we have shaded the area $[Fe^{2+}] \geq 10^{-6}$ and pH 7-9, which represents the area for granite-rock groundwater.

7. THE IRON-GROUNDWATER SYSTEM

There are three reasons for considering the iron-groundwater system here:

- The groundwater contains divalent iron. What is the consequence of this?
- Iron has been suggested as a thick canister material, instead of lead or copper. How resistant is iron against groundwater?
- The waste glass may be contained in an iron jacket. Again, how resistant is iron against groundwater?

In addition to these reasons for considering the iron-groundwater system, we have selected iron to illustrate Pourbaix diagrams. For this reason the reader is advised —before continuing— to study Appendix C.

The complete Pourbaix diagram for iron-water is shown in Fig. 6b. The following iron species have been considered (cf. Table C.1): Fe, Fe(OH)₂, Fe₃O₄, Fe(OH)₃, all solids, and the dissolved species Fe²⁺, Fe(OH)₄, Fe³⁺, Fe(OH)₂⁺ and FeO₄²⁻. The diagram is explained in Appendix C.

In groundwater, Fe(II) forms complexes with SO₄²⁻ and PO₄³⁻. However these complexes are much weaker than the hydroxy complexes. The carbonate complex is also weaker. The Cl⁻ and F⁻ complexes are so weak that they can be neglected. Using data in Table 5, one calculates that the fraction of Fe(II) in the form of phosphate or sulphate complexes is <5%; for F⁻ it is <0.1%. Thus, Fe(II) complexation in groundwater can be neglected, although the carbonate may limit its concentration due to formation of insoluble FeCO₃(s).

Fe(III) forms very strong complexes with OH⁻, F⁻ and HPO₄²⁻. From Table 5 one calculates that 99% of Fe³⁺ will be complexed by F⁻ and HPO₄²⁻ at the concentrations of these anions given in Table 5. Because OH⁻ forms stronger Fe(III) complexes than fluoride and phosphate (giving soluble FeOH²⁺ and Fe(OH)₂⁺), it is probable that most of the Fe(III) discovered in granitic groundwater will be found in hydroxy complexes. Carbonate complexing seems not to be important^{21,22}. Then, we can neglect complex reactions competing with OH⁻ in the case of Fe(III) also.

We conclude that Fig. 6b gives a reasonable picture of iron in groundwater. In groundwater analysis only dissolved species are considered. Because Fig. 6b contains solid hydroxides, which cannot be analyzed for, the solid species have been eliminated in Fig. 6c. Again, we have shaded the area for Fe(II) between pH₁ and pH₂ and the water reduction line (a). The line (c') borders on trivalent iron. Because all elements dissolved in groundwater will appear within this area, we have shaded it in all subsequent Pourbaix diagrams in this report.

From Fig. 6b it is seen that the line separating Fe(s) and Fe²⁺ lies below the hydrogen evolution line. Thus, solid Fe produces H₂ from water:

The corrosion rate is of the order of a few millimeters per year (Fig. 6d). So an iron slab one meter thick would completely corrode in a few hundred years. In the presence of oxygen, iron would be passivated (covered with a protective oxide layer), while at much lower Eh values iron would be immune to corrosion; see Fig. 6d. The relative rate of corrosion in various pH-Eh areas is shown in Fig. 6e. It therefore appears that iron (mild steel) is unsuitable as material for a container in contact with groundwater.

Finally, it should be noted that in this section we have been concerned only with general corrosion. Local corrosion, which would lead to earlier penetration, may be more important. Such local variations in corrosion rates cannot be treated thermodynamically.

FIG. 6b. Potential-pH equilibrium diagram for the system iron-water at 25°C [considering as solid substances only Fe, Fe(OH)₂ and Fe(OH)₃].¹³

FIG. 6c. Domains of relative predominance of the dissolved substances Fe²⁺, HFeO₂⁻, Fe³⁺, FeOH₂⁺, Fe(OH)₂⁻ and FeO₄²⁻.¹³

FIG. 6d-6e. Experimental conditions of corrosion, immunity and passivation of iron in the presence of agitated aqueous solutions. Rates of corrosion in Fig. 6d and intensity of corrosion in Fig. 6e.¹³

8. CANISTER-GROUNDWATER INTERACTIONS

Using Pourbaix diagrams, we shall analyze the resistance to corrosion in groundwater of the metals copper, lead and titanium, and the ceramic material corundum. In order to estimate the rate of dissolution, we shall assume that groundwater flows so slowly around the canisters that it becomes saturated with respect to soluble ions. We also assume the groundwater flow to be $0.2 \times 10^{-3} \text{ m}^3 \cdot \text{yr}^{-1} \cdot \text{m}^{-2}$ and flow cross section to be 10 m^2 (the approximate hole size in the KBS repository model). This is a flow of two liters per year per waste canister.^{8,9} Further, we shall discount the possibility that O_2 or any other species in groundwater (e.g., NO_3^-) may oxidize the canisters; under assumed Fe (II) conditions ($\geq 5 \text{ ppm Fe}^{2+}$) this seems reasonable. Finally, we shall assume that $[\text{HS}^-] = 0$, that is, that no sulphides are formed (cf. Reaction 3-1 and 3-4 in Table 2a). It should be observed that FeS is poorly soluble, while the presence of Fe^{2+} guarantees low HS^- concentration (in the ppm range).

8.1. COPPER GROUNDWATER

Figure 7 is the Pourbaix diagram. In the groundwater region (shaded), metallic copper is in equilibrium with monovalent Cu^+ . It is seen from Table 5 that Cu^+ forms insoluble hydroxide and chloride, but also soluble anionic chloride complexes (CuCl_2^- and CuCl_3^{2-} ; $\beta_3 = 10^{11}$). We thus have the following limitations and relations for the copper-groundwater system:

$$\text{Dissolved copper, } [\text{Cu}]_{\text{d}} = [\text{Cu}^+] + [\text{CuCl}_2^-] + [\text{CuCl}_3^{2-}] \quad (28)$$

$$[\text{Cu}^+][\text{OH}^-] = 10^{-14.7} \quad (29)$$

$$[\text{Cu}][\text{Cl}^-] = 10^{-9.7} \quad (30)$$

$$[\text{CuCl}_2^-] = 10^{11} [\text{Cu}^+][\text{Cl}^-]^2 \quad (31)$$

$$[\text{CuCl}_3^{2-}] = 10^{11} [\text{Cu}^+][\text{Cl}^-]^3 \quad (32)$$

Because $[\text{Cl}^-] = 3 \times 10^{-2}$ (1000 ppm) and $[\text{OH}^-] = 10^{-7} \text{ M}$, it can be shown that the solubility product for CuOH limits the Cu^+ solubility rather than the solubility product for CuCl . From Eq. (29), $[\text{Cu}^+]_{\text{max}} = 10^{-14.7+7.0} = 10^{-7.7}$. Introducing this value and $[\text{Cl}^-]$ into Eq. (31) yields $[\text{CuCl}_2^-] = 10^{-5.2}$ and introducing it into Eq. (32) yields $[\text{CuCl}_3^{2-}] = 10^{-1.80}$. Summation of these values yields $[\text{Cu}]_{\text{d}} = 2 \times 10^{-2} \text{ M}$.

With the expected water flow in the repository, 2.5 kg Cu(s) will dissolve in one million years, provided that no soluble complexes (other than those above) are formed, and that equilibrium prevails.

Copper therefore seems to be a good canning material, but the 0.2-m canister wall suggested by KBS seems unnecessarily thick.

It is obvious that divalent iron (i.e., a reducing groundwater potential) is essential for the integrity of the copper canister. If divalent copper is formed, the solubility of copper drastically increases.²³ We therefore conclude that, when using metal canisters for the waste, the repository should be selected in an area whose groundwater contains divalent iron; the Fe(II) concentration will be assumed to be $\geq 5 \text{ ppm}$ ($1 \times 10^{-4} \text{ M}$).

8.2. LEAD-GROUNDWATER

Figure 8 shows the Pourbaix diagram. Line (7), which divides the shaded area, represents the reaction

FIG. 7. Potential-pH equilibrium diagram for the system copper-water at 25°C. The solid substances Cu , Cu_2O , and $\text{Cu}(\text{OH})_2$ are considered. CuO is not considered.¹³

Pb^{2+} enters into the shaded area. From Table 5 it is seen that Pb^{2+} forms complexes with all anions in the groundwater.

By investigating the solubility products, we can find the maximum Pb^{2+} concentration. Obviously, the solubility will not be limited by F^- , Cl^- or SO_4^{2-} . If phosphate is present at 10^{-5} M the maximum lead concentration, $[\text{Pb}^{2+}]_{\text{max}}$, becomes $10^{-11.3}$, i.e., lead is practically completely insoluble. This points to the advantage of using vivianite, $\text{Fe}_3(\text{PO}_4)_2$, as an additional mineral in the clay buffer. In the absence of phosphate, the lead solubility is limited by the carbonate system at the higher carbonate concentration.

FIG. 8. Potential-pH equilibrium diagram for the system lead-water, at 25°C.¹³

range. Assuming $[\text{CO}_3^{2-}] = 10^{-3} \text{ M}$, $[\text{Pb}^{2+}]$ becomes about 10^{-10} . In comparison, at pH 7, the $\text{Pb}(\text{OH})_2(\text{s})$ is in equilibrium with $[\text{Pb}^{2+}] = 10^{-8.3}$. Possibly, a lead hydroxy carbonate may form.

Pb^{2+} forms the charged complexes PbOH^+ , $\text{Pb}(\text{OH})_3^-$ ($\beta_1 = 10^{6.3}$; $\beta_3 = 10^{13.3}$), and $\text{Pb}(\text{CO}_3)_2^{2-}$ ($\beta_2 = 10^{8.2}$). At pH 9 $[\text{PbOH}^+]/[\text{Pb}^{2+}] \approx 10^{1.3}$, and for $10^{-3} \text{ M CO}_3^{2-}$ $[\text{Pb}(\text{CO}_3)_2^{2-}]/[\text{Pb}^{2+}] \approx 10^{4.2}$ (It should be noted that in all estimates we try to maximize the concentration of dissolved metal.) For $[\text{Pb}^{2+}] = 10^{-8.3}$, one gets $[\text{PbOH}^+] = 10^{-7} \text{ M}$ and $[\text{Pb}(\text{CO}_3)_2^{2-}] = 10^{-4.1}$. Thus, the Pb species dominating the groundwater will be $\text{Pb}(\text{CO}_3)_2^{2-}$.

With a water flow of 2 liter/yr and a lead carbonate concentration of $10^{-4.1}$, about 0.03 g lead will dissolve per year, or 30 kg per million years. Therefore, lead appears to be a good protective material for granite groundwater conditions. In the KBS concept, the lead canning weighs over 3000 kg, which seems unnecessarily heavy.

8.3. TITANIUM-GROUNDWATER

Figure 9 shows the Pourbaix diagram. Only TiO_2 is stable under groundwater conditions. The reaction steps

are given by Baes-Becking, Kaplan and Moore.¹⁰ These equations yield

At pH 7, $[\text{TiO}_2^{\text{s}}] = [\text{Ti}(\text{OH})_2^{\text{s}}] = 10^{-9.9}$, while $[\text{Ti}(\text{OH})_3^+] \approx 10^{-2.2}$ (i.e., $6 \times 10^{-3} \text{ M}$).

With the 2 liter/yr water flow around a canister, ~0.5 g/yr will dissolve. For a canister surface of 5 m^2 , this dissolution corresponds to $0.02 \mu\text{m}/\text{yr}$. If the corrosion rate is even and a protective film is formed, a 6-mm-thick titanium canister (suggested by KBS) will last for about 300000 years. Pit corrosion may proceed faster.

8.4. ALUMINA-GROUNDWATER

As an alternative to metal canning, ASEA has suggested (see Appendix 1, Ref. 9) using α -aluminum oxide, commonly referred to as corundum. The potential-pH diagram, Fig. 10a, shows that we only have to be concerned with $\text{Al}(\text{III})$ oxide-hydroxides. Aluminum is known to form strong water-soluble F⁻ complexes, which also have to be considered.

Pourbaix gives the relation $\log [\text{Al}^{3+}] = 8.55 - 3\text{pH}$ for $\alpha\text{-Al}_2\text{O}_3$ solubility. The highest solubility will be at lowest pH (pH 7), in which case $\log [\text{Al}^{3+}] = -12.4$ —so low that it can be neglected.

From $K_{\text{eq}} = 10^{-33.5}$ for the formation of $\text{Al}(\text{III})$ in the pH range 7 to 9, $[\text{Al}^{3+}]$ is $10^{-26.5}$ to $10^{-24.5}$. Thus, although the maximum values of $[\text{AlOH}^{2+}]$, $[\text{Al}^{3+}]$ and $[\text{Al}(\text{OH})_2^+]/[\text{Al}^{3+}]$ are of the order 10^5 and 10^{11} (at pH 10), their concentration will be negligibly low. For example, $[\text{AlOH}^{2+}] = 10^5 [\text{Al}^{3+}] = 10^{-5.5}$ to $10^{-21.5}$. We can conclude that positively charged aluminum-hydroxy species are present at $< 10^{-13} \text{ M}$.

The F⁻ ions form stepwise water-soluble complexes: AlF^{2+} , AlF_2^+ , etc. If we assume that all F⁻ in the groundwater complexes aluminum, only forming AlF^{2+} , the 0.2 mM F⁻ in this water (2 liter/yr) can carry away 0.4 mmol of aluminum per year, or 0.01 g.

For the formation of aluminate ions, AlO_2^- , Pourbaix gives $\log [\text{AlO}_2^-] = -11.76 - \text{pH}$; a high pH value of 10 would give $\log [\text{AlO}_2^-] = -1.76$, or $[\text{AlO}_2^-] = 0.06 \text{ M}$, which is rather large. Figure 10b shows the solubility of various aluminum oxides. About 3 g/yr of aluminum will dissolve from 0.06 M aluminate in

FIG. 9. Potential-pH equilibrium diagram for the system titanium-water at 25°C. The diagram considers as derivatives of tri- and tetravalent titanium, the hydroxide $Ti(OH)_3$ and the hydrated oxide Ti_2H_2O .¹³

FIG. 10a. Potential-pH equilibrium diagram for the system aluminum-water at 25 °C.¹³

FIG. 10b. Influence of pH on the solubility of Al_2O_3 and its hydrates at 25°C .¹³

groundwater of pH 10. With a canister surface area of $\sim 15 \text{ m}^2$, the dissolution rate becomes $\sim 1 \mu\text{m/yr}$, or approximately one meter in a million years. At pH 9, the dissolution rate is 10 times slower.

Although corundum is thermodynamically stable, the high solubility of aluminates in basic solutions may be an obstacle to its use as a canning material. A more thorough analysis is desirable.

9. WASTE MATRIX-GROUNDWATER INTERACTIONS

Although numerous ceramics,²⁴ glasses and metals have been suggested as matrix for radioactive waste, only glasses (for the reprocessing waste) and the UO_2 (in the spent fuel elements) are of practical importance today. They will be briefly discussed here.

9.1. SILICA/GLASS-GROUNDWATER

The silicate system is extremely complex, comprising the silicate minerals in the rock and numerous types of glasses, in addition to soluble metal complexes. In this section we will make only a few comments, mainly based on the work of J. Van Muylder, J. Besson, W. Kunz and M. Pourbaix.¹³

The potential-pH diagram, Fig. 11a, shows that SiO_2 is the stable species, but many modifications occur:

	$\log [\text{HSiO}_3]$	$\log [\text{H}_2\text{SiO}_3]$	
a) Quartz (hexag.)	$-15.21 + \text{pH}$	5.21	(37a)
b) Cristobalite (cubic)	$-14.99 + \text{pH}$	-4.99	(37b)
c) Tridymite (hexag.)	$-14.89 + \text{pH}$	-4.85	(37c)
d) Vitreous silica	$-14.11 + \text{pH}$	-4.11	(37d)
e) Hydrated silica (amorphous)	$-11.84 + \text{pH}$	-1.84	(37e)

The right columns refer to the dissolution reactions

Figure 11b shows a plot of the influence of pH on the solubility of various forms of SiO_2 . For hydrated silica, the solubility is $10^{-3.8}$ at pH 8, $10^{-2.84}$ at pH 9, while at pH 10 it is $10^{-3.8}$ (Ref. 2). Since silicic acid (H_4SiO_4 , or H_2SiO_3) is formed through weathering of aluminosilicates of the rock, it seems probable that the groundwater is in equilibrium with Reactions (38) and (39). The 30 mg SiO_2 /liter (Table 1) corresponds to 5 mM, or $10^{-3.3}$ M. Because these figures are all compatible, one can conclude that high-pH groundwater leads to a high dissolution rate for waste glasses; this is also found experimentally.²⁴

In a more detailed analysis one has to consider other soluble silicate species, like $\text{SiO}_2(\text{OH})_2^-$ and $\text{Si}_3\text{O}_8(\text{OH})_6^{2-}$ (see Refs. 2, 25), and the incongruent dissolution of aluminosilicates (Table 2b). Unfortunately, many probable natural equilibria are insufficiently known. Still, the composition of ocean water has been well explained by Sillén^{1,22} and others²³ on the bases of equilibrium calculations for a system consisting of the components HCl, H_2O , CO_2 , SiO_2 , Al_2O_3 , NaOH, KOH, MgO and CaO, which includes the aluminosilicates. Similar calculations by Carett, Stumm and Morgan² for groundwater seem to be fairly successful. The critical relation between the solubility of silica and alumina is illustrated in Fig. 12.¹⁴ From Fig. 12 one expects to find a steep increase in dissolved alumina and silica when the pH of groundwater increases above 9 and approaches 10; however, this is not supported by Fig. 3. Sillén has concluded that the silicate system—not the carbonate system—is the main pH-buffering system in natural waters. Figure 11c² presents a more detailed picture of the silicate system than Fig. 11b; however, the solubility of monomeric silicic acid is the same.

The experience that the concentration of polymeric silica species is lower in groundwater than is to be expected from equilibrium data (for amorphous silica $\sim 2 \times 10^{-3}$ M, or ~ 120 ppm²) is interpreted as being due to slow kinetics. This seems a reasonable explanation if one also takes into account the effect of sorption on rock fractures, which may filter off the silica because of the silica's charge and high molecular weight.

FIG. 11a. Approximate potential-pH equilibrium diagram for the system silicon-water at 25°C. SiO_2 is considered to be in the form of quartz.¹³

For glasses which are mainly aluminosilicates, leach tests indicate an initial removal of basic hydroxides to form a hydrated, high-silica porous layer, which is then uniformly dissolved.⁵ This probably leads to the same dissolved silica species as are found in natural waters. The initial dissolution rate is 10^{-4} to $10^{-5} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ and decreases with time. Values as low as $10^{-10} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ have been observed after two years. At these long times the radionuclides seem to dissolve at the same rate as the glass itself.

Most nuclear waste glasses are of the borosilicate type. Leach tests with unlimited amounts of water show that the dissolution rate drops from 10^{-4} to $10^{-5} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ to 10^{-5} to $10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ after about two months. A dissolution rate of $10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ is commonly chosen as a conservative long-term

FIG. 11b. Influence of pH on the solubility of silica SiO_2 at 25°C . *a.* quartz; *b.* cristobalite; *c.* tridymite; *d.* vitreous silica; *e.* amorphous silica.¹³

FIG. 11c. Species in equilibrium with amorphous silica. The diagram is computed from equilibrium constants at 25°C . The line surrounding the shaded area gives the maximum soluble silica. The mononuclear wall represents the lower concentration limit, below which multinuclear silica species are not stable. In natural waters the dissolved silica is present as monomeric silicic acid.¹³

FIG. 12. The solubility of silica and alumina as a function of pH. At low pH (4-5) kaolinite may form, while at high pH (8-9) the formation of the clay montmorillonite is favored. For kaolinite Al_2O_3 : SiO_2 is 1:2, while for montmorillonite it is 1:4.²⁶

estimate. When this glass dissolves, $\text{B}(\text{OH})_3$ also dissolves. Although this may have little effect on the pH, boric acid is highly soluble in water and could produce metal borate complexes. Unfortunately, borate complexes are poorly known.

The dissolution rate increases with temperature: increases of a factor of 10-50 have been reported for a raise in the water temperature from 25° to 75°C. This increase in the dissolution rate observed in the laboratory may not be relevant in groundwater, because the groundwater may already be saturated with soluble silicates at the higher temperatures. Even the opposite, a slower dissolution, could conceivably occur. Therefore, glass dissolution studies must be carried out with natural groundwater in equilibrium with granite minerals at the temperature studied, in order to provide meaningful information for a real repository.

With an assumed dissolution rate of $10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$ and a waste glass canister of 400 kg and 2 m^2 surface area, 7.3 g glass should dissolve per year in 2 liter groundwater, providing a silica concentration of 2000 ppm, a concentration widely exceeding that of natural groundwater (data from Appendix F). The long-term dissolution rate will probably be limited by the silicate solubilities to 0.1-0.01 of this value, i.e., to 20-200 ppm.

9.2. URANIUM DIOXIDE-GROUNDWATER

Pourbaix considers the following soluble uranium species:

As pointed out in Appendix E, polymeric $\text{U}(\text{IV})$ and $\text{U}(\text{VI})$ species have been identified in solution. Figure 13a is valid for anhydrous oxides, 13b for the hydrous ones. When considering the dissolution of the UO_2 matrix in spent fuel elements, Fig. 13a is probably the best choice. In this figure, line 7' represents the domain of relative predominance of UOH^{3+} and UO_2^{2+} ($E_0 = 0.299 - 0.0880 \text{ pH}$). Thus both

FIG. 13. Potential-pH diagram for the system uranium-water at 25°C. a. Anhydrous oxides. b. Hydrated oxides.¹³

4- and 6-valent uranium is present; of these two, U(VI) dominates in our groundwater (not considering any supplemental complex formation).

From Table 5 it is seen that U(IV) forms stronger complexes with Cl^- , F^- , SO_4^{2-} (and also with $H_2PO_4^-$) than does U(VI). While the Cl^- complexes are so weak that they can be neglected, part of U(IV) is bound in SO_4^{2-} complexes. However, the U(IV) fluoride complexes are so much stronger that almost all U(IV) will be bound to F^- : $[UF_3^{2-}]/[U^{4+}] = 10^{5.3}$ and $[UF_2^{3-}]/[U^{4+}] = 10^{8.0}$. An F^- concentration of 0.2 mM would limit the free U^{4+} concentration to 6×10^{-14} M. However, U(IV) is bound in the soluble stepwise fluoride complexes to a much higher concentration. For U(VI) the ratio would be approximately $[U(VI) \text{ fluorides}]/[UO_2^{2+}] = 10$, at 0.2 mM F^- .

No more uranium can dissolve than there is F^- available (0.2 mM). By assuming the uranium to be complexed in soluble species with all available F^- and SO_4^{2-} , one obtains a rough estimate of the maximum solubility of the UO_2 matrix, namely, 0.4 mM. Thus, the dissolution is 0.2 g/yr for the reference waste repository; this corresponds to the dissolution of 1 ton of uranium in 5 million years. However, this estimate does not take into account the effect of the insolubility of the hydroxides. From Appendix E we have

$$[U^{4+}][OH^-]^4 = 10^{-45} \quad (40)$$

and

$$[UO_2^{2+}][OH^-]^2 = 10^{-22.4} \quad (41)$$

Then, at pH 7, $[U^{4+}] = 10^{-17}$ and $[UO_2^{2+}] = 10^{-8.4}$. Thus, U(IV) precipitates out preferentially. Introducing these $[U^{4+}]$ and $[UO_2^{2+}]$ into the fluoride fractions produces the true uranium fluoride concentrations: $[UF_2^{3-}] = 10^{-8.8}$, $[UF_3^{2-}] = 10^{-10.1}$ (assuming $\beta_3 = 10^{22}$), and $[U(VI) \text{ fluorides}] = 10^{-7.4}$. With

a value of 10^{-6} for all U-complexes the dissolution rate would be vanishingly small—0.5 mg/yr, or 0.5 kg in a million years.

U(VI) is known to form strong soluble carbonate complexes, which have not been considered above. The competition between hydrolysis, fluoride and carbonate complexation will shift the redox equilibrium between the U(IV) and U(VI) species even in an Fe(II)-redox buffered system. Unfortunately, exact information (i.e., complexity constants) is not available; this is highly desirable information worth a high-priority research effort. The importance of such knowledge is demonstrated in Fig. 13c. It shows the geological situation and the different zones around a uranium ore exposed to groundwater. In zones IA and IB uranium moves with the oxidizing ($E_h > 0.2$) groundwater as hexavalent carbonate complex, $UO_2(CO_3)_2^{2-}$. In zone II, the large amount of organic matter causes the groundwater to become reducing (E_h drops to negative values), and uranium precipitates out as a tetravalent hydroxide. In the final zone, the uranium content in the groundwater is a few ppm, compared to 10-100 ppm in the first zones. This picture, which is representative for how uranium mineral deposits are formed, illustrates the importance of pH, E_h , and complex formation in predicting uranium dissolution (or precipitation) rates and migration rates in the ground.

The KBS study reports the dissolution rates of a number of nuclides contained in a UO_2 matrix. The values level off at $\sim 10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$. For a glass cylinder of 1 m^2 this rate corresponds to about 1 g/yr, very much higher than the hydroxide solubility values indicate. There may be several explanations of this discrepancy, such as use of test water different from the groundwater, or use of too much test water, or neglect of the formation of soluble polymeric uranium hydroxide species. It is essential that solubility and dissolution rate studies are brought into agreement; this point is not always considered in the nuclear waste research efforts.

FIG. 13c. Different zones around a uranium ore percolated by groundwater."

10. NUCLEAR WASTE-GROUNDWATER INTERACTIONS

Nuclear waste consists of fission products (heavy elements (actinides) and activation products (radioactive nuclides of Fe, Cr, Ni, etc.), comprising some 50 elements, with at least one element in every column of the "chemical" periodic system (see Appendix F). Therefore, practically every kind of chemical property is represented in nuclear waste. In the next two sections, a few of the important aspects of waste-groundwater interaction are stressed; it will become apparent that a more detailed treatment is desirable.

It is reasonable to assume that the waste elements dissolve at the same rate as the matrix (glass, or UO_2), as long as their individual solubility products are not exceeded. We shall assume a glass dissolution rate of $10^{-6} \text{ g} \cdot \text{cm}^{-2} \cdot \text{d}^{-1}$, i.e., dissolution of a fraction of 1.8×10^{-6} of the total glass cylinder per year. To simplify the following discussion, we here assume that the UO_2 matrix dissolves at the same rate as the glass matrix, i.e., 1.8×10^{-6} of total matrix per year.

10.1. FISSION PRODUCTS

We shall consider only elements that retain significant radioactivity after 10 years of decay. Leaving out the gaseous fission products, the most essential ones are cesium, strontium, rare earths, technetium and iodine.

Cesium forms no important complexes under groundwater conditions. It is considered completely soluble as Cs^+ under all conditions. It has a stronger ion exchange affinity than Na^+ and H^+ and sorbs easily on minerals.

Strontium forms quite insoluble carbonate, fluoride, sulphate and phosphate complexes; see Table 5. Under groundwater conditions, the carbonate will limit the Sr solubility:

The lowest solubility will be at highest pH and highest total carbonate concentration. For $\text{pH} = 10$, where, according to Fig. 5, $[\text{HCO}_3^-] \approx [\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 10 \text{ mM}$, one obtains $[\text{Sr}^{2+}] = 2 \times 10^{-7} \text{ M}$. This is the lower solubility limit. At the other end of the scale, for $\text{pH} 7$ and 30 ppm HCO_3^- , one obtains $[\text{Sr}^{2+}] = 10^{-27}$. At $\text{pH} 7$, for air-saturated water Kragten²⁷ gives 10^{-13} , while Allard²⁸ for typical groundwater has calculated $[\text{Sr}^{2+}] = 10^{-27}$ (10^{-18} at $\text{pH} 9$); see Table 6. It is obvious that the Sr solubility strongly depends on the exact groundwater conditions. A value of $[\text{Sr}^{2+}]$ equal to 10^{-27} M corresponds for our specified flow conditions (2 liters per year) to the dissolution of 0.4 g of strontium per year.

A waste-glass cylinder from about 1 tonne of spent reactor fuel contains $\sim 0.50 \text{ kg}$ strontium. In the KBS conditions, assuming all canning has corroded away, this glass cylinder is washed by 2 liters of groundwater per year. With 1.8×10^{-6} of the glass dissolving per year (see above), 0.001 g Sr should dissolve per year — much less than strontium's solubility allows. Thus, all strontium exposed to groundwater is assumed to dissolve.

The **lanthanides** (Ln) form the largest fraction of the fission products, about 13 kg per waste glass cylinder. A fraction of 1.8×10^{-6} of the glass dissolving per year would allow 0.010 g Ln to dissolve annually in 2 liters of groundwater.

All lanthanides are trivalent in aqueous solutions, except for cerium, which can be tetravalent, and europium, which can be divalent. Figure 14 gives the Pourbaix diagrams for these two elements and for promethium, which is only trivalent, as the figure shows. It is seen that cerium can only be trivalent in groundwater, while there is a possibility that europium also forms Eu^{2+} ions in groundwater. Eu(II) will behave like Sr^{2+} ; since Eu(II) is not a large waste hazard, we will not consider it further.

In Table 5, samarium is chosen as a representative lanthanide; Allard et al., Table 6, refer to europium. Ln(III) forms strong hydroxide, carbonate and phosphate complexes:

TABLE 6. Maximum solubility ($-\log [M]$) of some waste elements in typical groundwater of various pH (Ref. 27).

	pH 7	pH 8	pH 9
Sr(II)	2.7	3.8	4.8
Eu(III)	9.3	10.3	11.1
Eu(III) ^a	5.7 ^b	7.3 ^b	8.5 ^b
Am(III)	8.7	8.3	6.9
Am(III) ^a	5.6 ^b	6.7 ^b	6.9 ^b
U(IV)	9.2 ^c	8.2 ^c	7.2 ^c
Th(IV)	12.0	11.6 ^c	10.7 ^c
U(VI)	2.3	2.6 ^c	2.6 ^c

^a Water without PO_4^{3-} .

^b Value uncertain.

^c Mainly anionic complexes.

$$[\text{Ln}^{3+}][\text{OH}^-]^3 = 10^{-25.4} \quad (4.3)$$

$$[\text{Ln}^{3+}]^2[\text{CO}_3^{2-}] = 10^{-32.5} \quad (4.4)$$

$$[\text{Ln}^{3+}][\text{PO}_4^{3-}] = 10^{-22.5} \quad (4.5)$$

FIG. 14. Potential-pH diagram at 25°C for lanthanides. a. Cerium-water. b. Promethium-water. c. Europium-water.¹³

At the anion concentrations given in Table 5, one finds that the phosphate determines the solubility; this result indicates again the advantage of vivianite as a filler in the buffer material around the waste canister. In the total absence of phosphate, the carbonate complex limits the solubility (to $10^{-8.8}$ M: Ln^{3+} at pH 7, and $10^{-13.5}$ M at pH 10). The large variation in natural carbonate concentration makes it difficult to choose a representative value. Thus, relying only on the hydroxide solubility, one finds that $[\text{Ln}^{3+}] \leq 10^{-4.4}$ M at pH 7 and $10^{-10.1}$ M at pH 9. Allard et al.²⁸ also consider the phosphate-no-phosphate case. For their typical groundwater, $[\text{Ln}^{3+}]$ is $10^{-5.7}$ at pH 7, while for aerated groundwater Kragten²⁷ gives $[\text{Ln}^{3+}] \approx 10^{-5.0}$. Assuming $10^{-5.0}$ as the highest possible $[\text{Ln}^{3+}]$, one finds that 0.003 g Ln dissolves per year in the typical groundwater. This is lower than the 0.010 g Ln dissolving per year at the glass dissolution rate given in the beginning of this paragraph. This could lead to some stabilization of the waste matrix, provided the Ln(III) does not form highly soluble silicates.

Figure 15 gives the potential-pH diagram for **technetium** in pure water. At groundwater conditions, neglecting complex formation, both Tc(IV), as a Tc^{4+} or TcO_2^{2+} species, and Tc(VII), as a TcO_4^- species, seem to exist.²⁹ Reaction 6 allows us to calculate the maximum TcO_4^- concentration:

$$E = 0.50 - \frac{0.059}{3} \log [\text{TcO}_4^-]/[\text{OH}^-]^3 \quad (10)$$

At a redox potential $E_h = 0$ and at pH 7, $[\text{TcO}_4^-] = 10^{-2.9}$, while for pH > 7.7 $[\text{TcO}_4^-] < 1$, i.e., there is no real limitation to the technetium solubility. A more thorough consideration of the technetium solubility is given by Allard.²⁹

Allard, Forstentfeld, Andersson and Rydberg³⁰ have also studied the **iodine** system, and conclude that the only stable species is I^- ions, with very high groundwater solubility and mobility. They suggest the use of special backfill materials for retaining the iodine. Cu(I) produced by dissolution of a copper canister would act as a getter for I^- because of the highly insoluble CuI .

10.2. ACTINIDES

The important waste actinides are uranium, neptunium, plutonium and americium. In water they can appear in different valency states:

Trivalent: Pu^{3+} , Am^{3+}

Tetravalent: U^{4+} , Np^{4+} , Pu^{4+}

Pentavalent: $(\text{UO}_2)^+$, NpO_2^+

Hexavalent: $(\text{UO}_2)^{2+}$

Figure 16 summarizes the redox diagrams for these species and potentials for some other redox couples in acidic solution. All these actinide species appear below the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple (i.e. where Fe(II) dominates). Thus in pure acidic water with a redox potential of -0.1 V, only U^{4+} , Np^{4+} , Pu^{4+} and Am^{3+} have to be considered. However, as already discussed above, groundwater is far from these ideal conditions, and other actinide valency states therefore may become important.

Allard³¹ has very recently carefully reviewed the actinide conditions in granitic-type groundwater, and concluded that the only complexes of importance are the hydroxy and carbonate species. In Fig. 17 we give the Pourbaix¹³ potential diagrams for Np, Pu and Am; the U diagram was given in Fig. 13.

In Section 9.2 it was concluded that $[(\text{UO}_2)^+] > [\text{U}^{4+}]$, but due to the stronger U(IV) complexes, the solutions would be dominated by tetravalent uranium. Figure 13 shows about equal stability for U(VI) and U(IV) in groundwater. In Fig. 18 Allard³¹ has calculated the maximum total solubility of uranium in reducing (-0.1 V) groundwater, considering all possible complexes and valency states. The minimum solubility is obtained at pH 8 due to formation of insoluble U(IV)---hydroxide/oxide; the solubility is

FIG. 15. Potential-pH diagram for the system technetium-water at 25 °C.²⁸

Equilibrium curves

1. $\text{Tc}^{2+} + 2\text{e}^- = \text{Tc(s)}$	$E^0 = 0.400 \text{ V}$
2. $\text{TcO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^- = \text{Tc(s)} + 2\text{H}_2\text{O}$	$E^0 = 0.272 \text{ V}$
3. $\text{TcO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- = \text{Tc}^{2+} + 2\text{H}_2\text{O}$	$E^0 = 0.144 \text{ V}$
4. $\text{TcO}_4^- + 4\text{H}^+ + 3\text{e}^- = \text{TcO}_2(\text{s}) + 2\text{H}_2\text{O}$	$E^0 = 0.738 \text{ V}$
5. $\text{TcO}_4^- + 6\text{H}^+ + 3\text{e}^- = \text{TcO}^{2+} + 3\text{H}_2\text{O}$	$E^0 = 0.58 \text{ V}$
6. $\text{TcO}_4^- + 3\text{H}_2\text{O} + 3\text{e}^- = \text{TcO(OH)}_2 + 4\text{OH}^-$	$E^0 = -0.50 \text{ V}$
7. $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	$E^0 = 0.771 \text{ V}$
8. $\text{Fe(OH)}_3 + \text{e}^- = \text{Fe}^{2+} + 3\text{OH}^-$	$E^0 = -1.12 \text{ V}$
9. $\text{Fe(OH)}_2 + \text{e}^- = \text{Fe(OH)}_2 + \text{OH}^-$	$E^0 = -0.67 \text{ V}$
10. $\text{Fe(OH)}_2 + \text{e}^- = \text{Fe}^{2+} + 3\text{OH}^-$	$E^0 = -1.52 \text{ V}$
11. $3\text{Fe}_2\text{O}_3(\text{s}) + 2\text{H}^+ + 2\text{e}^- = 2\text{Fe}_3\text{O}_4(\text{s}) + \text{H}_2\text{O}$	$E^0 = 0.221 \text{ V}$

For 1, 3, 4, and 10, two curves are given corresponding to different concentrations of the soluble species in solution (-4, -6, and -8 denote 10^{-4} M, 10^{-6} M, and 10^{-8} M, respectively).

$10^{-8.2}$ M. Carbonate complexes can be neglected at the low groundwater carbonate concentration (but not in the case of aerated water!). At higher pH anionic U(OH)_3 dominates, while at lower pH pentavalent UO_2^{2+} is the predominant species in the water. The calculations are quite sensitive to choice of redox-potential values and equilibrium constants. The hesitation before the conclusions in Fig. 18, which some readers may experience, indicates the demand for reliable data valid for groundwater conditions.

FIG. 16. Redox diagrams for the actinides and some other couples.⁷

FIG. 17. Potential-pH diagrams for the systems neptunium-water, plutonium-water and americium-water at 25°C.¹³

FIG. 18. Uranium concentration in granitic reducing groundwater, according to Allard.³¹

FIG. 19. Neptunium concentration in granitic reducing groundwater, according to Allard.³¹

For **neptunium**, line 2 in Fig. 17a is the isoconcentration line for $\text{Np}^{3+}/\text{NpO}_2^+$, while line 15 refers to

$$\text{NpO}_2(\text{s}) = \text{NpO}_2^+ + \text{e}^-; E = 0.530 + 0.059 \log [\text{NpO}_2^+] \quad (47)$$

Thus, Fig. 17 indicates that, at groundwater conditions, Np mainly occurs as insoluble hydroxide, the only soluble species being NpO_2^+ . At $E = 0.05$ V, one gets $[\text{NpO}_2^+] = 10^{-9.8}$. Taking hydroxy complexes into account Allard³¹ arrives at the conclusion that Np(IV) will dominate in the groundwater, with a concentration $< 10^{-8}$ M at pH > 9 . At higher pH the formation of Np(OH)_5 is assumed to increase total neptunium solubility; see Fig. 19. Considering the risk of easy transportation of neptunium as NpO_2^+ or Np(V) complexes by groundwater, better information is desirable.

The potential-pH diagram for **plutonium** is shown in Fig. 17b. The only stable species in groundwater here is PuO_2 (or Pu(OH)_4 , neglecting complexes). Line 2 is the isoconcentration line for $\text{Pu}^{3+}/\text{Pu}^{2+}$, while lines 15 are isoconcentration lines for $\text{Pu(III)}/\text{Pu(IV)}$. The calculations by Allard³¹ in Fig. 20 indicate that the latter lines should be shifted further to the right, Pu(III) dominating as the water-soluble species at pH < 8 . Minimum solubility is reached between pH 8 and 9, where it is $\sim 10^{-8}$ M. An assumed solubility of $\sim 10^{-5}$ M Pu (at pH 7) in the groundwater, and KBS reference data^{8,9} indicate that it would take about 2 million years to dissolve the 10 kg Pu in a waste canister.

A solubility maximum value of $\sim 10^{-7}$ M for plutonium in groundwater corresponds to the dissolution of 50 g per million years, or 50 kg per billion years. This does not seem unreasonable in view of the

FIG. 17. Potential-pH diagrams for the systems neptunium-water, plutonium-water and americium-water at 25°C.¹³

FIG. 18. Uranium concentration in granitic reducing groundwater, according to Allard.³¹

FIG. 19. Neptunium concentration in granitic reducing groundwater, according to Allard.³¹

For neptunium, line 2 in Fig. 17a is the isoconcentration line for $\text{Np}^{3+}/\text{NpO}_2^+$, while line 15 refers to

$$\text{NpO}_2(\text{s}) = \text{NpO}_2^+ + e : E = 0.530 + 0.059 \log [\text{NpO}_2^+]. \quad (47)$$

Thus, Fig. 17 indicates that, at groundwater conditions, Np mainly occurs as insoluble hydroxide, the only soluble species being NpO_2^+ . At $E = -0.05$ V, one gets $[\text{NpO}_2^+] = 10^{-8}$. Taking hydroxy complexes into account Allard³¹ arrives at the conclusion that Np(IV) will dominate in the groundwater, with a concentration $\sim 10^{-8}$ M at $\text{pH} > 9$. At higher pH the formation of $\text{Np}(\text{OH})_3$ is assumed to increase total neptunium solubility; see Fig. 19. Considering the risk of easy transportation of neptunium as NpO_2^+ or Np(V) complexes by groundwater, better information is desirable.

The potential-pH diagram for **plutonium** is shown in Fig. 17b. The only stable species in groundwater here is PuO_2 (or $\text{Pu}(\text{OH})_4$), neglecting complexes. Line 2 is the isoconcentration line for $\text{Pu}^{3+}/\text{PuO}_2^+$, while lines 15 are isoconcentration lines for $\text{Pu(III)}/\text{Pu(IV)}$. The calculations by Allard³¹ in Fig. 20 indicate that the latter lines should be shifted further to the right, Pu(III) dominating as the water-soluble species at $\text{pH} < 8$. Minimum solubility is reached between pH 8 and 9, where it is $\sim 10^{-8}$ M. An assumed solubility of $\sim 10^{-5}$ M Pu (at pH 7) in the groundwater, and EBS reference data^{8,9} indicate that it would take about 2 million years to dissolve the 10 kg Pu in a waste canister.

A solubility maximum value of $\sim 10^{-7}$ M for plutonium in groundwater corresponds to the dissolution of 50 g per million years, or 50 kg per billion years. This does not seem unreasonable in view of the

FIG. 20. Plutonium concentration in granitic reducing groundwater, according to Allard.³¹

fact that the few tons of plutonium formed 1.7 billion years ago at Oklo does not seem to have moved from its place of formation, although that area regularly has been percolated by rainwater.

The Pourbaix diagram of **americium** is given in Fig. 17c. The species present in (uncomplexing) groundwater are Am^{3+} and $\text{Am}(\text{OH})_4$. If $\text{Am}(\text{IV})$ had not formed such strong hydroxy complexes, only $\text{Am}(\text{III})$ would have been considered; also, the solution will contain almost only $\text{Am}(\text{III})$ americium. Line 14 represents the reaction

$$E_0 = 1.74\text{e} - 0.23\text{e}4\text{ pH} - 0.05\text{e}0 \log [\text{Am}^{3+}] \quad (48)$$

For $E_0 = 0\text{ V}$ and $\text{pH } 8$, $[\text{Am}^{3+}] = 10^{-2.5}\text{ M}$, i.e., considerable solubility compared to the value $10^{-8.2}$ given in Table 6. Experimental data indicate a solubility of $\approx 10^{-5}\text{ M}$.³¹ Again, basic data, such as stability and solubility constants for $\text{Am}(\text{III})$ complexes, are missing, hampering a quantitative treatment of the americium solubility in groundwater.

The above summation indicates that the Pourbaix diagrams¹³ for the actinides are outdated by more recent data. Taking such data into account, Skytte-Jensen³² has produced updated potential-pH diagrams for geochemically important radionuclides, including the actinides. However, the database needed for an accurate quantitative description of soluble actinide species of groundwater is simply not at hand.

11. SOME CONCLUSIONS

The dissolutions of canister, waste matrix and waste elements depend on the maximum solubilities of the chemical elements in groundwater and the kinetics of the dissolution process. Maximum solubilities (assuming no oversaturation) can never be exceeded. Thus, kinetics can only slow down the dissolution process, leading to unsaturated solutions.

A stringent calculation of maximum solubility in groundwater *requires detailed information* about the groundwater composition and all its natural equilibria with rock minerals. The rock minerals will act as concentration buffers for a number of groundwater species. That information can be available only when a specific site has been selected and carefully analyzed. Nevertheless, a detailed chemical-mathematical model may be set up before a site is selected. The second requirement for a maximum solubility calculation is that all relevant equilibria for redox, solubility and complex reactions are known and can be quantitatively accounted for. As pointed out above, much needed information is *lacking*. The labor involved in accurate determination of complex equilibria is considerable. In determination of solubility products, the mode of formation of the precipitate requires specific attention, and the developed model should as far as possible simulate the mode nature uses. No single laboratory has the resources to provide all needed information within a reasonable time (say, 5 years). Therefore an international program ought to be set up to meet this demand.

Once a detailed knowledge of the groundwater and the dissolved species leaving a waste repository is at hand, it should also be possible to predict the sorption—and delay times—for the individual elements (or nuclides) with the provision (1) that the geochemistry along the groundwater path is known, and (2) that sorption coefficients are available. Here we have not discussed the sorption coefficients (the so-called k_d -data). It is at present difficult to say how well such coefficients can be predicted. In several laboratories, experiments have started in *fairly idealized systems*, studying the sorption of one radionuclide on one kind of mineral in one type of selected groundwater, varying either temperature or one species of the groundwater (H^+ , Cl^- , SO_4^{2-} , etc.). This program may lead to an understanding of the physico-chemical processes contributing to the k_d -value. Even if the k_d -values so obtained cannot always be well explained, they may nevertheless serve in a useful model for predicting radionuclide migration in the ground.

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Appendix A. Equilibrium Constants from Thermodynamic Data

A1. CHEMICAL EQUILIBRIA

Consider the reaction in the *system*

between n_A moles of component A (element, ion, or compound) and n_B moles of component B, forming the reaction products C and D. The forward velocity (v_f), with which A and B react to form C and D is given by

$$v_f = K_f [A]^{n_A} [B]^{n_B}, \quad (A2)$$

while the velocity of the reverse reaction (backward reaction) is

$$v_b = K_b [C]^{n_C} [D]^{n_D}, \quad (A3)$$

where K_f and K_b are the reaction rate constants, and $\{\}$ is used to indicate chemical activity of a component. We have

$$\{i\} = f_i [i], \quad (A4)$$

where $[i]$ is the concentration and f_i the activity factor of component i . In the following we will simplify the writing by assuming ideal conditions, i.e., $f_i = 1$; thus, all $\{i\} = [i]$.

The reaction quotient (or ratio), Q , is then

$$Q = \frac{[C]^{n_C} [D]^{n_D}}{[A]^{n_A} [B]^{n_B}}, \quad (A5)$$

where

$$Q = (v_f / v_b) \times (K_f / K_b). \quad (A6)$$

At equilibrium, the analytical concentration of each component (i.e., $[i]$) must appear unchanged. This can occur only when

$$v_f = v_b \text{ (at equilibrium)}, \quad (A7)$$

and we specify

$$Q \text{ (at equilibrium)} = \frac{K_f}{K_b} = K, \quad (A8)$$

where K is the equilibrium constant. For further usage, we rewrite Eq. (A5) as

$$\frac{[C]^{n_C} [D]^{n_D}}{[A]^{n_A} [B]^{n_B}} = K \text{ (at equilibrium)}. \quad (A9)$$

A2. CHEMICAL POTENTIAL AND FREE ENERGY OF REACTION

Each chemical component has a power (or potential) to act in a chemical reaction. We define μ_i as the chemical potential of component i . The total chemical energy of the system is called the (Gibbs) free energy and is defined:

$$G = \sum n_i \mu_i. \quad (\text{A10})$$

When A and B react to form C and D, we have a change in the free energy of the system:

$$\Delta G = \sum \mu_i \Delta n_i. \quad (\text{A11a})$$

or for reaction (A1)

$$\Delta G = n_C \mu_C + n_D \mu_D - n_A \mu_A - n_B \mu_B. \quad (\text{A11b})$$

To provide a uniform scale, in which all chemical reactions will fit, standard and reference states must be assigned; the superscript 0 is used to indicate standard state. Thus, μ_i^0 is the chemical potential in the standard state. The deviation from this state follows the rule

$$\mu_i = \mu_i^0 + RT \ln \{i\} \quad (\text{A12a})$$

for a dissolved species i . In the standard state $\{i\} = 1$ and $\mu_i = \mu_i^0$. For a gas, $\{i\}$ in (A12a) must be replaced by the partial pressure p_i . As above, we approximate

$$\mu_i \approx \mu_i^0 + RT \ln \{i\}. \quad (\text{A12b})$$

It follows from (A11) and (A12) that

$$\Delta G = \Delta G^0 + RT \ln Q, \quad (\text{A13})$$

where μ_i^0 is the standard chemical potential and ΔG^0 is the standard (Gibbs) free energy.

At equilibrium, the energy of the system does not change, because it has reached its lowest state:

$$\text{spontaneous reaction} \quad \Delta G < 0 \quad (\text{A14})$$

$$\text{equilibrium} \quad \Delta G = 0 \quad (\text{A15})$$

$$\text{and} \quad \Delta G^0 = -RT \ln K. \quad (\text{A16a})$$

Introducing numerical values:

$$\Delta G^0 = -1363 \log K \text{ (cal)} = -5708 \log K \text{ (joule)}. \quad (\text{A16b})$$

Standard states are 25°C (298 K) and for a gas:

pressure $p_i = 1 \text{ bar} \approx 0.1 \text{ MPa} \approx 1 \text{ atm}$

solute: activity $\{i\} = 1$

solvent: mole fraction $N_i = 1$.

For solids $\{i\} = \{i\} = 1$.

The chemical potential for a pure element is set to zero. Also, its heat of formation (ΔH^0 , see next section) is zero. For the pure element, a specific state is chosen (always pointed out in reference tables like those in Ref. 12 or 13) as $H_2(g)$ for hydrogen, $O_2(g)$ for oxygen, C (graphite) for carbon, $Cl_2(g)$ for chlorine, $Fe(s)$ for iron, etc. Further, μ^0 (and ΔH^0) for $H^+ + e^- \rightarrow \frac{1}{2} H_2(g)$ is set to zero. This provides for a coherent energy scale.

A3. CALCULATION OF ΔG^0 VALUES

The free energy change accompanying the formation of a substance from its elements under standard conditions (1 atm, 25°C) is referred to by various names and symbols; those used by Stumm and Morgan,² Latimer,¹² and Pourbaix¹³ are given below.

(a) Stumm and Morgan use $\overline{G}_f^0$ ("standard molar free energy of formation").
Thus, for reaction (A1),

$$\Delta G^0 = n_C \overline{G}_{C,D}^0 + n_D \overline{G}_{D,D}^0 - n_A \overline{G}_{A,A}^0 - n_B \overline{G}_{B,B}^0, \text{ or, more simply,}$$

$$\Delta G^0 = n_C \mu_C^0 + n_D \mu_D^0 - n_A \mu_A^0 - n_B \mu_B^0,$$

where the chemical potential μ_i is based on formation energy.

(b) Latimer uses ΔF^0 ("free energy of formation").

(c) Pourbaix uses μ^0 ("standard chemical potential").

Since

$$\Delta G^0 = \Delta H^0 - T \Delta S^0,$$

where ΔH^0 is heat of reaction, called "standard molar enthalpy of formation ($\overline{H}_f^0$)" by Stumm and Morgan, and "heat of formation (ΔH^0)" by Latimer, and where ΔS^0 is entropy change, called "standard molar entropy of formation ($\overline{S}_f^0$)" by Stumm and Morgan and "entropy (S^0)" by Latimer.

When ΔH^0 and S^0 are known (measured and/or calculated), ΔG^0 can be calculated (Refs. 12 and 13 contain tables of such data). ΔH^0 and S^0 are directly additive units, but not ΔG^0 , as exemplified:

Example 1: What is the free energy of formation of CO_2 ?

From Latimer (p. 128):

	ΔH^0 (kcal)	ΔG^0 (kcal)	S^0 (cal/degree)
C (graphite)	0 (def)	0 (def)	1.3600
O_2 (g)	0 (def)	0 (def)	49.003
CO_2 (g)	-94.05	X	51.06

Thus, for $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, $\Delta H^0 = -94.05 - 0 = -94.05$, and $\Delta S^0 = 51.06 - 49.003 - 1.3600 = 0.70$.
Thus, $X = \Delta G^0 = \Delta H^0 - T \Delta S^0 = -94.05 - 298 \times 0.70 / 1000 = -94.26$. In Pourbaix (p. 450), μ^0 for CO_2 is -94259.8 cal.

Example 2: What is ΔG for $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$?

From Latimer:

	ΔH^0	ΔG^0	S^0
H_2	0	0	31.211
O_2	0	0	49.003
$H_2O(g)$	-57.80	X	45.106
$H_2O(l)$	-68.32	Y	16.716

$$\Delta S^0 [-H_2O(g)]: 45.106 - 31.211 - \frac{1}{2} 49.003 = -10.61 \text{ cal/degree}$$

$$T\Delta S^0 [-H_2O(g)]: 298(-10.61/1000) = -3.16 \text{ kcal.}$$

$$\Delta G^0 [-H_2O(g)]: -57.80 + 3.16 = -54.64 \text{ (p. 39 in Latimer) (=X).}$$

$$\text{For } H_2O(g) \rightarrow H_2O(l): \Delta H^0 = -68.32 + 57.80 = -10.52$$

$$T\Delta S^0 = 298(16.716 - 45.106)/1000 = -8.46$$

$$\Delta G^0 = -10.52 + 8.46 = -2.06.$$

For the formation of $H_2O(l)$ from H_2 and O_2 , -54.64 and -2.06 must be added, yielding -56.70 (Latimer: -56.690) (=Y).

A4. CALCULATION OF EQUILIBRIUM CONSTANTS AND ΔG

Equation (A16) provides the connection between ΔG^0 for a reaction and the equilibrium constant K .

Example 3: What is the equilibrium constant at 25°C for

From Latimer (who uses symbol ΔG^0) $\mu^0(\text{gas}) = -94.26 \text{ kcal}$ and $\mu^0(\text{aq}) = -92.31 \text{ kcal}$.

Therefore,

$$\Delta G^0 = -94.26 + 92.31 = -1.95 \text{ kcal [from Eq. (A11a)], and}$$

$$-1.363 \log K = -1.950 \text{ [from Eq. (A16b)]}$$

and

$$\log K = 1.43, \text{ or } K = 27.$$

Because we have

$$K = \frac{P_{\text{CO}_2}}{[\text{CO}_2]}$$

and the partial pressure of CO_2 in the atmosphere is $p = 0.00032$, one gets

$$[\text{CO}_2](\text{aq}) = 27 \times 0.00032 = 0.0086 \text{ M.}$$

The free energy of reaction for emitting CO_2 into the atmosphere from a solution containing 0.1 M $\text{CO}_2(\text{aq})$ is calculated as follows.

$$\mu_{\text{gas}} = -94.26 + 1.363 \log 0.00032 = -99.02 \text{ kcal}$$

$$\mu_{\text{aq}} = -92.3 + 1.363 \log 0.1 = -93.67 \text{ kcal}$$

$\Delta G = \mu_{\text{gas}} - \mu_{\text{aq}} = -5.35 \text{ kcal}$. The negative sign indicates (according to Eq. (A14)) that the release of CO_2 from the aqueous phase into the atmosphere occurs spontaneously.

Appendix B. Electrochemical Reactions and Conventions

In this appendix we quote extensively from Ahrland, Liljenzin, and Rydberg.³³

B1. BASIC RELATIONS BETWEEN E, ΔG, AND K

Every redox reaction can be split into two half-reactions—an oxidation reaction which liberates electrons, e^- , and a reduction reaction which consumes electrons. For example, the reduction of neptunyl(V) by iron (II) in acid solution,

can be split into the two half-reactions (B2) and (B3):

According to the IUPAC convention, all reactions involving electrons (half-reactions) should be written as reduction reactions,

with a corresponding equilibrium quotient, Q , defined as

$$Q = \frac{\{\text{Red}\}}{\{\text{Ox}\} [e^-]^n}, \quad (\text{B5})$$

where $\{\}$ is used to denote activities. The standard potential, E° , is then defined by

$$E = E^\circ + \frac{RT}{nF} \ln \frac{\{\text{Ox}\}}{\{\text{Red}\}}, \quad (\text{B6a})$$

where E is the reduction potential relative to the standard hydrogen electrode, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and n is the number of electrons taking part in the reaction. Because $(RT \ln 10)/F = 0.05916 \text{ V}$ (at 25°C), one commonly writes

$$E = E^\circ + \frac{0.059}{n} \log \{\text{Ox}\}/\{\text{Red}\}, \quad (\text{B6b})$$

also replacing activities by concentrations. Because at equilibrium $Q = K$, with these definitions and conventions the following relation between the equilibrium constant and the standard potential is obtained:

$$\ln K = \frac{nE^\circ F}{RT}, \quad (\text{B7a})$$

or

$$E^\circ = - \frac{0.059}{n} \log \{\text{Ox}\}/\{\text{Red}\}. \quad (\text{B7b})$$

When more than one redox system is present in the same solution, their redox potentials must be the same. This condition allows the calculation of equilibrium constants for any redox reaction when the standard potentials are known for the corresponding reduction reactions. The reduction of NpO_2^+ by Fe^{2+} (see reaction 1) will be used again as an example. The two reduction reactions are

and

The requirement that these reactions must have equal potentials gives rise to the following equation

$$E = 0.771 + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.7391 + \frac{RT}{F} \ln \frac{[\text{NpO}_2^+][\text{H}^+]^4}{[\text{Np}^{4+}][\text{H}_2\text{O}]^2}$$

which, after rearrangement of terms, becomes

$$\ln \frac{[\text{Fe}^{3+}][\text{Np}^{4+}][\text{H}_2\text{O}]^2}{[\text{Fe}^{2+}][\text{NpO}_2^+][\text{H}^+]^4} = \frac{0.7391 - 0.771}{RT/F} = \ln K,$$

where K is the equilibrium constant to be calculated. As mentioned, $RT/F \ln 10$ is 0.05916. Using this value, we obtain $\log K = -0.539$ or $K = 0.29$.

The free energy change of the reaction (B4) is

$$\Delta G = -\Delta G^0 + RT \ln Q, \quad (\text{A13})(\text{B8})$$

or, introducing Eq. (B5) and concentrations,

$$\Delta G = -\Delta G^0 + RT \ln [\text{Red}]/[\text{Ox}] \quad (\text{B9})$$

It is most important to observe that, although Eqs. (B6) and (B9) are very similar $[\text{Red}]/[\text{Ox}]$ in Eq. (B9) is inverted in Eq. (B6) (using + in the sum). At equilibrium $Q = K$ and

$$\Delta G^0 = -RT \ln K. \quad (\text{A16})(\text{B10})$$

we have

$$\Delta G = -nFE \text{ and } \Delta G^0 = -nFE^0 \quad (\text{B11})$$

Example 4. It is important to realize that different authors (e.g., Latimer, Pourbaix, and Stumm and Morgan) use different notations

Consider the release of O_2 from water:

(a) *Stumm and Morgan*, who adhere to IUPAC, write (p. 318)

(b) *Latimer* writes

and gives $E^0 = -1.229 \text{ V}$, in addition to thermodynamic data (ΔH^0 , ΔG^0 , S^0) for all components.

(c) Pourbaix (p. 101) writes (as Latimer)

and gives $E_0 = 1.228 - 0.059 \text{ pH}$.

Using IUPAC convention, we write the reduction reaction

for which

$$Q = \frac{[\text{H}_2\text{O}]^2}{P_{\text{O}_2}[\text{H}^+]^4[\text{e}^-]^4}.$$

Leaving out electrons, according to Eq. (B6)

$$E = E^0 + \frac{RT}{nF} \ln P_{\text{O}_2} [\text{H}^+]^4 = E^0 + \frac{0.059}{4} \log P_{\text{O}_2} [\text{H}^+]^4. \quad (\text{B12b})$$

For $n = 4$ electron, $\log K = 20.75$. Then

$$E^0 = 0.059 \times 20.75 = 1.22.$$

At 21%, O_2 in the atmosphere, $P_{\text{O}_2} = 0.21$. Substituting, we obtain

$$E = 1.22 + \frac{0.059}{4} \log 0.21 + \frac{0.059}{4} \times 4 \log [\text{H}^+]$$

$$E = 1.21 - 0.059 \text{ pH} \quad (\text{B13})$$

in agreement with Pourbaix (p. 99).

Latimer uses all equations above in the same way, *except* that:

1) he writes the reaction as an oxidation [cf. Eq. (B4)]

and consequently

$$Q_L = [\text{Ox}]/[\text{Red}], \quad (\text{L2})$$

which for reaction (B12) becomes

$$Q_L = [\text{O}_2] [\text{H}^+]^4 [\text{e}^-]^4 / [\text{H}_2\text{O}]^2, \quad (\text{L3})$$

where the "L" is used to distinguish it from (B12b) above, and

2) he writes the electrochemical Eq. (B6) as

$$E = E^0 - \frac{RT}{nF} \ln Q_L = E^0 - \frac{0.059}{n} \log [Ox]/[Red]. \quad (L4)$$

Observe the negative sign!

Then, introducing Latimer's $E^0 = -1.229$ V in Eq. (L4),

$$E = -1.229 - \frac{0.059}{4} \log [O_2] [H^+]^4 [e^-]^4 / [H_2O]^2,$$

which at equilibrium ($E = 0$) gives

$$\log [O_2] [H^+]^4 [e^-]^4 / [H_2O]^2 = 1.229 \times 4/0.059 = -83.3.$$

Thus, for the reaction

$$\log K = -83.3,$$

the same as Stumm and Morgan give (20.75×4 for the reverse reaction, $Q = Q_L^{-1}$).

Equation (B11) gives $\Delta G^0 = -nFE^0$ for the reaction $Ox + ne^- \rightarrow Red$. For Latimer, the negative value of nFE^0 requires that his ΔG refer to the reaction $Red \rightarrow Ox + ne^-$.

Pourbaix writes reaction formulae in any direction, but adheres to the IUPAC convention in Eq. (B6); see Appendix C.

B2. Eh AND $p\epsilon$ VALUES

The reference value for electrochemical reactions is

$$H^+ + e^- = 1/2H_2(g) \quad E^0 = 0 \text{ V}, \quad (B14)$$

and all redox potentials are conveniently related to this, providing an Eh scale, where h denotes the hydrogen reference. Commonly, the "h" is dropped, as has been done above.

Considering Eq. (B5), we can define

$$\log [e^-] = p\epsilon, \quad (B15)$$

which, with Eq. (B6a), gives

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]} = \frac{RT}{F} \ln [e^-].$$

For the hydrogen reference scale

$$E = \frac{RT}{F} \ln [e^-],$$

or

$$Eh = 0.059 p\epsilon. \quad (B16)$$

With $Eh^0 = 0.059 p\epsilon^0$, one gets

$$\epsilon^0 = n^{-1} \log K. \quad (B17)$$

All equilibrium reactions involving electrons can therefore be assigned an ϵ^0 value. Such relative electron affinities are provided (e.g., by Stumm and Morgan) and can be used instead of $\log K$ for comparative purposes. However, we will here continue to use the Eh scale, commonly dropping the "h" marking.

B3. GRAPHICAL PRESENTATION OF REDOX EQUILIBRIA

When several oxidation states of an element are encountered in solution, graphical presentations of the various relationships are very useful and greatly facilitate the understanding of these systems.

The most simple graph is the Latimer diagram (see Fig. B1), which only relates potentials and oxidation states. The sum of the potential times the number of electrons must be the same and independent of the way used in the Latimer diagram for any two oxidation states spanning one or more intermediate states. This is quite useful as an aid in evaluating potentials indirectly from other measured potentials, e.g., the $\text{PuO}_2^+/ \text{Pu}^{3+}$ potential from the $\text{PuO}_2^+/ \text{Pu}^{4+}$ and $\text{Pu}^{4+}/ \text{Pu}^{3+}$ potentials. In this example, the relation $2 \cdot E_{\text{IV}}^0 = 1 \cdot E_{\text{IV}}^0 + 1 \cdot E_{\text{IV}}^0$ was used.

Activity ratio potential diagrams are very often used because of their simplicity (see Fig. B2). However, as they use one of the oxidation states as reference basis they are not easy to use in predicting redox equilibria when more than one redox system is present in a solution. Relative concentration potential diagrams are generally more useful in predicting redox equilibria. Here the total concentration, C_M , is used as a common reference instead of one of the oxidation states.

In mass balance calculations it is necessary to use concentration instead of activities. In order to translate activities into concentrations in a simple way, activity factors are defined as in Eq. (A4). For simplicity we continue to use concentrations.

FIG. B1. The Latimer diagram for the plutonium formal potentials in 1 M HClO_4 . Values in bold type are measured, and the others are calculated from the measured potentials.

FIG. B2. Conventional redox diagram for uranium in 1 M HClO_4 . U^{4+} is used as the reference state (horizontal line) in the diagram.

B4. CONSTRUCTION OF REDOX DIAGRAMS

Let us consider the U(III)-U(IV)-U(VI) diagram, neglecting the U(V) species, and derive the relative concentrations of these species as a function of (1) the redox potential of the solution at 1 M H^+ , (2) the pH of the solution. Neglecting complexes and using the symbols [3], [4] and [o] for the concentration of the uranium ions in the three different valency states, the total uranium concentration C_U becomes

$$C_U = [3] + [4] + [o]. \quad (B18)$$

The Nernst expression for the redox reaction

becomes

$$E_{13} = E_{13}^0 + 0.059 \log [4] / [3]^{-1}, \quad (B20)$$

while for the redox reaction

the Nernst equation becomes

$$E_{04} = E_{04}^0 + \frac{0.059}{2} \log [o] / [H^+]^4 [4]^{-1}. \quad (B22)$$

In the same solution there can only be one E value; thus, $E = E_{13} = E_{04}$. In exponential form we write Eqs. (B20b) and (B22b):

$$[4] / [3]^{-1} = 10^{(E - E_{13}^0) / 0.059} = a_{13}, \quad (B20b)$$

$$[o] / [H^+]^4 [4]^{-1} = 10^{2(E - E_{04}^0) / 0.059} = a_{04}. \quad (B22b)$$

Let us now see how the U(IV) concentration, [4], varies with E . From the last equations we have

$$[3] = [4] a_{13}^{-1}, \quad (B20c)$$

$$[o] = [4] [H^+]^4 a_{04}, \quad (B22c)$$

which, introduced in Eq. (B18), give

$$C_U = [4] (a_{13}^{-1} + 1 + a_{04} [H^+]^4), \quad (B23a)$$

or, rewritten

$$\log [H] / C_U = - \log (a_{13}^{-1} + 1 + a_{04} [H^+]^4). \quad (B23b)$$

Introducing the standard redox potentials $E_{13}^0 = -0.596$ and $E_{04}^0 = 0.319$, one can calculate for $[H^+] \approx 1 M$ the values in Table B1.

TABLE B1. Values of $-\log a_{43}$, $\log a_{64}$ and $\log [U^{4+}/C_U]$ at different values of E.

	E(V)			
	-1.0	-0.5	0	+0.5
$-\log a_{43} = (1 - 0.596)/0.059$	$10^{-0.85}$	$10^{+0.4}$	$10^{+0.10}$	$10^{+0.96}$
$\log a_{64} = 2(E - 0.319)/0.059$	$10^{-4.4}$	$10^{-0.76}$	$10^{-0.61}$	$10^{+0.14}$
$\log [U^{4+}/C_U]$	-0.85	0.01	0	0.14

Figure B3 shows $\log [U^{4+}]/C_U$ as a function of the redox potential of the solution. The four calculated points are marked with o. The curve has three asymptotes, crossing each other at E_{13}^0 and E_{64}^0 (marked ●). The left asymptote has a slope of 0.059 V per concentration unit, while the right asymptote has a slope of $-0.059/2$. On the horizontal asymptote $[U^{4+}] = C_U$, i.e., practically all uranium is in the $U(IV)$ state.

In Fig. B4, the curve $\log [U^{4+}]/C_U$ as a function of E is replotted, with curves for $\log [U^{3+}]/C_U$ and $\log [UO_2^{2+}]/C_U$ produced in a similar way. Here also the pentavalent state is included; it is seen that it always will be $<0.001\%$ of total uranium.

Equation (B23) can be generalized to

$$\frac{[M^{z_1}]}{C_M} = \frac{1}{\sum_{i=1}^n \frac{1}{f_i} \exp\left(\sum_{j=1}^z \frac{f_j}{RT} (E - E_{ij}^0)\right)} = \frac{f_{11} [M^{z_1}]}{C_M} \quad (B24)$$

Equation (B24) is used to calculate the relative activity and relative concentration for any potential, E. The relative activities and relative concentrations for the remaining oxidation states are then calculated from Eqs. (B6a) and (A4). The values obtained are plotted in a logarithmic form with the logarithm of the relative concentration versus potential. It is very convenient to use a potential scale where 1 unit of length is $RT \ln 10/E$, a "pE" scale, as all lines then will have integral slopes except in the immediate vicinity of any formal (or standard) potential (see Fig. B4).

These diagrams can be used as follows to evaluate the equilibrium composition when two different redox systems are mixed. The appropriate redox diagrams are selected and potential scales are aligned and the concentration scales moved so that the actual total concentration ratio is given by the difference in the logarithmic concentration scales. The equilibrium concentrations of the different ions then correspond to the point of intersection of the ion lines with a vertical line drawn through the intersection of two lines representing the products formed. This can be exemplified using the reduction of NpO_2^+ by Fe^{2+} . If a solution is prepared which initially contains 0.001 M NpO_2^+ and 0.2 M Fe^{2+} in 1 M acid, what will the equilibrium composition be?

The actual redox diagrams are shown in Fig. B5 shifted according to the concentrations. The products formed are Fe^{3+} and Np^{4+} , which will be produced in equal amounts. A vertical line through the intersection of the Fe^{3+} and Np^{4+} lines shows that the equilibrium concentrations will be $[Fe^{2+}] \approx 0.2$ M, $[Fe^{3+}] = [Np^{4+}] \approx 10^{-3}$ M, $[NpO_2^+] \approx 9 \cdot 10^{-6}$ M and the redox potential will be 0.10 mV.

Using the same kind of diagrams, with total concentrations of each valence state plotted instead of the concentrations of the free ions, it is possible to treat cases of combined complex formation and redox reaction, provided that changes in the concentration of free ligand, acidity, etc., are negligible or duly considered.

For many practical purposes a potential pH diagram is very useful. Figure B8 (see Section B7) is an example of this type of diagram in which isoconcentration lines are used to show the composition at any pH and potential. Concentrations below 50% are usually not shown as they would make the diagram too difficult to read. When constructing such diagrams it is important to include all relevant effects, i.e., pH-dependent potentials, hydrolysis and ionic-medium effects.

FIG. B3 (upper). $\text{Log } [\text{U}^{4+}]/C_U$ as a function of the redox potential of the solution.

FIG. B4 (lower). The redox diagram for uranium in 1 M HClO_4 at 25°C. Observe that the crossing of U^{4+} and UO_2^+ is a higher potential than the crossing of UO_2^+ and UO_2^{2+} .

FIG. B5. Redox equilibrium after the reduction of 0.001 M Np(V) with 0.2 M Fe(II) in 1 M acid.

B5. ACIDITY-DEPENDENT REDOX DIAGRAMS

According to Eq. (B21), the reduction of UO_2^{2+} to U^{3+} involves hydrogen ions, which is included in the redox equation (B22). For Fig. B4 we assumed that $[\text{H}^+] = 1 \text{ M}$. For other values of $[\text{H}^+]$, $[\text{UO}_2^{2+}]$ will differ. For example, at 10^{-1} M H^+ one will get

$$[\text{U}] = a_{\text{U}} [\text{U}^{3+}] 10^{-4},$$

that is, the relative UO_2^{2+} concentration is reduced by 4 powers of ten. The calculations are otherwise carried out as before. Figure B6 shows the effect on the uranium system of changing the acidity one power of ten in either direction. It should be observed that the U(V) fraction increases with decreasing acidity.

FIG. B6. Redox diagram for uranium showing the effect of hydrogen ion on the relative concentration of the free ions. $[\text{H}^+] = 0.1, 1.0, 10.0 \text{ M}$. At the lowest hydrogen ion concentration and at the highest concentration minor corrections were omitted for hydrolysis of U^{4+} and ionic strength respectively.

B6. EFFECT OF COMPLEX FORMATION

It is assumed in this connection that only uncomplexed ionic species take part in the redox electron exchange reactions. (It should however be noted that this assumption is not valid in many organic and biochemical systems.) In some systems only a fraction of the total concentration of a metal in a valency state may be uncomplexed ion. For example, U^{3+} forms UOH^{2+} , $U(OH)_2^+$ and $U(OH)_3$ when it hydrolyzes. The overall complex reaction is then written

and the equilibrium constant is defined as

$$\beta_3^- = [H^+]^3 [U(OH)_3] / [U^{3+}] \quad (B26)$$

(β_3^- being the acidic complexity product). We then have

$$[U^{3+}] = \beta_3^{-1} [H^+]^3 [U(OH)_3] \quad (B27)$$

Furthermore, the total concentration of U(III), $C_{U(III)}$, is

$$C_{U(III)} = [U^{3+}] + [UOH^{2+}] + [U(OH)_2^+] + [U(OH)_3] = [U^{3+}] \sum \beta_i^{-1} [H^+]^i \quad (B28)$$

In the calculation of the redox diagram, given that

$$C_U = C_{U(III)} + C_{U(IV)} + C_{U(V)} + C_{U(VI)}$$

both C_U and concentrations of uncomplexed ions become pH-dependent. Introduction of hydrolysis effects therefore leads to complicated diagrams. Including other effects, such as additional complex formers (e.g., SO_4^{2-}) and ionic strength, adds further to the complexity of the redox diagrams. An example is shown in Fig. B7.

Under these circumstances, which fairly well reflect the natural conditions in a waste repository, another type of diagram is preferred, the so-called "Eh-pH diagram" (or "Potential-pH diagram" or "Pourbaix diagram").

FIG. B7. The redox diagram for uranium (total concentrations) at pH = 2, $I = 1$ and $[SO_4^{2-}] = 0$ (A), 0.01 (B), 0.1 (C), 0.33 M (D). The addition of sulphate increases the total amount of U^{4+} in various complexes at the expense of U^{3+} , UO_2^+ and UO_2^{2+} . The effect would have been larger if the preferential hydrolysis of U^{4+} had not stabilized U(IV) even in the absence of sulphate.

B7. POTENTIAL-pH DIAGRAMs

The hydrogen ions have a great influence on the composition of a solution at a given potential. This is due to a combination of three effects:

1. The potential for one of the reactants changes with pH.
2. The ions hydrolyze to a different degree, which changes the relative amounts of the different oxidation states.
3. The substitution of cations, e.g., H^+ for Na^+ , in the ionic medium changes the activity factors, $f_{\pm}$. The importance of the effect depends on the ionic strength and on the anions in the ionic medium.

It is possible to construct a series of redox diagrams at a series of pH values if due consideration is given to the three effects mentioned and if C_M is given a sufficiently low value so that polynuclear hydrolysis products are avoided. (If polynuclear species were included, C_M would have to be given a fixed value.) The results can be regarded as a three-dimensional potential-concentration-pH diagram which gives excellent information about the composition at any potential and pH. Such diagrams, are, however, generally not suited to presentation as two-dimensional projections, but with the sacrifice of some of the detail they can be reproduced as potential-pH diagrams with isoconcentration lines (see Fig. B8). Isoconcentration lines have been drawn at 98, 80, 63 and 50% of C_M as indicated by the numbers on the curves. The 50% lines separate areas where the indicated oxidation states dominate. Two dotted lines are drawn at 2% and 1%, since this oxidation state never passes 10% in this pH range.

The hydrolysis of U^{4+} prohibits the formation of larger amounts of $U(V)$ as the pH dependence of the 50% line between $U(IV)$ and $U(V)$ becomes smaller. The hydrolysis of U^{4+} also decreases the amount of $U(III)$, which is less prone to undergo hydrolysis.

Potential pH diagrams are further discussed in Appendix C.

FIG. B8. The potential-pH diagram for uranium in 1 M (H, Na)ClO₄. Isoconcentration curves are drawn at 98, 89, 80, 63, 50, 1, and 0.1% of the total concentration. Hydrolysis data for U³⁺ are estimated from the lanthanides and from Pu³⁺.

Appendix C. Construction and Interpretation of Potential-pH (Pourbaix) Diagrams

C1. SYMBOLS USED BY POURBAIX

ψ = electrode potential ("inner electric potential," p. 22*).

U_I = "equilibrium potential difference" (p. 25) at current I . For reaction $A + e^- \rightarrow B$, $U_I = \psi_B - \psi_A$.

$U_{I=0}$ = "electric tension of cell at current $I = 0$ ". $U_{I=0} = E_0 = E_{red}$ ("reduction chemical tension") (p. 25).

E = cell potential ("chemical tension of cell reaction").

E_0 = "equilibrium potential" of the electrochemical reaction, i.e. the cell potential at equilibrium conditions (or cell emf).

E_0^0 = cell potential at standard conditions (p. 45) and 25°C.

$E_1^{(0.5)}$ = coexistence potential, i.e., potential when $[Ox] = [Red]$ for reaction $Ox + ne^- \rightarrow Red$; same as 50% Ox and 50% Red .

C_i = overall metal concentration of system studied (p. 58).

A = "affinity" = $-\Delta G$; A_{red} = "reduction affinity."

μ = chemical potential; μ^0 at standard conditions, μ_0^0 at standard conditions and 25°C.

$\Sigma \nu \mu = \Delta G$ (Gibbs) free energy ("free enthalpy", p. 57). For example, for $2A + 3B \rightarrow C$,

$$\Delta G = \mu_C - 2\mu_A - 3\mu_B. \quad (C.1)$$

$\log(M) = \log K$, where K is the equilibrium constant.

R_i = reduced species i (we use Red_i).

O_i = oxidized species i (we use Ox_i).

x_i = fraction of oxidized species.

iso- C_i line: 50% ($x_i = 0.5$) of oxidized and of reduced species.

*Page numbers are from Ref. 13.

C2. CONVENTIONS USED BY POURBAIX

For reaction

$$\text{and} \quad \Delta G = \Delta G^0 + RT \ln Q \quad ; \quad \Delta G^0 = RT \ln K \quad (C2)$$

$$\text{and} \quad \Delta G = nFE_0 \quad ; \quad \Delta G^0 = nFE_0^0. \quad (C3)$$

Redox reactions are written either $\text{Ox} + n\text{e}^- = \text{Red}$ (according to IUPAC convention), or $\text{Red} = \text{Ox} + n\text{e}^-$, but the equilibrium potential is always written

$$E_0 = E_0^0 + (RT/nF) \ln [Ox]/[Red]. \quad (C4)$$

For E_0^0 from thermodynamic data

$$E_0^0 = \frac{\sum \nu \mu^0}{nF} \\ \sum \mu^0 / 23.06 n \text{ for } \mu^0 \text{ in kcal} \quad (C5)$$

Half-cell reactions are always written in the form Zn/Zn^{2+} , $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$ and $E_0^0 = E_{\text{red}}^0 - 0.76 \text{ V}$. Reference states are $\mu^0 = 0$ for pure element and $\text{H}^+(\text{aq})$, and $\Delta G^0 = 0$ for $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow 1/2 \text{H}_2(\text{g})$.

C3. THE IRON-WATER SYSTEM

We shall use this system to illustrate the construction and interpretation of Pourbaix diagrams. For this purpose we have taken Tables C1 and C2 and Fig. C1 from Pourbaix (p. 308).

C.3.1. THERMODYNAMIC DATA

Table C1 contains thermodynamic data (chemical potentials, μ°) for the species considered, and for species not considered. Of the oxides, only the hydrated ones (the "hydroxides") are assumed to be present in aqueous systems. Thus, from a chemical point of view we can consider FeO hydr $\text{Fe}(\text{OH})_2$, the only difference being one molecule of water. The formation reaction for FeO is

P12 means Eq. (12) in Pourbaix' book

TABLE C1. Substances considered and substances not considered (adapted from Ref. 13).

	Oxidation number (Z)	Considered	Not considered	$\mu^\circ(\text{cal.})^a$	Name, color, crystalline system
Solid substances	0	Fe	—	0	α -Iron, light grey, f.c. cub.
	2	FeO hydr.	—	-58 880 ^b	Ferrous hydroxide $\text{Fe}(\text{OH})_2$, white, rhomb.
	"	"	FeO anh.	—	Ferrous oxide, black, cub.
	2.67	Fe_3O_4 anh.	—	-242 400	Magnetite, black, cub.
	"	"	$\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$	—	Hydrated magnetite, green-black
	3	Fe_2O_3 anh.	—	-177 100	Haematite, red-brown, rhomb. or cub.
Dissolved substances	"	" hydr.	—	-161 930 ^c	Ferric hydroxide $\text{Fe}(\text{OH})_3$, red-brown, f.c. cub.
	2	Fe	—	-20 300	Ferrous ion, green
	"	H FeO_2	—	-90 627 (*)	Dihydroferrite ion, green
	"	"	FeO_2	—	Hypoferrite ion
	3	Fe	—	-2 530	Ferric ion, colorless
	"	FeOH^+	—	-55 940	Ferric ion, colorless
	"	$\text{Fe}(\text{OH})_2^+$	—	-106 200	Ferric ion, colorless
	"	"	FeO_2^-	—	Ferrite ion
	4	"	FeO^-	—	Ferryl ion
	"	"	FeO_4^{2-}	—	Perferrite ion
	5	"	FeO_2^-	—	Perferryl ion
	6	FeO_4^{2-}	—	-111 685? (*)	Ferrate ion, violet

^a These values are indicated by W. M. Latimer, except for the two values given below which were calculated by Pourbaix as follows:

(*) for HFeO_2 : Pourbaix assumed, as the solubility product $(\text{HFeO}_2) \cdot (\text{H}^+)$ relating to the reaction $\text{Fe}(\text{OH})_2 \rightarrow \text{HFeO}_2 + \text{H}^+$, the value $10^{-18.4}$ (Schrager, Chem. News, 138, 354, 1929);

(*) for FeO_2 : For want of more precise data Pourbaix provisionally assumed, for the standard equilibrium potential of the reaction $\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{FeO}_4^{2-} + 8\text{H}^+ + 3\text{e}^-$, the approximate value $E_0^{\circ} = 1.7$ V given in the Handbook of Chemistry & Physics (Volume 26, p. 951, Chemical Rubber Publ. Co., Cleveland, 1936), whose origin Pourbaix was not able to find. He points out that Latimer gives two approximate values for the equilibrium potentials of the oxidation-reduction reactions: $\text{FeO}_2^-/\text{FeO}_4^{2-} = V^{\circ} > +0.9$ V at pH 14 and $\text{Fe}^{++}/\text{FeO}_4^{2-} = V^{\circ} > +1.9$ V at pH 0.

^b This value of $\mu_{\text{FeO} \text{ hydr}}^\circ$ corresponds to $\mu_{\text{Fe}(\text{OH})_2}^\circ = -115 570$ cal.

^c This value of $\mu_{\text{Fe}_2\text{O}_3 \text{ hydr}}^\circ$ corresponds to $\mu_{\text{Fe}(\text{OH})_3}^\circ = -160 000$ cal.

TABLE C2. Reactions and equilibrium formulae (adapted from Ref. 13).

2.1 TWO DISSOLVED SUBSTANCES

2.1.1. Relative stability of the dissolved substances

2 $\rightarrow$ 2 2 $\rightarrow$ 3 + 2 $\rightarrow$ 3 + 2 $\rightarrow$ 6 + 3 $\rightarrow$ 6 2.1.2. $\log_{10}$ formulae of relative predominance of the dissolved substances

1.	$\text{Fe}^{2+} \rightleftharpoons \text{HFeO}_2^-$	pH = 10.53
2.	$\text{Fe}^{2+} \rightleftharpoons \text{FeOH}^{2+}$	pH = 2.43
3.	$\text{FeOH}^{2+} \rightleftharpoons \text{Fe(OH)}_2^+$	pH = 4.69
4.	$\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$	$E_0 = 0.771$
5.	$\text{Fe}^{2+} \rightleftharpoons \text{FeOH}^{2+}$	$E_0 = 0.914 - 0.0591 \text{pH}$
6.	$\text{Fe}^{2+} \rightleftharpoons \text{Fe(OH)}_2^+$	$E_0 = 1.191 - 0.1182 \text{pH}$
7.	$\text{HFeO}_2^- \rightleftharpoons \text{Fe(OH)}_2^+$	$E_0 = 0.675 - 0.591 \text{pH}$
8.	$\text{HFeO}_2^- \rightleftharpoons \text{FeO}_4^{2-}$	$E_0 = 1.001 - 0.0738 \text{pH}$
9.	$\text{Fe}^{2+} \rightleftharpoons \text{FeO}_4^{2-}$	$E_0 = 1.700 - 0.1580 \text{pH}$
10.	$\text{FeOH}^{2+} \rightleftharpoons \text{Fe(OH)}_2^+$	$E_0 = 1.652 - 0.1379 \text{pH}$
11.	$\text{Fe(OH)}_2^+ \rightleftharpoons \text{Fe(OH)}_4^-$	$E_0 = 1.559 - 0.1182 \text{pH}$

TABLE C2. (Continued.)

2.2. TWO SOLID SUBSTANCES

Limits of the domains of relative stability of iron and its oxides and hydroxides^a

0 → +2			
12.	$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}^+ + 2e^-$	$E_0 = -0.047 - 0.0594 \text{ pH}$	
0 → +2.67			
13.	$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8e^-$	$E_0 = -0.085 - 0.0591 \text{ pH}$	
0 → +3			
14.	$2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6e^-$	$a \ E_0 = -0.051 - 0.0591 \text{ pH}$ $b \ = -0.059 - 0.591 \text{ pH}$	
+2 → 2.67			
15.	$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+ + 2e^-$	$E_0 = -0.197 - 0.0591 \text{ pH}$	
+2 → +3			
16.	$2\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2e^-$	$a \ E_0 = -0.057 - 0.0591 \text{ pH}$ $b \ = -0.271 - 0.591 \text{ pH}$	
+2.67 → +3			
17.	$2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \rightarrow 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2e^-$	$a \ E_0 = -0.221 - 0.0591 \text{ pH}$ $b \ = -1.208 - 0.591 \text{ pH}$	

2.3. ONE SOLID SUBSTANCE AND ONE DISSOLVED SUBSTANCE

Solubility of iron and its oxides and hydroxides^a

Z → +2			
18.	$\text{Fe}^{2+} + \text{H}_2\text{O} \rightarrow \text{FeO} + 2\text{H}^+$	$\log(\text{Fe}^{2+}) = 13.29 - 2\text{pH}$	
19.	$\text{FeO} + \text{H}_2\text{O} \rightarrow \text{HFeO}_2 + \text{H}^+$	$\log(\text{HFeO}_2) = 18.30 - \text{pH}$	
Z → +3			
20.	$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$	$a \ \log(\text{Fe}^{3+}) = -0.72 - 3\text{pH}$ $b \ = -4.84 - 3\text{pH}$	
21.	$2\text{FeOH}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 4\text{H}^+$	$a \ \log(\text{FeOH}^{2+}) = 3.15 - 1\text{pH}$ $b \ = -2.41 - 2\text{pH}$	
22.	$2\text{Fe}(\text{OH})_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+$	$a \ \log(\text{Fe}(\text{OH})_2) = 7.84 - \text{pH}$ $b \ = -2.28 - \text{pH}$	
0 → +2			
23.	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$	$E_0 = -0.440 + 0.0295 \log(\text{Fe}^{2+})$	
24.	$\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{HFeO}_2 + 3\text{H}^+ + 2e^-$	$E_0 = 0.493 - 0.0886 \text{ pH} - 0.0295 \log(\text{HFeO}_2)$	
0 → +3			
25.	$\text{Fe} \rightarrow \text{Fe}^{3+} + 3e^-$	$E_0 = -0.037 + 0.0197 \log(\text{Fe}^{3+})$	
+2 → 2.67			
26.	$3\text{Fe}^{2+} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e^-$	$E_0 = -0.980 - 0.2364 \text{ pH} - 0.0886 \log(\text{Fe}^{2+})$	
27.	$3\text{HFeO}_2 + \text{H}^+ \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + 2e^-$	$E_0 = -1.819 + 0.0295 \text{ pH} - 0.0886 \log(\text{HFeO}_2)$	
+2 → +3			
28.	$2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2e^-$	$a \ E_0 = -0.728 - 0.1773 \text{ pH} - 0.0591 \log(\text{Fe}^{2+})$ $b \ = -1.037 - 0.1773 \text{ pH} - 0.0591 \log(\text{Fe}^{2+})$	
29.	$2\text{HFeO}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + 2e^-$	$a \ E_0 = -1.139 - 0.0591 \log(\text{HFeO}_2)$ $b \ = -0.810 - 0.0591 \log(\text{HFeO}_2)$	

^aFor the reactions involving Fe_2O_3 , the letter *a* relates to anhydrous Fe_2O_3 , whose free enthalpy of formation is -177 100 cal.; the letter *b* relates to $\text{Fe}(\text{OH})_3$, whose free enthalpy of formation is -166 000 cal.

with $\mu_{\text{H}_2\text{O}}^0 = -56.69$ kcal. Thus, although Eqs. (P12) and (C6) are the same when considering aqueous reactions, they are not the same thermodynamically, because the chemical potential values (Latimer, Pourbaix, etc.) are calculated for fixed stoichiometries.

In Table C1, the anhydrous and hydrous Fe_2O_3 appear, indicated by letters (a) and (b). Such letters sometimes appear in the diagrams (or refer to two different diagrams). It is then essential to check in the table what the differences are between these lines. In the iron-water system, the line (b) refers to the hydrated species; we shall also consider $\text{Fe}_2\text{O}_3 \text{ hydr.} \approx 2 \text{ Fe(OH)}_3$.

From Table 5 in the main text, we can see that stepwise complex formation is considered to involve the species:

Fe^{2+} , Fe(OH)^+ , Fe(OH)_2 and Fe(OH)_3 (last species only in Table C1).

Fe^{3+} , Fe(OH)^{2+} , Fe(OH)_2^+ and Fe(OH)_3 .

Pourbaix does not consider FeOH^+ , and writes out Fe(OH)_3 as HFeO_2^- . For the formation of FeOH^+ ,

we calculate from $\log K = 4.5$ that $\Delta G^0 = -6.13$ kcal, and

$$\log \{[\text{Fe}^{2+}]/[\text{FeOH}^+]\} = 9.5 - \text{pH} \quad (\text{C } 8)$$

In Fig. 6a (main text), we included Eq. (C 8) as line "(C8)", which falls inside the shaded area between lines (a) and (b). By considering FeOH^+ , the area of existence of soluble Fe(II) increases. The calculation of the lines in the Pourbaix diagrams is described in the next section.

General problems with Pourbaix diagrams are:

(i) The thermodynamic data on which the diagrams are based are quite old (mainly from Ref. 5, which appeared in 1953).

(ii) It is not clear what data should be chosen (or have been chosen) when the data in the literature are contradictory. (For example, hydrolysis constants for the same reaction sometimes differ by several powers of ten; cf. Appendix E.)

(iii) Solubility constants, especially for hydroxides, depend strongly on the method by which the precipitate has been produced (see, for example, Ref. 2).

(iv) Polymeric hydrolysis species often occur but are not included in the Pourbaix diagrams.

Consequently, the information provided by the Pourbaix diagrams must be used with care. A cooperative international program is desirable in order to update these diagrams and improve their reliability. With computer techniques, such diagrams can be displayed in a three-dimensional form, with the metal concentration as the third variable (concentration-potential-pH diagrams).

C.3.2. CALCULATION OF EQUILIBRIUM LINES

Because μ^0 is zero for H^+ , H_2 (g) and O_2 (g), and using $\mu_{\text{H}_2\text{O}}^0 = -56.69$ kcal, one can use the μ^0 values in Table C1 to calculate ΔG^0 by Eq. (C1) for any iron-water reaction involving the species in the table. With ΔG^0 one can then calculate equilibrium constants K [Eq. (C2)] or E^0 values [Eq. (C3)]. Values of E^0 are obtained faster with Eq. (C5).

Example 1:

This reaction is written according to IUPAC convention. However, using Pourbaix's data, one must follow his rule and write

$$\text{Fe(s)} = \text{Fe}^{2+} + 2e^- \quad (\text{P23})$$

so that [with Eq. (P1)]

$$E^0 = \frac{\Delta G^0}{nF} = \frac{\mu_{\text{Fe}^{2+}}^0 - \mu_{\text{Fe}}^0}{2 \times 23.06} = \frac{-20.30 - 0}{2 \times 23.06} = -0.440 \text{ V.}$$

If we had followed IUPAC convention, E^0 would have the wrong sign. Remembering that $RT \log 10/F = 0.059 \text{ V}$ and $[\text{Fe(s)}] = 1$ (as for all solid substances), one gets Pourbaix' Eq. (23) (see Table C.2):

$$E = -0.440 + \frac{0.059}{2} \log [\text{Fe}^{2+}]. \quad (\text{P23})$$

Example 2:

As pointed out before, we must write this relation in the "Latimer terminology":

Thus, $\Delta G^0 = -58.88 - 2 \times 0 + 20.30 + 56.69 = 18.11$

$$\Delta G^0 = -RT \ln K \approx -1.363 \log K$$

$$\text{and } \log K = \frac{18.11}{1.363} = \log [\text{H}^+]^2 [\text{Fe}^{2+}]^{-1}$$

$$\text{or } \log [\text{Fe}^{2+}] = 13.29 - 2\text{pH}. \quad (\text{P18})$$

Using the thermodynamic data for all species in Table C.1, one produces the reactions and equations in Table C.2. In the main text (section 6) only the species Fe^{2+} , $\text{Fe}(\text{OH})_2$, Fe^{3+} and $\text{Fe}(\text{OH})_3$ are considered (see Fig. 6). However, in section 7 all iron species are considered (we have also added FeOH^+ to Fig. 6).

C.3.3. INTERPRETATION OF POURBAIX DIAGRAMS

The main text has already described the principles for the production of Pourbaix diagrams. In the previous sections of this Appendix, we have added some cautionary remarks about reliability and completeness of these diagrams. However, these diagrams are extremely useful. We shall now interpret Fig. C.1 (same as Fig. 6b in the main text), assuming it to correctly describe the iron-water system.

In order to facilitate the understanding of Fig. C.1, we have marked the lines of Fig. 6a with the same Pourbaix equation numbers. Also in Fig. C.1 we have emphasized the lines already given in Fig. 6a. Below line (a) water is unstable with regard to H_2 production; at 1 M H^+ (pH 0), Fe(s) produces hydrogen gas from water. Above line (b) tetra-oxo ions, FeO_4^{2-} , are formed. Line (9') is the iso-concentration line for Fe^{3+} and FeO_4^{2-} . Lines (11') and (8') refer to other species ($\text{Fe}(\text{OH})_2^+$ and HFeO_2^- , respectively) in equilibrium with FeO_4^{2-} . Line (2') divides the area between uncomplexed Fe^{3+} and its first hydrolysis complex, FeOH^{2+} . Observe that all complexity reactions (but not those involving redox reactions) appear as vertical lines! The line starting at -0.5 V and marked (23), continuing in lines (18), (20) and (21), refers to reactions involving one dissolved iron species at concentration 1 , 10^{-2} , 10^{-4} and 10^{-6} M we have thickened the line for 10^{-4} M , used in Fig. 6b.

In section 7 of the main text, this Pourbaix diagram is further discussed, and later sections treat the diagrams for other metals of importance for the safe storage of highly radioactive waste.

Appendix D. Determination of Redox Potential in Swedish Groundwater

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D1. INTRODUCTION

It is often possible to determine from the redox potential of the system whether general corrosion of metallic material is possible. This use of the redox potential is illustrated by a relative diagram for copper in an aquatic system of roughly the same composition as the groundwater studied here. As is evident from Fig. 7 (main text), metallic copper is not stable at redox potentials greater than approximately -45 mV.

The redox potential in most groundwaters is determined by various mineral equilibria, e.g., oxide phases and silicates of iron(II) and iron(III). Redox potentials in systems such as we are dealing with here are normally calculated on the basis of the standard free formation energy, G_f° . It is obviously of great value if the result can be verified by direct experiment, but measurements of this type are often complicated by the relatively low redox buffer capacity of the system; furthermore, in some cases soluble sulphides are present, which can "poison" the redox electrodes.

The results of redox potential measurements in Swedish water (Stripa and Finnsjö) are reported in this Appendix. The samples were taken from a depth of approximately 400 m and kept in rubber-stoppered flasks in order to prevent contact with oxygen. The sampling technique and the test flasks were developed by Orrje & Co.

D2. MEASUREMENT METHOD

The redox potential is calculated on the basis of the voltage measured in a galvanic cell, where one half-cell consists of the sampling flask with electrode and the other of an external reference electrode. Voltages are measured with respect to the reference electrode. The two half-cells are connected by a salt bridge. The galvanic cell is illustrated in Fig. D1.

A silver electrode in 10 mM AgClO_4 solution is used as a reference electrode. Two different types of redox electrodes were tested—a platinum electrode, which was present in the sampling flask at the time of sampling, and a gold electrode. The gold electrode was a needle-shaped solid gold rod which was pushed through the rubber stopper after sampling. The part of the salt bridge connected to the water sample consisted of a needle-shaped capillary tube, which could also be pushed through the rubber stopper.

FIG. D1. Apparatus for measuring redox potential.

D3. RESULTS

Groundwater from the Stripa area gave a half-cell potential of 225 mV, measured with the platinum electrode, compared to a standard hydrogen-gas electrode. This corresponds to a pH value of 3.8, i.e., within the corrosion range for copper. Other analyses of the same water indicate the presence of Fe(II) and Mn(II) as well as sulphides, probably dissolved. At the pH in question, Fe(II) and Mn(II) cannot occur at the measured redox potential. Thus, there is reason to believe that the measured potential does not represent the redox potential of the system. A possible explanation may be that sulphides present in the system "poison" the platinum electrode.

In a new series of experiments, the platinum electrode was replaced by a gold electrode. Since gold electrodes are said to work much better than platinum electrodes in sulphide-containing solutions (according to Mr. Rennerfeldt of Orrje & Co.), the measured emf values and the calculated half-cell potentials are presented in Table D1.

A stable (± 2 mV) potential was obtained after approximately 30 min. Stability was checked over a 12-hour period.

Two of the measured results deviate significantly from the others. Before the results are discussed, it is necessary to verify that the measured potential is influenced by the oxygen content of the system. This was done by injecting 5 ml air through a syringe into the sample. If all of the oxygen dissolves, the injected quantity corresponds to ~ 3.5 ppm oxygen. The measured results are presented in Table D2.

The experiment shows that the addition of an oxidant increases the measured emf. This indicates that the potential of the gold electrode correctly indicates the system's redox potential.

It is possible that the redox potentials for samples 8 and 14 are different because oxygen entered the system in the course of sampling. These solutions have much lower iron (II) and manganese (II) than the Finnsjö water. The redox buffer capacity is thus low and the water is more sensitive to contamination with oxygen than the water from Finnsjö.

If we disregard these two samples, the average redox potential in deep groundwater from both Stripa and Finnsjö is -0.17 ± 0.04 V. The results lie within the interval -0.25 ± 0.10 V obtained by Brotzén from a thermodynamic model calculation. Approximately the same results are obtained from the Pourbaix diagrams.

TABLE D1. Measured emf values and calculated half-cell potentials (mV) referred to a standard hydrogen-gas electrode for groundwater from Stripa and Finnsjö.

Sample No.	Place	Measured emf	Half-cell potential
7	Stripa	-834	-152
8	Stripa	-713	-31
18	Stripa	-855	-173
19	Finnsjö	-873	-191
21	Stripa	-892	-210
14	Stripa	-707	-26
20	Finnsjö	-839	-157
24	Stripa	-821	-140

TABLE D2. Measured emf values and calculated half-cell potentials (mV) in groundwater from Stripa, Sample 24, before and after oxygenation by the injection of air.

Air injected (ml)	Measured emf	Half-cell potential
0	-821	-140
5	-670	-12
15	-498	-164

D4. CONCLUSION

The results of the measurements show that redox potentials can be determined experimentally in groundwater and that thermodynamic model calculations provide a sufficiently good description of actual systems to serve as a basis for a determination of the properties of the systems.

Appendix E.

Hydrolysis Constants of Actinide Ions

The data available in the literature^{1,2} do not quite satisfy the demand for accurate knowledge about actinide oxidation states and complexes in different groundwater systems. The most recent tables of stability constants are by Sillén and Hogfeldt,³ published in 1971, and by Smith and Martell,⁴ published in 1976. Thorough reviews of metal complex formation with hydrophilic ligands were presented by Baes and Mesmer in 1976⁵ and by Burgess in 1978.⁶ A summary of actinide hydrolysis constants is in Table E1.

An exact description of actinide species in natural waters requires detailed information on water composition (pH, complex formers, redox potential, etc.) as well as equilibrium constants for all actinide complexes which can be formed.¹

Table E2 summarizes techniques used in studying hydrolysis. Some techniques give information only about the structure of the complexes formed (x-ray diffraction, NMR), or its average molecular weight (freezing point, ultracentrifugation, self-diffusion), or average molecular size (conductivity, electromigration). Other techniques (spectrophotometry, Raman fluorescence, ion exchange) "fingerprint" specific species, but these techniques require an additional constant (the relation between the species and measured signal type and strength) which is not always easy to determine. The more "selective" techniques (emf, solvent-extraction, sometimes ion-exchange and polarography) measure the concentration of a metal species — usually only one — in the solution. This selectivity makes them amenable to exact mathematical treatment of the complex-formation reactions, and therefore they are also most widely employed for determination of complexity constants. While emf and polarographic methods require macroscopic amounts of the metal, solvent-extraction and ion-exchange methods do not.

TABLE E1, Part 1. Hydrolysis constants ($L = OH^-$) for trivalent actinides.^a

Metal ion	Equilibrium	Log K 25°C, 0.5	Log K 25°C, 1.0	Log K 25°C, 0	ΔH 25°C, 0	ΔS 25°C, 0
Pu ³⁺	ML/ML	6.7 ^a		7.0		
Am ³⁺	ML/ML	7.9 ^a				
Cm ³⁺	ML/ML	7.9 ^a - 0.1				
Bk ³⁺	ML/ML	8.2 ^a				
Cf ³⁺	ML/ML	8.2 ^a				

^a 25°C, 0.1.

TABLE E1, Part 2. Hydrolysis constants (L = OH⁻) for pentavalent and hexavalent actinides.^a

Metal ion	Equilibrium	Log K	Log K	Log K	ΔH	ΔS
		25°C, 0.5	25°C, 1.0	25°C, 0	25°C, 0	25°C, 0
Pa(V)	ML ₄ /ML ₃ L		13.13 ^a	14.5		
	ML ₅ /ML ₄ L		9.68 ^a	9.5		
UO ₂ ²⁺	ML/ML	8.0 ± 0.0 (7.7) ^d	8.1 ^a	8.2	(-2) ^b	(30) ^c
	M ₂ L/M ² L		9.6			
	M ₂ L ₂ /M ² L ²	21.55 ± 0.02 21.73 ^d	21.64 ± 0.02 22.32 ^a	22.4	16.7 ^a	46 ^a
	M ₃ L ₃ /M ³ L ³		42.4 43.5 ^a			
	M ₃ L ₅ /M ³ L ⁵	52.4 ± 0.1	52.6 ± 0.1 54.4 ^a	54.4	41.1 ^a	111 ^a
	M ₄ L ² /ML ₂ (s)			-22.4		
NpO ₂ ²⁺	ML/ML		8.6	8.9		
	M ₂ L ₂ /M ² L ²		20.9	21.6		
PuO ₂ ²⁺	M ₃ L ₅ /M ³ L ⁵		50.7	52.5		
	ML/ML		7.8 7.9 ^a	8.4		
	M ₂ L ₂ /M ² L ²		19.1 20.1 ^a	19.6		
	M ₃ L ₅ /M ³ L ⁵		46.8 49.2 ^a	48.4		

^a 25°C, 3.0.

^b 25-95°C, 0.5.

^c 25°C, 0.5.

^d 25°C, 0.1.

TABLE E1, Part 3. Hydrolysis constants ($L = OH^-$) for tetravalent actinides.^a

Metal ion	Equilibrium	Log K 25°C, 0.5	Log K 25°C, 1.0	Log K 25°C, 0	ΔH 25°C, 0	ΔS 25°C, 0
Th ⁴⁺	ML/M.L		9.6 9.1 ^{c,d}	10.8	(-8) ^a	(20) ^b
	ML ₂ /M.L ²		19.89	21.1	(-13) ^a	(50) ^b
	M ₂ L ₂ /M ² .L ²		22.97	(21.9)	(-12) ^a	(60) ^b
	M ₂ L ₃ /M ² .L ³		23.58 ^{c,d}			
	M ₂ L ₆ /M ² .L ⁶		33.8 ^{c,d}			
	M ₃ L/M ³ .L		(53.7) ^{c,d}			
	M ₃ L ₃ /M ³ .L ³		(12.7) ^{c,d}			
	M ₃ L ₆ /M ³ .L ⁶		(35.7) ^{c,d}			
	M ₄ L ₈ /M ⁴ .L ⁸		91.2	(90.9)	(-51) ^a	(250) ^b
	M ₆ L ₁₃ /M ⁶ .L ¹⁴		162.1 ^{c,d}			
	M ₆ L ₁₅ /M ⁶ .L ¹⁵		169.8	173.2	(-96) ^a	(470) ^b
	M.L ⁴ /ML ₄ (s)			-44.7 ^e		
Pa ⁴⁺	M.L ⁴ /MO ₂ (s)			49.7		
	ML/M.L		14.04 ^c	14.8		
	ML ₂ /M.L ²		27.64 ^c	28.0		
	ML ₃ /M.L ³		40.7 ^c			
U ⁴⁺	ML ₄ /M.L ⁴		51.4 ^c			
	ML/M.L	12.24	12.23-0.01	13.3	(-2) ^f	(50)
		12.50 ^g				
		12.31 ^h	(12.1) ^c			
Np ⁴⁺	M ₂ L ₁₃ /M ⁶ .L ¹⁵		196.1 ^c	192.8		
	ML ₅ /M.L ⁵			54.0		
	M.L ⁴ /MO ₂ (s)			56.2		
	ML/M.L	11.7 ^h		12.5		
Pu ⁴⁺	ML/M.L	12.14	12.1			
		12.23 ^h				
	M.L ⁴ /ML ₄ (s)			-47.3	(-6) ⁱ	(40) ^b

^a 0-95°C, 1.0 molal.^b 25°C, 1.0.^c 25°C, 3.0.^d NaCl used as background electrolyte.^e 22°C, 0.^f 10-43°C, 0.^g 25°C, 0.1.^h 25°C, 2.0.ⁱ 15-25°C, 2.0.

TABLE E2. Techniques considered for study of actinide hydrolysis.

Technique	Comments
Emf	Metal-sensitive electrodes down to μM concentrations. Accurate determinations of H^+ . High selectivity.
Solvent extraction, radioactive tracers	Often 100% selective (measures only one species). Covers even lowest metal concentrations. Accuracy good.
Spectrophotometry	Requires additional constants (ϵ), clear solutions and macro concentrations. Moderate sensitivity and accuracy. Useful for identifications of valency states.
Ion exchange, radioactive tracers	Like solvent extraction. Demand for additional constants can be circumvented by using several different ion exchangers (laborious!). Surface sorption can be a problem.
Conductivity	Requires additional constants (Λ^0). Limited to zero bulk electrolyte concentration.
Electromigration	Can be used with tracer. Like conductivity, but can be used for any ionic strength and composition.
Freezing point	Inaccurate. Requires macro amounts.
Solubility	Requires macroscopic amounts, but radioactive tracers useful for high sensitivity. Rarely provides stepwise constants.
Ultracentrifugation	Measures only macroscopic polymers.
Raman Fluorescence	Demand for high-power tunable laser. Conclusions from spectrum perturbations. Spectrum not calculable. Claimed to be sensitive down to 10^{-8} M .
X-ray diffraction	Necessary to check if precipitates are amorphous or crystalline. Solid structure not necessarily same as in solution. Diffraction on liquids helpful for specie identification.
NMR	Can provide valuable information on structure of dissolved complexes, but rather high concentrations seem to be required.
Polarography	Possibly useful. Can be used on tracer concentrations (radiopolarography).
Self-diffusion	Gives only average molecular weight. Can be helpful in study of polymeric species.

E1. SOLUBILITY

Actinide solubilities are usually presented as solubility products. For example,

$$[M^{3+}][OH^-]^3 = k_{so}. \quad (E1)$$

If k_{so} and pH are known, $[M^{3+}]$ can be calculated.

The mononuclear hydrolysis reaction proceeds step-wise (leaving out charges):

These step-wise reactions are summarized by

where β is the stability product. Hydrolysis reactions are more commonly written as deprotonation reactions, e.g.,

indicating the acid properties of the metal. Because Reactions (2)-(4) must be taken into account in the pH range where appreciable amounts of the intermediate hydrolysis species MOH and $M(OH)_2$ exist, Eq. (1) cannot be used for calculation of $[M]$ as long as k_1 , k_2 and k_3 are unknown.

The situation is even more complicated. Solubility measurements are usually carried out as concentration measurements of a dissolved fraction of a preformed precipitate. It is hardly believable that adding alkali to an acid Pu^{3+} solution leads to the precipitation of stoichiometric $Pu(OH)_3$ in equilibrium with monomeric $Pu(OH)_3$ species in the solution.⁷ It is most likely that polymeric species are formed in the precipitation reaction. Also, secondary treatment after the precipitation may dehydrate the precipitate (e.g., formation of some Pu_2O_3). Thus, the measured solubility may not reflect the "solubility product" as defined by Eq. (1), although it is commonly interpreted as that (cf. e.g., Ref. 8)

E2. TRIVALENT ACTINIDES

The only stable trivalent actinides in natural waters are Pu(III), Am(III) and Cm(III). The first stepwise constant is given according to Eq. (2): to $\log k_1 = 6.7$ (for Pu), 7.9 (for Am) and 8.9 (for Cm).^{4,9} Although much larger values have been suggested, the values above seem reasonable in comparison with those of the trivalent lanthanides. The tendency of stronger hydrolysis with increasing actinide number (decreasing radius) agrees with what is expected. From these data one calculates that at pH ~ 6 only 10% of Pu(III) is hydrolyzed as $\text{Pu}(\text{OH})^{2+}$. Although no second hydrolysis constant is available, one may estimate that the concentration of higher hydrolyzed Pu(III) species is $\leq 1\%$. However, at pH 8, >90% of Pu(III) is hydrolyzed. At this pH, the solubility product value $k_{sp} = 10^{-19.7}$ indicates that the $\{\text{Pu}^{3+}\} \sim 10^{-2}\text{M}$; the value refers to a fresh precipitate.⁹ In comparison with the lanthanides ($\text{Nd } 10^{-23}$), the solubility product seems to be too high.

In summary, in natural water Pu(III) is largely hydrolyzed; at the low concentrations expected in water effluents from a waste repository, the solubility product of the hydroxide is not exceeded. However, at these pH levels the trivalent actinides strongly sorb on any surface. Though the actinide may not precipitate out, it may sorb out.

Polynuclear hydrolysis products have been observed for a number of trivalent ions (Bi^{3+} , In^{3+} , Sc^{3+} , Ce^{3+} , Ti^{3+} , etc.), which have many similarities to the trivalent actinides.^{10,11} It is thus highly probable that such species also are formed at macro-concentrations of Pu(III). Such concentrations will hardly be reached through leaching of spent fuel elements or of high-active waste glass.

E3. TETRAVALENT ACTINIDES

Table E3 summarizes values for the first hydrolysis step ($-\log \beta_1^*$). The first column shows the range in reported equilibrium constants (a factor of 400 for Th^{4+}). The second column shows recommended "critical" constants. Taking an approximate value of $\log \beta_1^* = 2$ (or $k_1 = 10^{13}$), one finds that in 1 M acid $[\text{MOH}] \ll [\text{M}]$, while at pH 2 $[\text{MOH}] \approx [\text{M}]$.

Polymeric species are formed at higher pH (lower acidities). According to Costanzo et al.¹² ~ 1% of $\text{Pu}(\text{IV})$ is polymeric at pH 1 for $[\text{Pu}]_{\text{tot}} = 0.01$ M, while Ockenden et al.¹³ claimed that ~50% is polymeric at the same conditions. Many different species have been suggested—e.g., $\text{Th}_2(\text{OH})_2$, $\text{Th}_3(\text{OH})_8$, $\text{Th}_6(\text{OH})_{15}$. Hietanen¹⁴ explained the $\text{Th}(\text{IV})$ and $\text{U}(\text{IV})$ hydrolysis according to the core-and-links hypotheses,¹⁵ covering a metal concentration range of 0.0005 to 0.035 M and pH range of 1 to 4.

Using this model and data for $\text{U}(\text{IV})$ one finds that at $[\text{U}] \leq 0.1$ M polymerization is negligible at pH 0, while polymerization exceeds 50% at pH 1. For $[\text{U}] \leq 0.01$ M, polymerization can be neglected at pH 1 but dominates at pH 2. Assuming that $\text{Pu}(\text{IV})$ hydrolyzes somewhat more easily than $\text{U}(\text{IV})$, one can conclude that in 0.01 M solutions of $\text{Pu}(\text{IV})$ considerable polymerization occurs even at pH 1 (cf. Refs. 12 and 13). Using the same relation and argument, one arrives at the conclusion that $\text{Pu}(\text{IV})$ may be highly polymerized in neutral solutions even at concentrations as low as 10^{-10} M.

Bell et al.¹⁶ have shown that the rate of polymerization increases with $[\text{Pu}(\text{IV})]$ concentration (first power) and decreases with acidity (second power). Since "polymerization equilibrium" is reached in an hour in $0.04 \text{ M } 1.1 \times 10^{-3} \text{ O}_2$ for 0.01 M $\text{Pu}(\text{IV})$, polymerization will be very rapid at pH ~ 7 even at Pu concentrations as low as 10^{-10} M. The obvious conclusion is that $\text{Pu}(\text{IV})$ in natural waters always is polymerized. However, rather improbable that such polymers will freely migrate in the water, they will sorb on particulate impurities ("radiocolloids") and other solid matter.

Solubility products for $\text{M}(\text{OH})_4$ are uncertain, and measurements seem only to have been made on Th and Pu, giving a range of 10^{-11} – 10^{-12} for Th, and 10^{-47} – 10^{-50} for Pu. Kraus⁹ estimated the following values: $\text{Th}(\text{IV})$ 10^{-30} , $\text{U}(\text{IV})$ 10^{-45} , $\text{Pu}(\text{IV})$ 10^{-52} , and $\text{Am}(\text{IV})$ 10^{-50} . The solid phases given either as $\text{M}(\text{OH})_4$ or MO_2 , indicating the uncertain experimental conditions discussed in Section 1. Smith and Martell¹⁷ recommend the values

$$\frac{[\text{Th}^{4+}][\text{OH}^{-}]^4}{[\text{Th}(\text{OH})_4]} = 10^{-41.7}$$

$$\frac{[\text{Th}^{4+}][\text{OH}^{-}]^4}{[\text{ThO}_2]} = 10^{-19.7}$$

If one assumes K_{sp} for $\text{Pu}(\text{IV})$ to be 10^{-50} , one finds that at pH > 4 $[\text{Pu}] < 10^{-26}$. The latter value has hardly any analytical meaning, because it implies that there would be less than one $\text{Pu}(\text{OH})_4$ molecule in one liter of solution. The value 10^{-15} has been used in the main text. However, the analysis by Allard (see Section 10.2 of the main text) indicates a larger range of stability for the pentavalent states of U, Np and Pu under groundwater conditions.

TABLE E3. Equilibrium constants of tetravalent actinides.

Actinide	$-\log \beta_1^*$	
	Range	Critical
Th^{4+}	2.4–5.0 ^a	4.4 ^b
Pa^{4+}	0.1	0.0
U^{4+}	0.7–2.0	1.8
Np^{4+}	2.3	2.0
Pu^{4+}	1.3–1.7	1.9

^a From Ref. 6.

^b From Ref. 4.

E4. PENTAVALENT ACTINIDES

No aqueous M^{5+} species are known; all aqueous pentavalent actinide ions are -yl ions: PaO^{3+} and/or PaO_2^+ (Refs. 17, 18), NpO_2^+ , and PuO_2^+ . The latter is not very stable and disproportionates into other valency states.

The most stable neptunium ion is NpO_2^+ . The first hydrolysis constant, β_1' , is $10^{-5.4}$; thus, 50% of Np(V) is hydrolyzed at pH 5.4.

E5. HEXAVALENT ACTINIDES

Hexavalent actinides appear as MO_2^{2+} ions in acidic solutions. The first mononuclear hydrolysis constant, $\log k_1$, is 8.1 for uranium, 8.6 for neptunium and 7.8 for plutonium.⁴ The value of $\log k_1$ for uranium indicates that 50% of U(VI) is hydrolyzed at pH 5.9. Smith and Martell⁴ also give constants for the formation of polymeric $(\text{MO}_2)_2(\text{OH})_2$, $(\text{MO}_2)_3(\text{OH})_4$, and $(\text{MO}_2)_3(\text{OH})_5$ species; for the latter $\log k_{35}$ is 53, 51 and 47, respectively. From $\log k_{35}$ for uranium one finds that in a 10^{-6} M solution at pH 7, >50% of U(VI) is in the form of $(\text{UO}_2)_3(\text{OH})_5$, while at pH 8 polymerization can be neglected for {U(VI)} only at $<10^{-8}$ M.

Ahrland et al.¹⁹ suggest the core-and-link hypothesis for U(VI) polymerization in acid solutions. Their parameter values indicate that no complexes higher than tetramers have to be considered in the concentration range {U(VI)} 1-100 mM up to pH 5. At pH 7 polymerization dominates for {U(VI)} $> 2 \times 10^{-6}$ M, while at pH 8 polymerization dominates at {U(VI)} $> 5 \times 10^{-8}$ M. Since uranium concentrations in natural waters often are in the 10^{-8} M range, natural uranium may be partly polymeric (neglecting the formation of other hydrophylic complexes).

Schedin²⁰ has shown that the PuO_2^{2+} ion behaves very like the UO_2^{2+} ion.

Of the hexavalent actinide hydroxides, a solubility product has been reported²¹ only for $\text{UO}_2(\text{OH})_2$ — $K_{so} = 10^{-22.4}$. Neglecting polymerization, this value shows that at pH 7 {U(VI)} $\leq 4 \times 10^{-6}$; at higher pH the uranium concentration must be even less. When U(VI) appears in higher concentration in natural waters it is probably in colloid form or complexed with hydrophilic ligands (primarily CO_3^{2-}).

In order to estimate the hydrolysis conditions for Np(VI) and Pu(VI), since we lack experimental data, it is reasonable to assume that their equilibrium values are the same as those for U(VI).

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Appendix F. Some Data for the KBS Waste-Handling Concept

TABLE F1. Some data for the storage of high-level waste (HLW) and spent uranium fuel (SUF) as suggested by KBS.

Property	Storage of HLW	Storage of SUF
Reprocessing	By vitrification	Not reprocessed
Equivalent waste amount ^a	From 1 tonne SUF ^b	1.3 tonne SUF
Central part composition	420 kg borosilicate glass with 9% FP ^c	550 fuel pins + lead in voids
Central part weight	450 kg, incl. 3 mm stainless steel cladding	2 tonne fuel + 2.5 tonne lead
Outer canning	100 mm lead + 6 mm titanium	200 mm copper
Total canister:		
Dimensions	0.6 × 1.8 m	0.8 × 4.7 m
Weight	3.9 tonne	20 tonne
Canister surface temp:		
Max ^d	65 °C	77 °C
After 1000 y	35 °C	50 °C
Depth of bentonite backfill (outer barrier)	0.2 m	0.4 m
Dimensions of rack hole	1.0 × 5.0 m	1.5 × 7.7 m

^aAt 33,000 MWd/tonne U burn-up.

^b38 kg fission products (FP), + 3 kg U, + 0.05 kg Pu, + 1 kg other transuranium elements.

^cGlass of this composition will be returned to Sweden after reprocessing at the French site at La Hague.

^dMaximum temperature reached about 15 years after fuel discharge from the reactor.

TABLE F2. Important properties of French borosilicate glass obtained in the vitrification of high-level waste.

Property	Value
Leaching rate at 25 °C	$2 \cdot 10^{-7}$ g per cm ² per day
Factor for increase of leaching rate at 70 °C	10 times
Transformation point (temperature below which crystallization does not take place)	550 °C
Increase of leaching rate if crystallization occurs	50%
Density	$2 \cdot 10^3$ g per cm ³
Thermal conductivity	1.2 W per meter per degree Celsius

TABLE F3. The chemical composition of French waste glass from light-water reactors (wt%).

SiO ₂	54.9	Actinide oxides (total) ^a	1.1
Na ₂ O	11.7	Fission products (total) ^b	9.0
B ₂ O ₃	20.0		
Al ₂ O ₃	2.2		
NiO + Fe ₂ O ₃	1.1 ^c		

^aSee Table F4.

^bSee Table F5.

^cFrom structural components of the fuel bundles.

TABLE F4. Typical composition of the actinide oxides (wt%).

UO ₂	0.8
NpO ₂	0.19
PuO ₂	0.0074 ^a
Am ₂ O ₃	0.14
Cm ₂ O ₃	0.003
Total	1.1

^aCOGEMA calculates that 0.15% of the plutonium in spent fuel is retained in the waste glass at La Hague, which corresponds to a level of 0.0074% PuO₂. The safety analysis, however, has assumed a PuO₂ level in the glass which corresponds to 0.5% of the level in the spent fuel.

TABLE F5. Typical^a contents of the most important fission products (wt%).

MoO ₃	1.63	Pr ₂ O ₃	0.40
Nd ₂ O ₃	1.21	PdO	0.40
ZrO ₂	1.15	Rb ₂ O	0.27
CeO ₂	0.66	Ti ₂ O ₃	0.27
RuO ₂	0.61	Sm ₂ O ₃ + Eu ₂ O ₃	0.27
BaO	0.55	Y ₂ O ₃	0.18
Cs ₂ O	0.54	Rh ₂ O ₃	0.18
Gd ₂ O ₃	0.54	SrO	0.14
Total			9.0

^aThe distribution of the fission products varies with the degree of burnup of the spent fuel and the time after discharge.

Note: Dimensions are in mm

Note: Dimensions are in mm

FIG. F1. KBS concepts for storage in the ground of high-level waste (HLW), a, and spent uranium fuel (SUF), b.

H 4·10 ⁻⁵ 0.39																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P / / / /	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr / / / /	Mn	Fe / / / /	Co	Ni / / / /	Cu	Zn	Ga	Ge 4·10 ⁻⁴ 0.007	As 8·10 ⁻⁵ 0.005	Se 0.05 4·10 ⁻⁴	Br 0.015 0	Kr 0.36 5.8
Rb 0.35 2·10 ⁻⁸	Sr 0.78 60	Y 0.47	Zr 3.78 2·10 ⁻³	Nb 4·10 ⁻⁶	Mo 3.47 0	Tc 0.84 0.014	Ru 2.15 0.42	Rh 0.39	Pd 1.16 1·10 ⁻⁴	Ag 0.06 1·10 ⁻⁵	Cd 0.08 3·10 ⁻⁵	In 0.001 0	Sn 0.059 5·10 ⁻⁴	Sb 0.011 0.61	Te 0.56	I 0.27 4·10 ⁻⁵	Xe 5.46 0
Cs 2.31 92	Ba 1.81 85		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra																

La 1.27 0	Ce 2.48 0.10	Pr 1.2	Nd 4.1 0	Pm 0.007 7.0	Sm 0.86 1.1	Eu 0.16 4.4	Gd 0.12 1·10 ⁻⁴	Tb 0.002	Dy 0.001 0	Ho 7·10 ⁻⁸	Er	Tm	Yb	
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Ac	Th 0.0003	Pa 0.0003	U 955 0.0036	Np 0.48 0.018	Pu 10.4 86	Am 0.14 0.16	Cm 0.023 1.7	Bk	Cf	Es	Fm	Md	No	Lw
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FIG. F2. Composition of 1 tonne spent uranium fuel, originally enriched to 3.3% in ²³⁵U, after 33 000 MWd/tonne U burn-up at a flux of $3 \cdot 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ (30 MW/tonne U) at a cooling time of 10 yr. The upper numbers are weight in kg, and the lower numbers are the radioactivity in kCi. Total weight is 35 kg fission products (FP) and 11 kg transuranium (TU) elements. Total radioactivity is 312 kCi from the FP and 2.35 kCi from the TU elements. Thermal power is 1.02 kW from the FP and 0.070 kW from the actinides. Most common corrosion products in HAW are shaded. P is a radiolysis product. Arrows indicate mother-daughter relations.