

**SKBF**  
**KBS**

**TEKNISK**  
**RAPPORT**

**79-26**

**Leakage of Niobium-94 from an  
Underground Rock Repository**

K Andersson  
B Torstenfelt  
J Rydberg

Department of Nuclear Chemistry  
Chalmers University of Technology, 1979-11-05

**SVENSK KÄRNBRÄNSLEFÖRSÖRJNING AB / PROJEKT KÄRNBRÄNSLESÄKERHET**

*POSTADRESS: Kärnbränslesäkerhet, Box 5864, 102 48 Stockholm, Telefon 08-67 95 40*

LEAKAGE OF NIOBIUM-94 FROM AN UNDERGROUND  
ROCK REPOSITORY

K Andersson  
B Torstenfelt  
J Rydberg

Department of Nuclear Chemistry  
Chalmers University of Technology  
Göteborg, 1979-11-05

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

A list of other reports published in this series is attached at the end of this report. Information on KBS technical reports No. 1 - 120 in an earlier series is available through SKBF/KBS.

## Contents

	page
1. Summary	1
2. Background	2
3. Design of a Repository	2
4. Chemical Conditions in a Repository	3
4.1. Ground water	3
4.2. Concrete	3
5. The Chemistry of Niobium	4
5.1. Corrosion	4
5.2. Equilibria	5
6. Transport of Niobium Through a Buffer Material	5
6.1. Calculations	5
6.2. Results	7
7. Retention of Niobium in the Rock	8
7.1. Experiments	9
7.2. Results	9
7.3. Expected Retention	11
8. Discussion and Conclusions	12

### References

### Figures:

- Fig. 1 pH-potential diagram
- Fig. 2 Column experiment

### Appendices:

- Appendix 1 Composition of some Swedish groundwaters
- 2 Corrosion of niobium
- 3 Equilibrium constants
- 4 Short study on the chemistry of niobium in groundwater
- 5 Synthetic groundwater

## 1. Summary

Metal parts, that have been activated in a nuclear reactor, are planned to be stored in tunnels at great depth in granitic rock. This metal waste containing the long-lived isotopes  $^{59}\text{Ni}$  and  $^{94}\text{Nb}$ , will be placed in concrete blocks, surrounded by a bentonite/quartz mixture.

If the metal is exposed to groundwater, it may corrode, with a possibility of release of these nuclides to the groundwater. The release of niobium is discussed here; nickel has been treated in an earlier report (7).

Niobium is added in small amounts ( $\sim 1\%$ ) to alloys where the main component is nickel. Since niobium corrodes at high pH ( $>13$ ) and nickel at low pH ( $\leq 6$ ), a simultaneous corrosion is unlikely. (The pH in the repository is held at a high level  $>10$  by the concrete for a long period of time,  $>10^5$  years).

If the niobium corrodes, the solubility of the components formed in the prevailing pH range is low. Therefore a transport of niobium away from the repository would be slow even if an instantaneous dissolution is assumed. The release of niobium to the groundwater would be low (about 1 mg/year from a 300 m long tunnel).

In contact with the rock, niobium velocity will be reduced by at least a factor 1000 in comparison with the groundwater velocity due to the sorption on rock surfaces.

Experiments have given approximate distribution coefficients ( $K_d$ -values) for niobium-granite ranging from 0.1 to  $10 \text{ m}^3/\text{kg}$ .

## 2. Background

Beside spent fuel, metal waste of low and medium activity will be obtained from nuclear reactors. This metal waste with neutron induced activity has to be stored until the activity has decayed. The metal will be stored in concrete cubes. The dose rate from these cubes will be of the same order of magnitude as that from concrete blocks containing spent ion-exchange resin from purification of reactor cooling water.

The radioactive isotopes from the metal remaining after one thousand years of storage and therefore liable to be spread into the geosphere include  $^{14}\text{C}$ ,  $^{59}\text{Ni}$ ,  $^{63}\text{Ni}$ ,  $^{93}\text{Zr}/^{93\text{m}}\text{Nb}$  and  $^{94}\text{Nb}$  (6).

Among these the nuclides with the longest half-lives are  $^{59}\text{Ni}$  ( $7.5 \cdot 10^4$  y) and  $^{94}\text{Nb}$  ( $2 \cdot 10^4$  y). The possibilities of nickel leakage from the repository has been investigated by Neretnieks and Andersson (7).

The purpose of this investigation is to evaluate the possibilities of dissolution and leakage of niobium into the groundwater.

## 3. Design of a Repository

The metal parts will be moulded in concrete cubes with 1.6 m sides and piled in two layers of three horizontal rows in a tunnel of 300 m length. The tunnel will be located at a large depth in plutonic rock and is 8.5 m high and 9 m wide. Around the cubes a mixture of bentonite and quartz sand will be placed. The bentonite/quartz mixture might be replaced by concrete.

The tunnel is planned to be located in a bedrock with extremely low groundwater flow. A maximum flow of  $0.2 \text{ l/m}^2$ , year, is expected. The permeability of the bentonite/quartz mixture is much lower than that of the rock. This means that no water will flow through an undamaged repository.

Maximum water flow through the repository occurs if there is no flow resistance in the repository i.e. if the bentonite/quartz

has disappeared and if the flow direction of the groundwater is perpendicular to the tunnel. In that case all water from an area twice as big as the projection of the tunnel would pass through it. This is equal to an area of  $5100 \text{ m}^2$  or a water flow of 1020 l/year through the repository.

#### 4. Chemical Conditions in a Repository

##### 4.1 Groundwater

The composition of groundwater in plutonic rock at a depth of 500 m has been determined at several locations in Sweden (8). Data are given in Appendix 1. The redox potential in this type of water has been theoretically calculated to be  $(-0.15) - (-0.27) \text{ V}$ . Measurements have given values in the range  $(-0.15) - (-0.21) \text{ V}$  according to Allard et al. (13).

The data in Appendix 1 on the groundwater composition has been used in the following analysis of mass transport from the repository.

##### 4.2. Concrete

The concrete will influence the chemical environment in the repository due to its partial dissolution in the groundwater (9). The parameters most strongly affected are pH and the concentration of calcium.

Primarily, as water penetrates the concrete, the pH of the water will rise to 13-14, due to the dissolution of NaOH and KOH. Thereafter, the pH will decrease to about 12,6 when free calciumhydroxide is dissolved. This state will prevail for at least several hundred years (7). During this period the concentration of calcium is about 0.02 M. Then pH decreases and remains around 10 during at least  $10^5$  years, when the calcium concentration in the water is 0.002 M. After this only the ballast will remain in the concrete. Calcium concentration and pH will then attain the values of the surrounding groundwater (9).

## 5. The Chemistry of Niobium (cf Appendix 4)

Niobium is a metal in the vanadium group (V, Nb, Ta). In nature, niobium is associated with tantalum and other metals in oxidic minerals as columbite-tantalite  $(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6$ , pyrochlore  $((\text{Na, Ca})\text{Nb}_2\text{O}_6\text{F})$  and euxenite  $((\text{Y, Ca, Ce, U, Th})(\text{Nb, Ta, Ti})_2\text{O}_6)$ .

The natural occurring niobium is 100%  $^{93}\text{Nb}$ .

Niobium is used in alloys such as Inconel, because it prevents inter-crystalline corrosion and enhances strength at high temperatures (1).

Because of its small neutron capture cross section (1 b) it is used in nuclear reactor technology (1).

### 5.1 Corrosion

Niobium is oxidized by air at temperatures above  $350^\circ\text{C}$ . In water vapour oxidization starts at  $250^\circ\text{C}$ . A protective layer of niobium oxide inhibits further oxidization. As metallic niobium is very reactive it must be protected by an inert atmosphere or vacuum when being processed at higher temperatures (1).

The metal resists most mineral acids at ambient temperature, but is dissolved in HF and warm, concentrated mineral acids. The hydrogen gas evolved at acid attack embrittles the metal (1). Most liquid metals do not react with metallic niobium. Inorganic salts and compounds not containing fluorine or strong complex forming agents do not attack the metal at pH below 10. Corrosion is however caused by alkali metal hydroxides and carbonates (4).

In the table in Appendix 2 it is shown that NaOH-solutions at ambient temperature are corrosive (3). The pH-potential diagram in Fig. 1 (11) shows that niobium is passive under the conditions expected. At the high pH-values that will occur in the repository during the first centuries corrosion might give  $\text{NbO}_4^{3-}$  ions.

## 5.2 Equilibria

Equilibrium data for niobium compounds are sparse in the literature.

The most common oxidation state of niobium is +5, but also +4, +3, +2, +1, 0 and -1 are observed (1). In groundwater probably only the valences +3 and +5 would occur.

Equilibrium data of some fluorides and solubility products of a number of metal niobates are listed in Appendix 3 (10).

If niobates are formed in the repository the total solubility will be limited by the calcium niobate, which has a very low solubility. As large quantities of calcium are available, due to the concrete dissolution, the maximum niobium concentration in solution will be about 10  $\mu\text{g/l}$ .

The low solubility of niobium makes experimental work difficult since the concentration has to be low to avoid precipitation. In experimental work the water-soluble oxalate- or tartrate complexes are used. The oxalate is precipitated in alkaline solutions, while the tartrate is unstable for these long periods of time (2).

In alkaline water solutions large complexes with molecular weights of 1000 g/mol can be formed (2).

Niobium fluorides are prepared by high temperature reactions or by reaction with bromine trifluoride or hydrofluoric acid (2).

## 6. Transport of Niobium Through a Buffer Material

### 6.1 Calculations

The mass-transfer from a repository containing spent metal has been calculated for  $^{94}\text{Nb}$  in a similar way as for  $^{59}\text{Ni}$  (7). Calculations have been performed for an intact backfill barrier



as well as for a repository with free water flow.

In both cases an instantaneous dissolution of niobium is assumed. This is probably a very conservative assumption since niobium is present in low concentration in the metal alloys. The matrix of these alloys consists of nickel, which is stable at pH >6 (11).

The parameters needed to convert the results of the mass-transfer calculation for nickel to niobium are the concentration gradient, determined by the solubility of niobium and the diffusion coefficient of niobate ions in concrete and clay.

The total solubility of niobium has been assumed to be equal to the solubility of the calcium niobate (i.e. 10 µg/l, see 5.2).

The diffusion coefficient of niobate ions in both concrete and clay has been assumed to be  $10^{-9} \text{ m}^2/\text{s}$ , i.e. the same value as was used for nickel (7). This choice was made with reference to measurements of  $\text{Sr}^{2+}$ -diffusion in compacted bentonite (6), where the diffusion coefficient was found to be  $10^{-11} \text{ m}^2/\text{s}$ . The diffusion coefficient of ions in concrete is usually  $10^{-12} - 10^{-14} \text{ m}^2/\text{s}$  (14). The diffusion coefficient of large molecules ( $M = 24\ 000 \text{ g/mol}$ ) was found to be  $< 3 \cdot 10^{-14} \text{ m}^2/\text{s}$  (6).

If niobate ions would polymerize, which is possible according to Fairbrother (2), the diffusion coefficients in clay and concrete will probably be less than  $10^{-14} \text{ m}^2/\text{s}$ .

The mass transfer rate has been calculated for different groundwater fluxes, fissure sizes and distances in the rock: see Table 1. These values are the same as those for nickel (7).

## 6.2 Results

The results of the calculations are shown in table 1-4.

Table 1. Mass transport through buffer.

Case	$u_o$ [m/y]	S [m]	B [mm]	Res 1 (concrete)	Res 2 (clay)	Res 3 ("film")	N/L [g/m,y]
1	$1 \cdot 10^{-3}$	1	0.1	1	31	239	$8.4 \cdot 10^{-6}$
2	$1 \cdot 10^{-3}$	0.4	0.2	1	26	107	$17.0 \cdot 10^{-6}$
3	$0.2 \cdot 10^{-3}$	1	0.1	1	31	534	$4.0 \cdot 10^{-6}$
4	$0.2 \cdot 10^{-3}$	0.4	0.2	1	26	239	$8.6 \cdot 10^{-6}$

$u_o$  = water flux in rock [ $m^3/m^2, y$ ]

S = distance between cracks [m]

B = width of cracks [mm]

Res = Relative transport resistance (from (7))

N/L = transport rate per m tunnel [g/m,y]

The transport rate has been calculated for four different cases, as shown in Table 1. The main mass transfer resistance is the film resistance.

Table 2. Flow of niobium from repository.

Case	N [g/y]	t [y]
1	$2.5 \cdot 10^{-3}$	$800 \cdot 10^6$
2	$5.1 \cdot 10^{-3}$	$400 \cdot 10^6$
3	$1.2 \cdot 10^{-3}$	$1700 \cdot 10^6$
4	$2.6 \cdot 10^{-3}$	$800 \cdot 10^6$

N = flow of niobium [g/y]

t = time for all niobium in repository (= 2 ton) to reach the groundwater at a flux of N.

It takes at least 400 millions of years to transfer all niobium to the groundwater: see Table 2. The most probable case considering the properties of the rock, case 3, leads to a transport time of 1700 millions of years and a flux out of the repository of 1,2 mg/y.

Table 3. Flow of niobium in repository without concrete and clay.

Case	Solubility 0,01 mg/l		Solubility 50 mg/l	
	N [g/y]	t[y]	N [g /y]	t[y]
1, 2	51 10 <sup>-3</sup>	41 10 <sup>6</sup>	255	7.8 10 <sup>3</sup>
3, 4	10 10 <sup>-3</sup>	196 10 <sup>6</sup>	50	40 10 <sup>3</sup>

Table 3 shows the hypothetical case when the concrete and clay has disappeared from the repository. This case gives the maximum amount of water that can get in contact with the dissolving metal. The amount of niobium transferred into the water is here dictated by the limited solubility of niobium. With the most probable solubility (0.01 mg/l) and assuming saturation of all water that can pass through the repository a release of 10 mg Nb/year and a time of dissolution of 200 million years (in a bedrock with 5 times higher water flux than the expected 0.2 l/m<sup>2</sup>, year the corresponding release rate will be 50 mg/year).

If the solubility of niobium in the groundwater is 5000 times higher than expected, i.e. the solubility is determined by the formation of sodium niobate instead of calcium niobate, a flow of niobium of 50 g/year (or with higher water flux, 250 g/y) would be possible.

### 7. Retention of Niobium in the Rock

The retention of a nuclide in rock is given by the retention factor R:

$$R = u_{aq} / u_{nucl} = 1 + K_d \rho(1-\epsilon) / \epsilon = 1 + K_a a(1-\epsilon) / \epsilon$$

where  $u_{aq}$  = water velocity [m/s],  $u_{nucl}$  = velocity of nuclide [m/s],  $K_d$  = distribution coefficient = (conc. in rock)/(conc. in water), [m<sup>3</sup>/kg],  $\rho$  = density of rock [kg/m<sup>3</sup>],  $\xi$  = porosity of rock,  $K_a$  = surface related distribution coefficient [m<sup>3</sup>/m<sup>2</sup>],  $a$  = specific surface [m<sup>2</sup>/m<sup>3</sup>].

The retention factor can be determined by  $K_d$ -measurements in batch experiments.  $K_d$  can also be determined in column experiments, where water flows through a column filled with crushed rock.

### 7.1 Experiments

Both batch and column experiments have been performed with niobium. In both cases a synthetic groundwater with composition according to Appendix 5 has been used. The batch experiments were performed under oxic conditions at pH 8 and 10.5 and under reducing conditions at pH 8. Granites from the Stripa mine and the Finnsjö area have been investigated. A column experiment under oxic conditions at pH 8 has been performed with granite from Stripa.

The niobium isotope best suited for these experiments is <sup>95</sup>Nb ( $t_{1/2}$  = 35 d). This isotope is difficult to obtain free from the mother nuclide <sup>95</sup>Zr. In the experiments a mixture of <sup>95</sup>Zr and <sup>95</sup>Nb has been used. The nuclides are easy to distinguish and measure separately by  $\gamma$ -spectroscopy. The Zr-concentration was lower than the Nb-concentration. The isotopes were in the form of oxalate complexes.

### 7.2 Results

The results from the batch experiments are shown in Table 4.

Table 4. Batch experiments.

Rock	Conditions	pH	$K_d$ m <sup>3</sup> /kg	
			Cont. time	
			6 d	20 h
Stripa	Oxic <sup>1)</sup>	8.0	10	
"	"	10.5	0.1	
Finnsjö	"	8.0	4	
"	"	10.5	0.1	
Stripa	Reducing <sup>2)</sup>	8.0		1.2

1) Aerated solution

2) Addition of Fe(II) <5ppm

Addition of a complex forming agent such as fluoride (in concentration comparable to that found in natural groundwater) does not affect the  $K_d$ -value.

The column experiment was performed at a water velocity corresponding to 3 mm/min in the column. The experiment lasted 29 h, which corresponds to a flow of 74 column volumes of water. A very small amount of the niobium pulse (~0.2%) passed through the column without retention (possibly as oxalate complex). During the rest of the experiment no niobium could be detected in the water. After the experiment, the activity distribution along the column length was measured in intervals of 0.5 cm. (The column was moved inside a lead block with a 5 mm slit). The result of this measurement is shown in Fig. 2.

The main part of the niobium (and zirconium) is retained in the upper part of the column: see Fig. 2. The transport in the column corresponds to a  $K_d$ -value of  $0.08 \text{ m}^3/\text{kg}$  or  $K_a = 6.3 \cdot 10^{-3} \text{ m}$ .

### 7.3 Expected retention

From the measured  $K_d$ -values the expected velocity of the nuclide in a fissured rock matrix can be calculated. Results for the highest and lowest  $K_d$ 's obtained are seen in Table 5.

The retention factor R is given by:  $R = 1 + \frac{K_a}{\xi}(1 - \xi)$ , where  $\xi$  = porosity of rock (here  $10^{-5}$ ).

Table 5. Retention in Rock.

Measurement type	$K_d$ ( $\text{m}^3/\text{kg}$ )	$K_a^x$ ( $\text{m}^3/\text{m}^2$ )	R	$u_n$ (m/y)	$t_{1 \text{ km}}$ (y)
Batch (low)	0.10	$2.4 \cdot 10^{-3}$	480	$6.3 \cdot 10^{-2}$	$16 \cdot 10^3$
-'' (high)	10	0.24	47 000	$6.4 \cdot 10^{-4}$	$1 600 \cdot 10^3$
Column	0.08	$6.3 \cdot 10^{-3}$	1 260	$2.4 \cdot 10^{-2}$	$42 \cdot 10^3$

R = retention factor

$u_n$  = nuclide velocity

$t_{1 \text{ km}}$  = time to transport nuclide 1 km

$x$  = different particle size in batch and column experiments

All values refers to the fissure width 0.01 mm, the fissure spacing 1 m, permeability  $10^{-9} \text{ m/s}$ , and fissure area  $2 \text{ m}^2/\text{m}^3$  rock.

As seen in the table, it takes at least one half-life to transport dissolved niobium 1 km through the rock. With the highest  $K_d$ 's measurement it takes about 100 half-lives.

## 8. Discussion and Conclusions

For the corrosion of niobium a high pH is necessary. These conditions can be expected during the first centuries of the storage, due to the dissolution of concrete.

Niobium, however, constitutes a very small fraction of the metal in these alloys (about 1 % in Inconel, which contains 70-80 % nickel). Thus, to dissolve the niobium, the surrounding metal matrix has to corrode as well. Nickel is passive at  $\text{pH} > 6$  (11), i.e. nickel corrosion will not occur simultaneously with niobium corrosion. If, despite this, niobium is dissolved from the metal matrix, its solubility is very low in the repository where no agents capable of forming soluble complexes with niobium are likely to occur.

Thus the concrete leads to corrosion of niobium due to high pH. It also causes low solubility of the dissolved niobium, due to high calcium concentration. The low solubility leads to a very low flow of niobium from the repository. If no resistance to corrosion due to low solubility of the nickel matrix occurs, the flow will be only 1-5 mg/y. The release of all niobium from a repository would in this case take 400 - 1 700 million years.

In the conservative case, where no concrete or clay remains in the repository and groundwater flows freely through it, the transport will take at least 40 million years. Under these conditions and if the solubility of the Na-niobate (50 mg/l in the groundwater) is assumed to determine the maximum Nb-concentration the transport time will be 8 000 - 40 000 years. with a flow of 50 - 250 g/y.

If complexes with high molecular weight are formed the diffusion coefficient of niobium in bentonite would probably be higher than the value used in the present calculations ( $10^{-9} \text{ m}^2/\text{s}$ ). Thus, transport time out of the repository will probably be much longer.

Retention of niobium in rock is considerable, as shown in the column experiment. Due to experimental factors any deduction of accurate retention factors seem to be doubtful. However, a value of 1 000 seems to be a conservative estimate.

The high retention of niobium is also observed at Oklo (12).

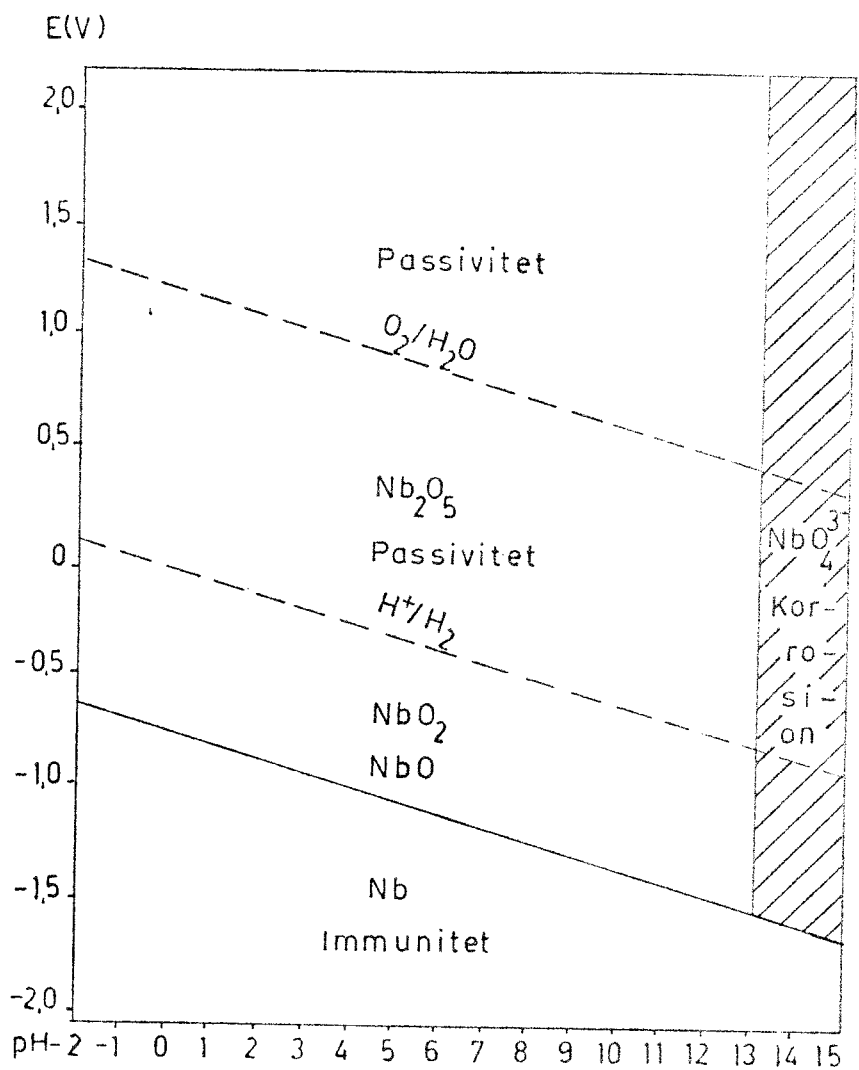


## References

1. Bailar C (ed), Comprehensive Inorganic Chemistry, Pergamon Press, London 1973.
2. Fairbrother F, The Chemistry of Niobium and Tantalum, Elsevier Publishing Company, Amsterdam 1967.
3. Hampel C A (ed), The Rare Metals Handbook, 2nd ed., Reinhold Publishing Chapman and Hall, London 1961.
4. Kirk-Othmer, Encyclopedia of Chemical Engineering, 2nd ed.
5. Lönnerberg B, Konstruktionsdetaljer, direktdeponering, (Construction Details, Deposition of Unreprocessed Fuel), KBS-TR-39, Kärnbränslesäkerhet, Stockholm 1977 (in Swedish).
6. Neretnieks I, Skagius C, Diffusivitetmätningar i våt lera Na-lignosulfonat,  $\text{Sr}^{2+}$ ,  $\text{Cs}^+$ . (Diffusivity Measurements in Wet Clay Na-lignosulfonate,  $\text{Sr}^{2+}$ ,  $\text{Cs}^+$ ) KBS-TR-87, Kärnbränslesäkerhet, Stockholm 1978.
7. Neretnieks I, Andersson K, Utläckning av Ni-59 från ett bergförvar (Leakage of Ni-59 from an Underground Rock Repository) KBS-TR-101. Kärnbränslesäkerhet, Stockholm 1978 (in Swedish).
8. Rennerfelt J, Jacks G, Sannolik sammansättning av grundvatten i urberg på större djup, (Probable Composition of Groundwater in Plutonic Rock at large Depths), Teknisk rapport 90, underbilaga A1, 1978 (in Swedish).
9. Rombén L, Tuutti K, Slutförvaring av aktiverade ståldetaljer (Final Storage of Activated Steel Details) KBS-TR-119, Kärnbränslesäkerhet, Stockholm 1978 (in Swedish).
10. Sillén L G, Martell A E, Stability Constants of Metal-ion Complexes, The Chemical Society, London 1964 and Högfeldt E, Martell A E, Stability Constants of Metal-ion Complexes, Supplement No 1, The Chemical Society, London 1971.
11. Wranglén G, Metallens Korrosion och Ytskydd, Almqvist & Wiksell (The Corrosion and Surface Protection of Metals) Stockholm 1967 (in Swedish).
12. Bryant E A, Cowan G A, Daniels W R, Maeck W J, Oklo an Experiment in Long Term Geologic Storage, ACS Symposium Series, American Chem Soc 1976.
13. Allard B, Kipatsi H, Torstenfelt B, Sorption av långlivade radionuklider i lera och berg, del 2 (Sorption of Long-lived Radionuclides in Clay and Rock, part 2) KBS-TR-98, Kärnbränslesäkerhet, Stockholm 1978 (in Swedish).

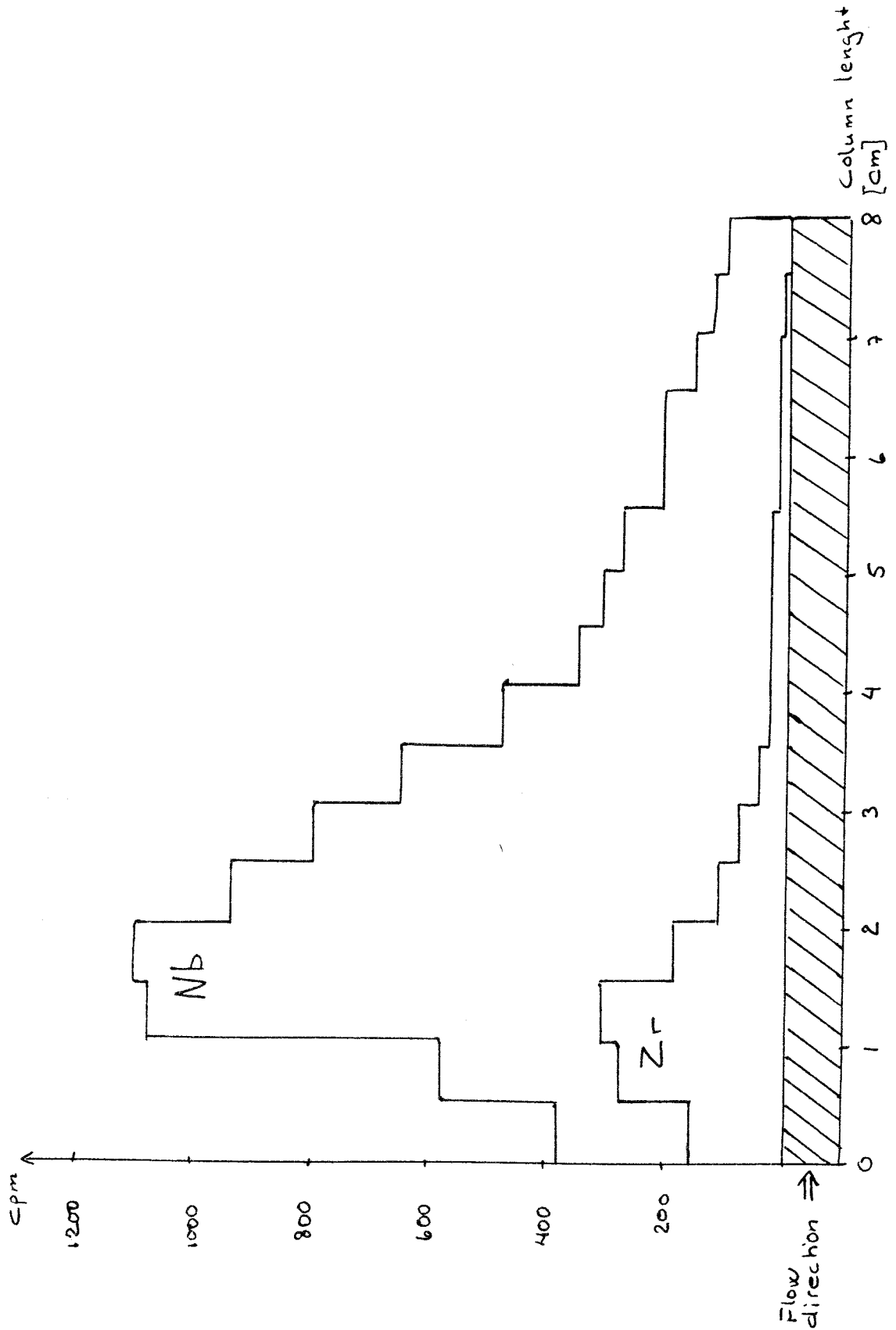
14. Rombén L, Private Communication, Cement- och Betonginstitutet,  
Stockholm.

Figure 1 (11)



pH - Eh diagram for niobium.

Figure 2. Column experiment, Stripa granite. Particle size 65 - 250  $\mu\text{m}$ . Water flow 0.02 ml/min. Time 29 h. Activity measurements along the column.



Appendix 1

Probable composition of groundwater in plutonic rock at great depth, according to Rennerfelt and Jacks.

Analysis		Probable Range	Min. value	Max value
Conductivity	$\mu\text{S/cm}$	400 - 600		1100
pH		7.2 - 8.5		9.0
$\text{KMnO}_4$ -cons:	mg/l	20 - 40		50
$\text{COD}_{\text{Mn}}$	"	5 - 10		12.5
$\text{Ca}^{2+}$	"	25 - 50	10	60
$\text{Mg}^{2+}$	"	5 - 20		30
$\text{Na}^+$	"	10 - 100		100
$\text{K}^+$	"	1 - 5		10
Fe-tot	"	1 - 20		30
$\text{Fe}^{2+}$	"	0.5 - 15		30
$\text{Mn}^{2+}$	"	0.1 - 0.5		3
$\text{HCO}_3^-$	"	60 - 400		500
$\text{CO}_2$	"	0 - 25		35
$\text{Cl}^-$	"	5 - 50		100 xx)
$\text{SO}_4^{2-}$	"	1 - 15		50
$\text{NO}_3^-$	"	0.1 - 0.5		2
$\text{PO}_4^{3-}$	"	0.01 - 0.1		0.5
$\text{F}^-$	"	0.5 - 2		8
$\text{SiO}_2$	"	5 - 30		40
$\text{HS}^-$	"	<0.1 - 1		5
$\text{NH}_4$	"	0.1 - 0.4		2
$\text{NO}_2$	"	<0.01 - 0.1		0.5
$\text{O}_2$	"	<0.01 - 0.07		0.1

Appendix 2. Corrosion of niobium. (3)

Medium	Temp [°C]	Corrosion, [mm/y]
NaOH, dil.	20	0.025
"-	100	0.45
NaOH, 1%	100	0.73
"-, 5%	100	2.5
"-, 10%	ambient	0.012
"-, conc.	20	Fast
"-, "-	100	"-

Appendix 3 Stability Constants of Niobium in Water.

Nb(V) - Fluoride	log K	Medium
$\text{Nb(OH)}_3\text{F}_2 \text{ (s)} \rightleftharpoons \text{Nb(OH)}_3\text{F}_2^\circ$	-4.82	3 M $\text{HNO}_3$
$\text{Nb(OH)}_3\text{F}_2 + \text{HF} \rightleftharpoons \text{Nb(OH)}_2\text{F}_3 + \text{H}_2\text{O}$	4.2	"-
$\text{Nb(OH)}_4\text{F(s)} \rightleftharpoons \text{Nb(OH)}_4\text{F}^\circ$	-5.22	0.5 M $\text{KNO}_3$
$\text{Nb(OH)}_4\text{F} + \text{HF} \rightleftharpoons \text{Nb(OH)}_4\text{F}_2^- + \text{H}^+$	3.64	"-

Solubility Product of Niobates	log $K_s$	Temp. °C
$\text{M}^+\text{NbO}_3^-$ , where $\text{M} = \text{Na}^+$	-6.84	25
"- $\text{M} = \text{K}^+$	-6.15	"-
"- $\text{M} = \text{Cs}^+$	-8.13	"-
$\text{M}^{2+}(\text{NbO}_3^-)_2$ , where $\text{M} = \text{Mg}^{2+}$	-16.64	20
$\text{M} = \text{Ca}^{2+}$	-17.06	"-
$\text{M} = \text{Pb}^{2+}$	-16.62	"-
$\text{M} = \text{Ba}^{2+}$	-16.49	"-
$\text{M} = \text{Sr}^{2+}$	-17.38	"-

## Short study on the chemistry of niobium in ground water

### General on niobium

Niobium, also called columbium, belongs to group 5 of the Periodic Table of Elements.

In minerals niobium occurs as niobite,  $\text{Fe(II)Nb}_2\text{O}_6$ , or complex oxides based on  $\text{Nb}_2\text{O}_5$ .

The most stable state of oxidation of vanadium, niobium and tantalum is the fifth yielding a rare gas configuration. The states II, III and IV are also known but are of significance only for vanadium.

The group V elements are hard to melt. They are chemically resistant, chiefly due to passivation by a protective oxide film, at moderate temperatures. The durability increases in the order  $\text{V} < \text{Nb} < \text{Ta}$ .

The only acids attacking Nb and Ta are hydrofluoric acid and concentrated sulphuric acid. Vanadium is attacked by strong oxidizing acids. Only very strong alkaline solutions attack the metals.

All three of the group 5 elements become prone to reactions above about  $300^\circ\text{C}$ .

### Assumptions

#### Ground water composition, Ref 1

Available analyses for ground water from great depth (Storjuktan, Stripa, Kråkemåle, Finnsjön, Forsmark etc) are collected in table 1. Maximum and minimum values are shown as well as probable interval.

In the pH range 7-9 anion concentrations are according to table 2.

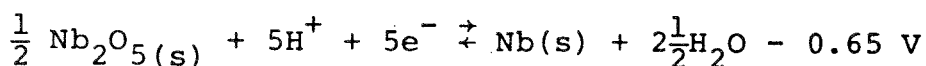


Ground water composition in the presence of concrete, Ref 2

The ground water chemistry will be affected by the great amounts of concrete present in the repository. In the first stage the pH increases to 13-14 because of the dissolution of small amounts of NaOH and KOH from the concrete. Later the free  $\text{Ca(OH)}_2$  in the concrete dissolves stabilizing the pH of 12.6.  $\text{Ca(OH)}_2$  constitutes a few per cent of the concrete. After a period of time the Ca dissolves from silicates and aluminates at which time the mechanical strength of the concrete disappears. The ground water pH will then be about 10. These compounds constitutes about 10-15 % of the concrete weight.

Redox conditions in the ground water, Ref 1

Figure 1 is a potential pH graph showing the area of interest for deep ground water shaded.

Electrode potentials for niobium, Ref 5In which form does niobium occur?

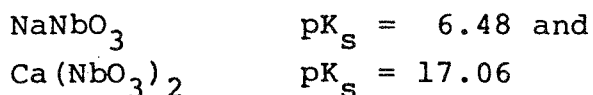
In the potential-pH graph, figure 1, where the shaded area represents the area of interest for deep ground water, the electrode potential for the reaction  $\frac{1}{2}\text{Nb}_2\text{O}_5(\text{s}) + 5\text{H}^+ + 5\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Nb}(\text{s}) + 2\frac{1}{2}\text{H}_2\text{O}$ ,  $e_0 = -0.65 \text{ V}$  has been drawn as a dashed line. The stable form in ground water will be  $\text{Nb}_2\text{O}_5$ .

A theoretical potential-pH graph with some empirical data is shown in figure 2 /Ref 6/. In this figure the pH ranges for ground water (marked 1) and for ground water in the presence of concrete (marked 2) have been introduced.

Considering figure 1 Nb will strive towards  $\text{Nb}_2\text{O}_5$  in the

pH range of the unaffected ground water. In the presence of concrete this will also be true for the main portion of the time when the pH is between 10 and 12.6. Initially, however, when the pH is 13-14 there will be some corrosion yielding  $\text{NbO}_4^{3-}$ . This ion will diffuse towards the rock meeting water of a lower pH. Reasonable reactions are that  $\text{NbO}_4^{3-}$  then converts to  $\text{Nb}_2\text{O}_5$  or  $\text{NbO}_3^-$ .

$\text{NbO}_3^-$  forms sparingly soluble salts with alkali metals and still less soluble salts with alkaline earths. The salts that, with respect to the cation concentrations in table 1, can be of interest are:



If the calcium concentrations are according to table 1 this would give a niobium solubility of 0.1 mg/l given that the available amount of calcium is sufficient. This seems probable considering the calcium content of the concrete but has not been verified. No solubility values have been found for  $\text{Nb}_2\text{O}_5$ .

It has not been possible to find complex constants for Nb with the anions in table 2. The fluoro- and chloro-complexes of Nb(V) are formed in strongly acidic solutions.

#### Comparison with nickel

The solubility of niobium in the repository itself increases due to the presence of concrete while the solubility of nickel is kept low because of the buffering effect the concrete has on the pH. It seems very probable that the niobium eventually diffusing out of the repository precipitates when meeting undisturbed ground water. The solubility of nickel is, however, higher in the undisturbed ground water than in the concrete.

Soil measurements with nickel have yielded a retention

factor of about 6 000. As no certain complex constants are available for niobium it is difficult to predict the retention factor for niobium. The most probable case seems to be that it precipitates as  $\text{Ca}(\text{NbO}_3)_2$ ,  $\text{Fe}(\text{NbO}_3)_2$  or  $\text{Nb}_2\text{O}_5$ , all occurring as natural minerals and very sparingly soluble.  $\text{Nb}_2\text{O}_5$  is even so inert that it has been difficult to determine its redox potential. The above given values therefore are based on thermal data.

Tabell 1. Data för naturvatten sammanställda från tillgängliga analyser av djupgrundvatten.<sup>2</sup> (Inom parentes anges motsvarande halter enligt 3.

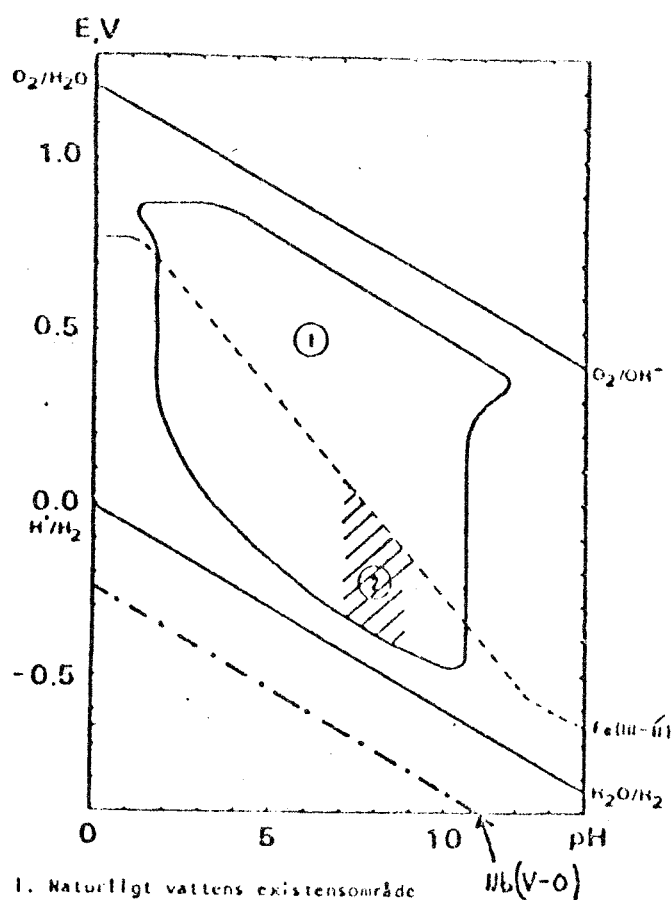
	Naturvatten mg/l			Syntetiska vatten				
	Max. värde	Min. värde	Troligt Intervall	CTH <sub>1105</sub>	CTH <sub>293</sub>	Lund	Stodsvik	Orrje
pH	8,65 (9,0)	7,10 (6,5)	7,2-8,5 (7,2-8,5)					
NH <sub>4</sub> <sup>+</sup>	0,3 (5)	0	0,05-0,3 (0,1-0,4)	0	0	0,1	0	0,2
Na <sup>+</sup> 1)	190 (200)	8	15-150 (20-40)	288	42	306	121	100
K <sup>+</sup>	14	0,2	0,5-5	10	5	14	1	5
Mg <sup>2+</sup>	19 (1-0)	0,5	2-6 (15-30)	15	7,5	30	3	10
Ca <sup>2+</sup>	82 (100)	5	20-45 (20-60)	75	37,5	66,9	6	40
Mn <sup>2+</sup>	1,1 (3)	<0,02	0,05-0,5 (0,1-0,5)	0	0	1,0	0	0,5
Fe	19 (30)	<0,02	0,1-20 (0,5-20)	0	0	4,0	0	13
HCO <sub>3</sub> <sup>-</sup>	390 (500)	32	90-350 (150-400)	200	100	120	300	300
SiO <sub>2</sub>	26 (60)	3	15-25 (15-40)	0	0	30	10	20
NO <sub>2</sub> <sup>-</sup>	0,1 (0,5)	0	0-0,1 (0,01-0,1)	0	0	0,2	0	0,1
NO <sub>3</sub> <sup>-</sup>	11 (10)	0,08	0,1-1,0 (0,1-2)	0	0	0,3	0	1
PO <sub>4</sub> <sup>3-</sup>	0,11 (1)	0,01	0,01-0,1 (0,1-0,6)	0	0	0	0	0
HS <sup>-</sup>	5 (10)	0	0-0,5 (-0,2-5)	0	0	0	0	0
SO <sub>4</sub> <sup>2-</sup>	43 (100)	<1	3-30 (20-40)	15	7,5	100	11,8	16,6
F <sup>-</sup>	7,5 (8)	1,0	1-4 (0,5-3)	1,5	0,75	1,5	1,5	1
Cl <sup>-</sup> 1)	280 (400)	2	5-100 (20-100)	500	93	600	12,3	40

1) Vid saltvattenintrusion kan högre värden erhållas

Tabell 2. Haltintervall för anjoner i grundvattnet (pH 7-9; mmol/l)

$H_2O$	$-\log [OH^-]$	14,0-pH
	$-\log [CO_3^{2-}]$	6,2-3,5
$H_2CO_3$	$-\log [HCO_3^-]$	2,9-2,2
	$-\log [H_2CO_3]$	<u>5,5-2,9</u>
		$\Sigma$ 2,8-2,2
	$-\log [H_2SiO_4^{2-}]$	12,6-8,2
$H_4SiO_4$	$-\log [H_3SiO_4]$	6,5-4,1
	$-\log [H_4SiO_4]$	3,7-3,2
	$-\log [H_2(H_2SiO_4)_2^{2-}]$	<u>12,5-7,8</u>
		$\Sigma$ 3,6-3,2
$NO_3^-$	$-\log [NO_3^-]$	5,8-4,5
	$-\log [PO_4^{3-}]$	12,7-8,6
$H_3PO_4$	$-\log [HPO_4^{2-}]$	7,4-5,2
	$-\log [H_2PO_4^-]$	8,8-5,4
	$-\log [H_3PO_4]$	<u>15,6-10,2</u>
		$\Sigma$ 7,0-5,2
$SO_4^{2-}$	$-\log [SO_4^{2-}]$	4,5-3,4
	$-\log [HSO_4^-]$	<u>11,5-8,4</u>
		$\Sigma$ 4,5-3,4
$F^-$	$-\log [F^-]$	4,6-3,7
	$-\log [HF]$	<u>9,9-7,7</u>
		$\Sigma$ 4,6-3,7
$Cl^-$	$-\log [Cl^-]$	3,9-2,4

Figur 1. Potential-pH-diagram för vatten samt Fe(III)/Fe(II)-jämviktskurvan.



1. Naturligt vattens existensområde
2. Grundvatten innehållande  $\text{Fe}^{2+}$  (representativt för svenskt djupgrundvatten).

Markerat område i figur 1 förefaller alltså väl representera aktuella djupgrundvatten.

Figur 2.

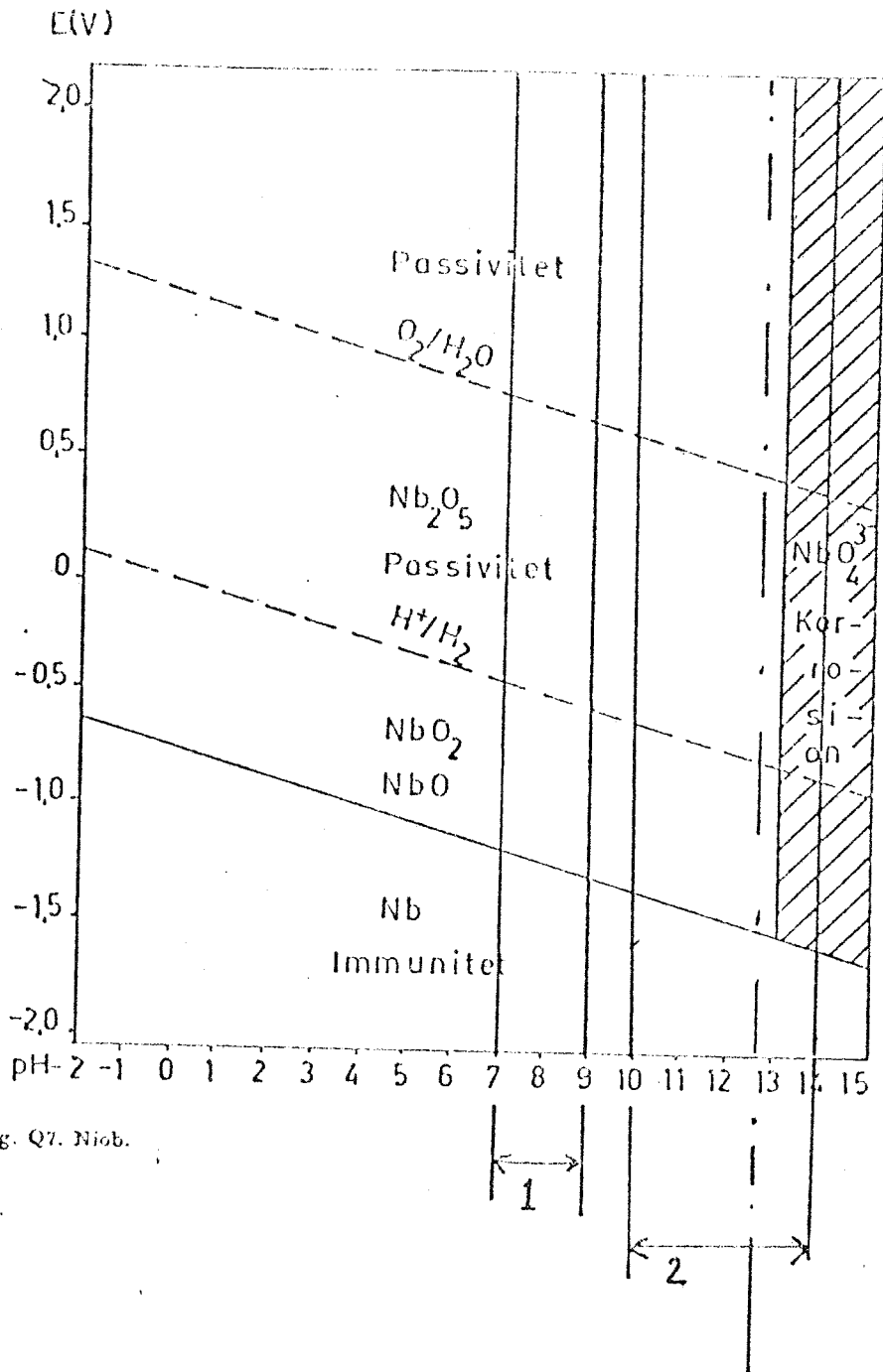


Fig. Q7. Niob.

Referenslista

1. KBS teknisk rapport 98 kap. 2 och 3.
2. KBS " " 101 kap. 4.
3. Gunnar Hägg; Allmän organisk kemi.
4. Latimer, Hildebrand; Reference Book of Inorganic Chemistry, 3rd ed, New York.
5. L-G Sillén; Stability Constants of Metal-Ion Complexes, Chem. Soc. Spec. Publ No 17.
6. Gösta Wranglen; Metaller's korrosion och ytskydd.



## Appendix 5

### Artificial groundwater for sorption measurements

#### Preparation

I. Dissolve in small volumes of water (distilled):

1. 24.65 mg/l  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$   
15.80 mg/l  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$   
7.46 mg/l KCl

2. 37.84 mg/l  $\text{Na}_4\text{SiO}_4$

Neutralize with ca 8.2 ml 0.1 M HCl to pH 8

3. 65.82 mg/l  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

4. 169.20 mg/l  $\text{NaHCO}_3$

II. Bubble  $\text{N}_2$  through distilled water

Add solutions 1, 2, 3 and 4

Adjust pH to 8.0 - 8.2 (if necessary) with NaOH or HCl and add water until the final solution volume is obtained

Store in closed bottle with  $\text{CO}_2$  trap.

#### Composition

Total concentrations are given. The values suggested for standard water according to KBS TR 36 and TR 55 are given within parentheses for comparison (TR 36 value first)

$[\text{HCO}_3^-]$	$2.014 \cdot 10^{-3}$ M,	123 ppm	(300 ppm, 100 ppm)
$[\text{H}_4\text{SiO}_4]$	$2.056 \cdot 10^{-4}$ M,	12 ppm	(20 ppm, 0 ppm)
$[\text{SO}_4^{2-}]$	$1.000 \cdot 10^{-4}$ M,	9.6 ppm	(16.6 ppm, 7.5 ppm)
$[\text{Cl}^-]$	$1.973 \cdot 10^{-3}$ M,	70 ppm	(40 ppm, 93 ppm)
$[\text{Ca}^{2+}]$	$4.477 \cdot 10^{-4}$ M,	18 ppm	(40 ppm, 37.5 ppm)
$[\text{Mg}^{2+}]$	$1.774 \cdot 10^{-4}$ M,	4.3 ppm	(10 ppm, 7.5 ppm)
$[\text{K}^+]$	$1.000 \cdot 10^{-4}$ M,	3.9 ppm	(5 ppm, 5 ppm)
$[\text{Na}^+]$	$2.836 \cdot 10^{-3}$ M,	65 ppm	(100 ppm, 42 ppm)

pH 8.0 - 8.2

Ionic strength: 0.0085

FÖRTECKNING ÖVER KBS. TEKNISKA RAPPORTER

1977-78

- 121 KBS Technical Reports 1 - 120.  
Summaries. Stockholm, May 1979

1979

- 79-01 Clay particle redistribution and piping phenomena in bentonite/  
quartz buffér material due to high hydraulic gradients  
Roland Pusch  
University of Luleå 1979-01-10
- 79-02 Försöksområdet vid Finnsjön  
Beskrivning till berggrunds- och jordartskartor  
Karl-Erik Almén  
Lennart Ekman  
Andrzej Olkiewicz  
Sveriges Geologiska Undersökning november 1978
- 79-03 Bergmekanisk bedömning av temperaturbelastning vid slutförvaring  
av radioaktivt avfall i berg  
Ove Stephansson  
Bengt Leijon  
Högskolan i Luleå 1979-01-10
- 79-04 Temperatur- och spänningsberäkning för slutförvar  
Taivo Tarandi  
VBB Vattenbyggnadsbyrån, Stockholm februari 1979
- 79-05 Kompletterande berggrundsundersökningar inom Finnsjö- och  
Karlshamnsområdena  
Andrzej Olkiewicz  
Sören Scherman  
Karl-Axel Kornfält  
Sveriges Geologiska Undersökning 1979-02-02
- 79-06 Kompletterande permeabilitetsmätningar i Karlshamnsområdet  
Gunnar Gidlund  
Kenth Hansson  
Ulf Thoregren  
Sveriges Geologiska Undersökning februari 1979

- 79-07 Kemi hos berggrundvatten i Blekinge  
Gunnar Jacks  
Institutionen för Kulturteknik, KTH, februari 1979
- 79-08 Beräkningar av grundvattenrörelser inom Sternöområdet i Blekinge  
John Stokes  
Institutionen för Kulturteknik, KTH, februari 1979  
Preliminär utgåva
- 79-09 Utvärdering av de hydrogeologiska och berggrundsgeologiska  
förhållandena på Sternö  
Kaj Ahlbom  
Leif Carlsson  
Gunnar Gidlund  
C-E Klockars  
Sören Scherman  
Ulf Thoregren  
Sveriges Geologiska Undersökning, Berggrundsbyrån,  
februari 1979
- 79-10 Model calculations of groundwater condition on Sternö peninsula  
Carl-Lennart Axelsson  
Leif Carlsson  
Geological Survey of Sweden september 1979
- 79-11 Tolkning av permeabilitet i en befintlig berganläggning  
Ulf Lindblom  
Alf Norlén  
Jesús Granero  
Kent Adolfsson  
Hagconsult AB februari 1979
- 79-12 Geofysisk borrhålmätning i 2 st borrhål på Sternö  
Kurt-Åke Magnusson  
Oscar Duran  
Sveriges Geologiska Undersökning februari 1979
- 79-13 Bildning av fritt väte vid radiolys i lerbädd  
Trygve Eriksen  
Johan Lind  
Institutet för Kärnkemi KTH 1979-03-28
- 79-14 Korrosionsprovning av olegerat titan i simulerade  
deponeringsmiljöer för upparbetat kärnbränsleavfall.  
Slutrapport.  
Sture Henrikson  
Marian de Pourbaix  
Studsvik Energiteknik AB 1979-05-07
- 79-15 Kostnader för hantering och slutförvaring av högaktivt avfall  
och använt kärnbränsle  
Arne W Finné  
Åke Larson Byggare, april 1979
- 79-16 Beräkning av permeabilitet i stor skala vid bergrum i Karlshamns  
hamn  
Ulf Lindblom  
J J Granero  
Hagconsult AB Göteborg, 23 augusti 1979

- 79-17 Water percolation effects on clay-poor bentonite/quartz buffer material at high hydraulic gradients  
R Pusch  
Div. Soil Mechanics, University of Luleå, 1979-05-31
- 79-18 Sammanställning och utvärdering av genomförda GETOUT- och BIOPATH-körningar  
M Elert  
B Grundfelt  
C Stenquist  
Kemakta AB, Studsvik Energiteknik AB, 1979-08-13
- 79-19 Diffusion in the rock matrix - An important factor in radionuclide retardation?  
Ivars Neretnieks  
Royal Institute of Technology May 1979
- 79-20 Hydraulisk konduktivitet bestämd i stor skala i ytliga partier av Blekinge kustgnejs  
Ulf Lindblom, Hagconsult AB, Göteborg  
Torbjörn Hahn, Fortifikationsförvaltningen, Stockholm  
Göteborg juni 1979
- 79-21 Teknik och kostnad för rivning av svenska kärnkraftverk  
Utarbetad av en särskild arbetsgrupp inom SKBF/KBS,  
oktober 1979
- 79-22 Technology and costs for dismantling a Swedish nuclear power plant. Prepared by a special working group within SKBF/KBS,  
October 1979
- 79-23 Release of  $^{129}\text{I}$  to the coolant  
Hilbert Christensen  
Studsvik Energiteknik AB 1979-07-20
- 79-24 Development of glass compositions with 9% waste content for the vitrification of high-level waste from LWR nuclear reactors  
Tibor Lakatos  
Swedish Glass Research Institute, Växjö October 1979
- 79-25 Svenska torv- och lerlager - Egenskaper av betydelse för slutlagring av låg- och medelaktivt avfall  
Ove Landström  
Hans Tollbäck  
Studsvik Energiteknik AB, November 1979
- Mäktiga lerformationer i Sydsverige - En litteraturstudie  
Henrik Norlander  
Kvartärgeologiska Institutionen  
Stockholms Universitet, September 1979
- 79-26 Leakage of Niobium-94 from an Underground Rock Repository  
K Andersson  
B Torstenfelt  
J Rydberg  
Department of Nuclear Chemistry  
Chalmers University of Technology, 1979-11-05