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**Canister materials proposed for final disposal of high level nuclear waste – a review with respect to corrosion resistance**

Einar Mattsson

Swedish Corrosion Institute, Stockholm, June 1981

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OF HIGH LEVEL NUCLEAR WASTE - A REVIEW WITH RESPECT  
TO CORROSION RESISTANCE

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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 during 1981, is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28) and 1980 (TR 80-26) is available through SKBF/KBS.

## CANISTER MATERIALS PROPOSED FOR FINAL DISPOSAL OF HIGH LEVEL NUCLEAR WASTE - A REVIEW WITH RESPECT TO CORROSION RESISTANCE

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Einar Mattsson, Swedish Corrosion Institute, Stockholm

### Summary

Spent fuel from nuclear reactors has to be disposed of either after reprocessing or without such treatment. Due to toxic radiation the nuclear waste has to be isolated from the biosphere for 300-1,000 years, or in extreme cases for more than 100,000 years.

The nuclear waste will be enclosed in corrosion resistant canisters. These will be deposited in repositories in geological formations, such as granite, basalt, clay, bedded or domed salt, or the sediments beneath the deep ocean floor. There the canisters will be exposed to groundwater, brine or seawater at an elevated temperature. Species formed by radiolysis may affect the corrosivity of the agent.

The corrosion resistance of candidate canister materials is evaluated by corrosion tests and by thermodynamic and mass transport calculations. Examination of ancient metal objects after long exposure in nature may give additional information. On the basis of the work carried out so far, the principal candidate canister materials are titanium materials, copper, and highpurity alumina.

### 1. The nuclear waste to be disposed of

In nuclear reactors the fuel has to be unloaded from the core after a certain burn-up, due to loss of reactivity and damage to the fuel cladding. The spent fuel, which has a quite high radioactivity level can be treated in various ways:

- The spent fuel can be reprocessed; useful fissile isotopes are then extracted and recycled into nuclear reactors for further energy production. The remaining waste products are vitrified and have to be disposed of.
- Alternatively the spent fuel can be disposed of as it is, i.e. without

any reprocessing or vitrification.

Due to decay processes the vitrified waste as well as the non-reprocessed spent fuel will emit radiation ( $\alpha$ ,  $\beta$  and  $\gamma$ ), which is high initially; therefore the waste is designated high level waste (HLW). The radiation, however, decreases significantly with time as shown in fig. 1 and 2. The decay will also be associated with the generation of heat (fig. 3). As the radiation is toxic to human beings and other living organisms the waste has to be isolated from the biosphere of our planet for a period, until the radiation has decreased to a sufficiently low level. The general approach to this problem is to encapsulate the waste in canisters and to deposit these in appropriate geological formations, thus creating a number of barriers between the waste and the biosphere.

The nuclear waste will generally be placed in an intermediate storage before the final deposition in the repository. The waste may be kept there for a long period, up to decades, until the radiation has decreased to a moderate level. As for the lifetime of the canisters to be used for final deposition, the following requirements have been put forward (3):

- Until most high activity fission products  
in reprocessed vitrified waste have decayed 300-1,000 years
- Until the temperature in the repository  
has approached the ambient temperature 20,000-50,000 years
- Until the fission products in unrepro-  
cessed spent fuel have decayed satisfac-  
torily more than 100,000 years.

It should be added that in many countries there is a request that the deposited canisters shall be retrievable.

Different ways have been chosen to solve the nuclear waste disposal problem. In Sweden the Parliament passed the so called "Stipulation Law" in 1977, which states that new nuclear power reactors may not be charged with fuel unless the owner is able to demonstrate that terminal storage of either the high-level waste from the reprocessing of spent fuel or unreprocessed spent fuel can be accomplished in an absolutely safe manner. To fulfil these requirements the Swedish power utilities formed the Nuclear Fuel Safety Project (KBS), which has worked out rather complete conceptual programs for how a final storage of

vitriified high level reprocessing waste (1) as well as of unreprocessed spent nuclear fuel could be implemented (2). From this basis KBS is now continuing the studies to reach improved and more optimized solutions. Such development work is also in progress in several other countries.

The solutions arrived at for disposal of wastes from nuclear reactors might also largely be applicable for disposal of HLW generated in connection with the production of nuclear weapons. The quantity of military waste produced since 1942 might be more than a power of ten larger than the quantity of civilian waste.

## 2. The canister package

As the terminology for the canister package varies, the meaning of some terms related to the canister and the repository will be explained as to the sense in which they are used in this report:

- The waste may be in the form of a glass (e.g. borosilicate glass) or in the form of spent fuel rods.
- A container, often made of chromium-nickel steel, provides mechanical support to the waste during transportation, handling and encapsulation operations, and also during the final storage in the repository.
- A  $\gamma$ -screen of metal, e.g. lead, may be placed around the container to provide shielding of radiation from the waste.
- An overpack is enclosing the components earlier mentioned to provide corrosion resistance to the canister when exposed to the environment. One barrier may fulfil the combined function of  $\gamma$ -screen and overpack.
- The canister is the combination  $\gamma$ -screen - overpack used for encapsulation of the waste.
- A buffer (or backfill) may be emplaced around the canister in the repository. This buffer may have several functions; it may comprise a soft, formable bed for the canister to rest upon; it may inhibit groundwater penetration and distribute the groundwater uniformly over the surface of the canister; it may serve as a chemical buffer regulating the pH value of the water and its oxygen content; finally the buffer may retard the transport of corrosive reactants to and of radioactive substances away from the canister. Bentonite and mixtures of bentonite and quartz sand have been proposed as buffer materials. Upon contact with water the bentonite swells, which counteracts the formation of water-

bearing fissures in the material and makes mass transport possible only by diffusion.

- A hole sleeve may be placed around the canister to aid retrievability. This sleeve may consist of e.g. mild steel, cast iron, concrete, a ceramic, graphite or a polymer.

### 3. Corrosion conditions

#### 3.1 Geological formations considered for repositories

Different geological formations are considered for the repository to provide the ultimate long-term barrier.

In Sweden the plans are to place the canisters in vertical boreholes extending from horizontal tunnels 500 m below ground in stable igneous rock selected for low permeability (1, 2); the water flow in the rock would be of the order of 0.1 l per m<sup>2</sup> per year (fig. 4).

Similarly in Canada the main concept under investigation is disposal deep within stable, hard-rock geological formations in the Canadian Shield (3).

In the United States several alternatives are studied for HLW isolation in geological formations (4). Bedded salt deposits in south eastern New Mexico (at the site of the Waste Isolation Pilot Plant, WIPP) is one alternative. Others are basalt formations on the Hanford reservation and a number of shale, argillite and tuff formations at the Nevada Test Site. Disposal of HLW is also considered in sediments or hard rock beneath the deep ocean floor in the North Pacific (fig. 5). Certain regions there belong to the least valuable real estate on earth without important fishing, petroleum or mineral resources, and are in addition among the most stable parts of the earth's surface, without earthquakes, large rock movements or glaciations (5).

In West-Germany, domed salt at Gorleben is being studied as a host rock for the final disposal of HLW canisters (6). In Belgium the clay formation underlying the site of the nuclear research centre at Mol is envisaged for this purpose (7). In France and the United Kingdom the choice is crystalline rock (7).

### 3.2 The corrosive environment

The corrosive environment in deep hard-rock repositories in granite and basalt formations is groundwater, the chemistry of which is site specific.

A typical example of groundwater composition (500 m below ground) at a potential repository site in Sweden is given in table 1. The oxygen content at this depth is very low (0.1 mg/l), in equilibrium with the rock material. During an initial period immediately following deposition of the canister, a thin surface zone along the walls of the repository has an elevated oxygen content. The Cl<sup>-</sup>-content expected is max. 100 mg/l, except during the phase for drainage and filling when it may rise to 400 mg/l.

The groundwater at Hanford, USA, has a similar composition (8). As found in Canada, however, high salinity water is not particularly uncommon in deep hard-rock mines of the Canadian Shield (3) and this might apply to other regions also.

In seabed sediment and rock repositories the intrusion of seawater is very likely (4).

In bedded or domed salt repositories hydrologic flow of brine is unlikely, not taking into account accidental water inrush through the shaft of the repository. Migration of brine inclusions up the thermal gradient, toward the HLW canister may occur, however, during the first period after emplacement, when the thermal gradient is greatest (4). The amount of brine expected to intrude is of the order of 1-10 liters per 100 years (9). Intrusion of groundwater will also be possible dissolving salt so that a brine is formed, which may interact with the overpack. Different brine compositions have been recommended for corrosion tests representative of repositories in bedded and domed salt (8, 10). Largely they are concentrated solutions containing Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. The canister, however, will mainly be exposed to dry salt.

### 3.3 Temperature of the canister

Due to the heat generation in the waste, the temperature will rise in the repository. The resulting temperature can to some extent be regulated, as it is determined by the time of intermediate storage of the waste before final disposal, the amount of waste in the canister, the number of canisters per area unit, and the heat conductivity of the environment. Thus,

depending on the arrangements, different maximum values are expected for the canister temperature shortly after deposition:

- The Swedish Nuclear Fuel Safety Project (KBS) has specified a maximum canister temperature of 70-80°C shortly after deposition in deep hard-rock repositories (11, 12, 13). In the United Kingdom higher temperatures are evidently anticipated as canister materials for the repositories there are tested at temperatures up to 150°C (7). Above 100°C of course there is a risk of steam formation, if the pressure is not sufficiently high.
- Belgish exposure tests of canister materials for repositories in clay are carried out in groundwater at temperatures up to 100°C.
- In concepts for deposition in bedded or domed salt, the canister temperature will initially be higher. Tests of canister materials for such repositories are carried out by exposure to brines or dry salts at temperatures up to 300°C (7, 8, 14).

### 3.4 Radiolysis

If the water solution around the canister is exposed to radiation from the waste, radiolysis of the solution can take place leading to the formation of oxygen, hydrogen, and hydrogen peroxide in groundwater; in brines also HCl and  $OC1^-$  are formed (4). These species may considerably affect the corrosivity of the environment. A  $\gamma$ -screen in the canister, however, can eliminate the radiolysis.

## 4. Methods for evaluation of the corrosion properties of candidate canister materials

A very long lifetime is required for the canisters; 300-1,000 years or in some cases more than 100,000 years. Predictions for such long periods have hitherto been very unusual in corrosion technology, so much consideration has been devoted to methods for evaluation of the corrosion properties of candidate canister materials.

### 4.1 Corrosion tests

The plan made up at the Battelle Pacific Northwest Laboratory (PNL) for evaluation of the corrosion properties of candidate canister materials will be quoted (8) as its philosophy seems to have a wider application:

"The candidate barrier materials, selected initially on the basis



of literature surveys and consultations with other investigators, are undergoing laboratory-scale corrosion and mechanical-property screening tests. These tests will serve to reduce the initial large number of candidate materials to the few that can be tested in the in-depth fashion required for actual barrier service certification. Where possible, the tests will be performed under conditions relevant to specific candidate repositories, e.g. WIPP brine and Hanford basalt. - Materials appearing most useful to barrier systems applications after completion of the screening studies will be tested in a rigorous fashion to reveal any susceptibility to degradation under severe-service simulation conditions. Where known potential susceptibilities exist, such as hydrogen embrittlement of titanium alloys, the phenomena will be investigated in depth to determine safe application limits. The severity of the test(s) will be relied upon, in general to reveal unanticipated modes of material degradation. --- It is anticipated that the prototype packages will be validated eventually by means of in-situ tests that are wholly relevant to the specific disposal sites for which the packages are intended. The in-situ tests should duplicate the most severe conditions expected in each environment, including effects of temperature, pressure, stress, and radiation."

The aim of the more rigorous studies is to get information of the long-term behaviour of the metals with respect to corrosion mechanism and corrosion rate. For practical reasons the exposure time will, even in the rigorous tests, be restricted to months, years or exceptionally decades. An extrapolation of the results to hundreds, thousands or even hundreds of thousands of years will of course involve uncertainties. Small errors in the determined rate of corrosion or crack propagation may result in misleading conclusions after extrapolation. Further, the corrosion mechanism may change, and even unforeseen corrosion phenomena may appear during the extreme time spans to be considered.

#### 4.2 Thermodynamic calculations

Thermodynamic calculations are useful tools for prediction of the long-term corrosion behaviour of metals. On the basis of thermodynamic data one can determine which species of a metal is stable under given condi-

tions and also whether a certain corrosion reaction is possible or not. The results may be conveniently surveyed in potential-pH-diagrams (cf. fig. 8) - so called Pourbaix diagrams - or other diagrams of similar type. Thermodynamic calculations, however, give no information on the rate of a corrosion reaction, which has been found thermodynamically possible. As such a reaction will require the supply of certain reactants to the metal surface, the transport rate for one of these reactants may control the rate of the whole reaction. So thermodynamic calculations in combination with mass transport calculations may in favourable cases be used for prediction of the corrosion of a metal, even over long time spans. This technique has been used in Sweden for prediction of the corrosion of copper canisters (see chapter 5.2).

#### 4.3 Examination of ancient metal objects

Effort has been made to get information on the long-term corrosion behaviour of metals by examination of ancient metal objects. Johnson Jr. and Francis at PNL (15) have carried out such an investigation including:

- Archeological objects - artifacts - of gold, silver, copper, lead, iron, tin, and mercury, the oldest ones from 6,000-7,000 BC. Thousands of metallic artifacts exist, which have been exposed for millenia in soils of various compositions, caves, tombs, graves, submerged shipwrecks etc.
- Metal meteorites of iron-base alloys with 5-60 % nickel and minor amounts of cobalt, phosphorus, and sulfur. Approximately 530 metal meteoritic masses have been identified with terrestrial ages up to one million years, some buried in the ground, others exposed to the atmosphere.
- Native metals, mainly gold, silver, copper, and mercury. Of particular interest are copper masses transported by glaciers, so called "float" copper, of which some have been cold worked - bent or distorted - by glacial action. So now native copper objects with residual stresses are available for examination after at least 8,000 years' exposure in the ground, i.e. the time elapsed since the last glacier receded.

Generally it is not possible to determine the corrosion rates for ancient metal objects available in the museum, because their original dimensions and weights are unknown; furthermore the exposure conditions are unknown. Still an examination may show which types of corrosion have occurred

during the very long exposure and what is the morphology of the attack. In the future it might be possible to gain still more information from finds of ancient metal objects by a closer cooperation between archeologists and corrosionists, the latter contributing by determination of environmental parameters of importance to the corrosion, such as pH value, redox potential, soil resistivity, and by description of the objects from corrosion point of view, before cleaning and conservation treatment is carried out. To get information applicable to a certain case, like the corrosion of buried canisters, it might even be possible to search for ancient metal objects at locations with an environment representative of the actual case.

## 5. The corrosion properties of some candidate canister materials

To fulfil the requirements of the "Stipulation Law" in Sweden KBS has proposed three canister alternatives for disposal of nuclear waste; a titanium canister with lead lining, a copper canister and a canister of highpurity alumina (fig. 6). Introductory investigations in other countries have also resulted in some candidate canister materials being indentified.

### 5.1 Titanium materials

Titanium materials are among the principal candidate overpack materials in most countries, e.g. in Belgium, Canada, France, Sweden, UK, and USA (1, 3, 7, 8, 14). Among the titanium materials taken into consideration the following grades may be mentioned (compositions given in percentage by weight):

- Ti-50A; unalloyed, commercially pure titanium
- ATi-24; unalloyed titanium, which contains max. 0.05 Fe, 0.05 C, 0.10 O, 0.03 N, and 0.012 H (a special variant has only 0.002 H)
- Ti-0.20Pd; contains 0.20 Pd
- Ti-12; contains 0.8 Ni and 0.3 Mo.

Titanium is not thermodynamically stable in water (11, 16). Nevertheless the metal has a very good corrosion resistance in water solutions over a wide pH range (pH 2-14) due to its ability to form spontaneously a dense,

thin passivation layer of titanium dioxide ( $\text{TiO}_2$ ) on the surface when exposed to water, both in the presence and in the absence of dissolved oxygen:



The rate of uniform corrosion in warm ( $60\text{-}90^\circ\text{C}$ ) chloride solutions has been found generally to be in the range  $0.1\text{-}0.25 \mu\text{m}/\text{year}$ . Pitting or crevice corrosion may occur in warm chloride solutions above certain critical values of temperature and chloride contents that depend on the pH value (fig. 7).

The grades Ti-50A, Ti-12 and Ti-0.20Pd have been tested at the Sandia National Laboratories (14) in oxygenated and nonoxygenated concentrated NaCl and Mg-K-NaCl brines and in seawater at temperatures up to  $250^\circ\text{C}$ . Ti-12 and Ti-0.20Pd were found very corrosion resistant. An increase in the oxidizing potential, due to radiolysis of the solution or oxygen addition, was found to improve the passivation and decrease the corrosion rate (tables 2 and 3). The uniform corrosion rate increased with the temperature, but pitting or crevice corrosion was not detected at temperatures up to  $300^\circ\text{C}$ . Crevice corrosion was observed, however, in Ti-50A at  $250^\circ\text{C}$ , making it an unlikely candidate for high temperature applications (14). Similar tests at PNL seem to largely support the results obtained at Sandia (8).

The stress corrosion resistance of Ti-12 has also been studied at Sandia by slow strain rate technique (14, 17). Tests have been carried out in oxygenated brine and seawater at temperatures up to  $250^\circ\text{C}$ ; then the macroscopic tensile properties were not affected by the exposure.

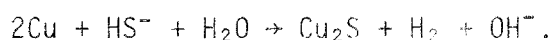
Titanium may be damaged by absorbed hydrogen. Hydrogen embrittlement may occur if the solubility of hydrogen (at room temperature 20 ppm) is exceeded and titanium hydride forms. Significant effects will be obtained, however, only at hydrogen contents of some hundreds ppm or more. Another type of damage is delayed fracture, at stress below the ultimate strength due to enrichment of hydrogen at defects and other stress raisers. Delayed fracture has been observed in ( $\alpha + \beta$ )-alloys, but so far not in unalloyed titanium (11, 16). Even if the probability of delayed fracture seems very low, the risk cannot be fully excluded. Should delayed fracture happen in the titanium overpack of a canister it may be locally penetrated

in comparatively short time. On the evaluation of the titanium canister concept proposed by KBS (fig. 6), having a 6 mm overpack of titanium and a 100 mm thick lining ( $\gamma$ -screen) of lead, the titanium overpack has not been ascribed any appreciable life due to the risk of delayed fracture (11, 16). The whole life of the canister in fact was based on the corrosion resistance of the lead lining. It seems important to clarify the mechanism of delayed fracture in unalloyed titanium, so that reliable lifetime predictions can be made.

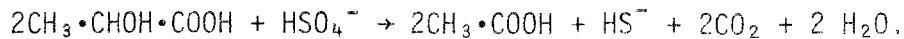
## 5.2 Copper

As mentioned earlier KBS has proposed that spent unprocessed nuclear fuel shall be disposed of by encapsulation in copper canisters with 200 mm thick walls (2, 12). The canisters are to be placed in vertical boreholes in igneous rock, 500 m below ground, and embedded in a buffer of compacted bentonite (fig. 6). The bentonite buffer will possess a very low permeability ( $10^{-12}$  m/s) and, in addition, a very high swelling capacity on moistening. So, for mass transport through the buffer, only diffusion needs be taken into consideration. The canister surface will reach a maximum temperature of 80°C after one or two decades. After 1,000 years the temperature will have decreased to 50°C. The radiolysis is negligible due to the screening effect of the copper.

The thermodynamic possibilities of various corrosion reactions on copper under the prevailing conditions have been studied (12, 16, 18). Copper can be attacked by water containing dissolved oxygen, but only at a comparatively high redox potential - above 50 mV SH at 25-100°C. The corrosion products will be  $\text{Cu}_2\text{O}$  or  $\text{CuO}$  (fig. 8). The maximum corrosion rate possible will then be determined by the supply of oxygen to the canister surface. Oxygen entrapped in the buffer material at the time of the closing of the repository was found to be an important oxidant. Sulphide in the groundwater was found to be another important reactant, for in the presence of  $\text{SH}^-$ , copper can be oxidized even by  $\text{H}^+$ , e.g. in water. One condition is then a low redox potential, below about -200 mV at 25°C or below -500 mV at 100°C (fig. 8). One possible reaction is:



Sulphide can also be formed by bacterial reduction of sulphate according to, e.g. the following equation:



Here  $\text{CH}_3\cdot\text{CHOH}\cdot\text{COOH}$  may be substituted by other organic matter. The supply of organic matter that is required by the bacteria for their life process is, in fact, the limiting factor for reduction in the presence of a surplus of sulphate.

Considering the supply of rate-limiting reactants mainly by diffusion through the bentonite the average penetration (assuming uniform attack) was calculated as:

Time of exposure, years	$10^3$	$10^4$	$10^5$	$10^6$
Average penetration, mm	0.02	0.1	0.5	2.4
Max. pit depth; 25 x average penetration, mm	0.5	2.3	13	60.

The possibility of pitting, however, cannot be excluded. The relation between pit depth (P) and time (t) may be expressed by the empirical equation  $P = A(t-t_0)^n$ , where  $t_0$  is the incubation time before pitting starts, and A and n are constants.

A statistical analysis of results from Denison and Romanoff's (19) investigation of copper corrosion in various types of soil in the USA during 14 years of exposure has shown that n has a value between 0 and 1 (generally between 0.1 and 0.6) and that this value decreases with the time of exposure. With such a value of n, the growth rate of the pit depth decreases with time and eventually becomes negligible if the wall thickness is large enough. Further attack then takes place by the initiation of new pits and by widening of old ones. Thus, when the wall thickness is very large, as in this case 200 mm, corrosion after very long times takes the form of an attacked surface zone with local variations in depth.

The relation between the maximum depth of attack and the average penetration is generally called the pitting factor. In Denison and Romanoff's field tests, the greatest pitting factor found for copper was 24. An examination of the results from these tests has shown, as was expected, that the pitting factor decreases with time of exposure. So, for the copper canisters local variations have been taken into account by multi-

plying the average penetration by a pitting factor of 25, a value which is conservatively chosen (see above).

On the basis of the estimated values of the maximum pit depth a copper canister with a wall thickness of 200 mm was estimated to have a life of hundreds of thousands of years.

In the evaluation described it has been assumed that the pitting factor is not greater than 25. The examinations of ancient copper objects exposed for millenia in various natural environments carried out by Johnson Jr. and Francis (15) seem to show that very deep pits do not occur on the ancient copper objects, so that the assumption made concerning the pitting factor is conservative. Johnson and Francis' examinations also seem to support another assumption made, i.e. that pure copper is resistant to stress corrosion cracking in ground environments. Further confirmation, however, is desirable, e.g. by constant strain rate testing and by more extensive studies of ancient copper objects.

A more solid knowledge of the long-term corrosion behaviour of copper might make it possible to reduce the wall thickness of the copper canisters.

Copper as canister material is also being considered, e.g. in Canada and Switzerland.

### 5.3 Highpurity alumina

KBS has also proposed that spent unreprocessed nuclear fuel shall be disposed of by encapsulation in canisters of highpurity alumina sintered under isostatic pressure (fig. 6) (13). The canisters will have a wall thickness of 100 mm and are to be placed in vertical boreholes extending from horizontal tunnels 500 m below ground in igneous rock. In each borehole one canister is deposited embedded in a quartz sand/bentonite buffer. The maximum temperature of the canister surface will be 70°C. Outside the canister, oxygen and hydrogen are formed due to radiolysis of water.

The alumina is not thermodynamically stable in water (13, 16). In pure water hydration will occur, below 100°C leading to the formation of either  $Al(OH)_3$  in the amorphous state or crystalline gibbsite ( $Al_3O_3 \cdot 3H_2O$ ). Corrosion may take place by slow dissolution or flaking off of a surface

layer. Various immersion tests showed that the corrosion rate will be less than  $0.1 \mu\text{m}/\text{year}$ , probably one or two powers of ten lower.

If the alumina canister in the storage has sufficiently large surface defects and is under sufficiently high mechanical tension the defects may grow slowly into propagating cracks, ultimately leading to fracture, so called delayed fracture. On the basis of results from fracture mechanical studies and after introduction of safety factors with respect to possible unknown features of the delayed fracture it was judged possible to eliminate the risk of delayed fracture if the the canisters pass the following production control:

- Proof testing at  $150 \text{ MN}/\text{m}^2$ , using acoustic emission technique to ensure that crack growth does not occur during the unstressing cycle. Canisters that can withstand this proof stress would not have surface defects larger than 0.4 mm.
- Surface acoustic wave examination with respect to surface inclusions, canisters with inclusions larger than  $100 \mu\text{m}$  within a  $100 \mu\text{m}$  deep surface zone being rejected.

Canisters which pass the production control mentioned are estimated to have a life of hundreds of thousands of years, or probably considerably more, under the conditions specified.

It may be questioned whether the very hard production control prescribed is reasonable. As the knowledge of delayed fracture in ceramics will increase, however, it will certainly be possible to relax the conservative requirements.

The choice of highpurity alumina as a corrosion resistant canister material is supported by test results obtained at PNL (8).

#### 5.4 Nickel base alloys

Several nickel base alloys are among the candidate canister materials (7, 8, 20), the following being of primary interest (composition given in percentage by weight):

SS 316:	17 Cr, 12 Ni, 2.5 Mo, bal Fe
Incoloy 825:	22 Cr, 42 Ni, 3 Mo, 30 Fe, 2 Cu, 0.9 Ti, 0.03 C



Inconel 600: 15 Cr, 76 Ni, 8 Fe, 0.04 C  
Inconel 625: 22 Cr, 63 Ni, 9 Mo, 3 Fe, 4 Nb, 0.2 Ti, 0.05 C  
Hastelloy C-276: 15 Cr, 59 Ni, 17 Mo, 5 Fe, 4 W, max. 0.02 C  
Hastelloy C-4: 16 Cr, 69 Ni, 15 Mo, max, 0.015 C, max. 0.70 Ti.

SS 316 and other austenitic stainless steels have shown very low corrosion rates when exposed to groundwater or brine at 250°C for 6 months (8). These alloys are susceptible, however, to stress corrosion cracking in oxygenated chloride solutions at temperatures above 60°C and also to localized corrosion. As oxygen may be added, e.g. by radiolysis or air access to the repository, austenitic stainless steels do not seem suitable as overpack materials.

In the same tests some "superalloys" with high nickel contents, i.e. Incoloy 825, Inconel 600, Inconel 625 and Hastelloy C-276 also showed very low corrosion rates. An increase of the nickel content improves the resistance to chloride induced stress corrosion, but to eliminate the susceptibility to pitting and crevice corrosion a molybdenum content of at least 6 % is required (21). For that reason Inconel 625 and the Hastelloy C family seem to be of primary interest for further investigation. From the Hastelloy C materials, which are known for very good resistance to seawater, should be chosen variants like Hastelloy C-276 or Hastelloy C-4, which, due to very low carbon content and/or addition of Ti, have improved resistance to intergranular corrosion after welding. In accordance Hastelloy C-4 and Inconel 625 belong to the principal candidate canister materials studied in France (20).

### 5.5 Zirconium alloys

Also certain zirconium alloys have been selected as candidate canister materials; Zircaloy-2 in USA (8), and Zircaloy-4 in France (20). These alloys have the following compositions in percentage by weight:

Zircaloy-2: 1.5 Sn, 0.12 O, 0.13 Fe, 0.10 Cr, 0.05 Ni, bal Zr  
Zircaloy-4: 1.5 Sn, 0.12 O, 0.21 Fe, 0.10 Cr, bal Zr.

The corrosion resistance of zirconium depends upon a passivating surface film in a similar manner as with titanium. Zirconium does not equal titanium in resistance to certain oxidizing media, but is superior in non-oxidizing acids, and in caustic alkalis. The behaviour in chloride solu-

tions appear to depend upon whether the solution is oxidizing or reducing, and in general zirconium is not as resistant as titanium (22).

Zircaloy-2 has been included in the screening tests at the Battelle Pacific Northwest Laboratory, earlier mentioned (8). On exposure to brine at 250°C for 6 months Zircaloy-2 showed very low corrosion rate, but on exposure to groundwater a higher corrosion rate was determined. Whether this observation was significant or accidental has not been clarified. In any case further investigation of the zirconium alloys is required before any conclusions can be drawn about their feasibility for nuclear waste canister production.

#### 5.6 Lead

The titanium-lead canister proposed by the Swedish KBS has a 6 mm thick overpack of titanium and a 100 mm thick lining of lead. This canister has been ascribed a life of thousands of years only due to the corrosion resistance of the lead (11, 16). - If the titanium sheath should be penetrated by corrosion or mechanical damage, the exposed lead may corrode by anodic dissolution, the corresponding cathodic process being reduction of oxygen or other oxidant at the surrounding passivated titanium surface. The corrosion rate, however, will be limited by the supply of oxygen to the canister surface, and on this basis the time required for perforation of the lead lining has been estimated to thousands of years.

Archeological finds have shown that lead directly exposed to soil may be attacked by intergranular corrosion. Thus, the weld on Roman lead piping, which had been buried in the ground for 2,000 years was destroyed by intergranular corrosion, while the other part of the pipe was apparently uncorroded (23) . The attack of the weld has been ascribed to the coarse grain structure of the weld region. The nature of the soil is also of importance; high contents of nitrate or organic acid as well as too high or too low pH values make the soil corrosive to lead (22).

#### 5.7 Cast iron

Some interest has even been devoted to cast iron as canister material, due to its low price. In the screening tests at PNL (8) the cast iron materials were seriously attacked in brine

at 250°C, but their corrosion rate in groundwater at 250°C, although significant, was not intolerable; it corresponded to an average penetration of about 25 mm in 1,000 years.

The corrosion of cast iron is often of type graphitic corrosion, the iron being selectively dissolved leaving behind a porous residue of carbon with poor mechanical properties. The corrosion of cast iron in soil is not always uniform but may result in the formation of pits; in one reported case the deepest pits were deeper than 7.5 mm after five years' exposure to sandy clay liable to tidal immersion (22). So cast iron cannot be considered a fool proof material for canisters.

### 5.8 Ceramic materials

At PNL screening tests have also been carried of 16 ceramic materials considered for use as elements in the canister overpack or hole sleeve (8). Samples were exposed to demineralized water, groundwater and brine under dynamic as well as static conditions at temperatures up to 250°C. The exposure generally lasted for about one month.

The leach rates increased with temperature. In the static tests at 150°C and 250°C they were generally highest in the demineralized water and lowest in the brine solution. Localized attack or alteration reactions became a serious problem at temperatures above 150°C with most of the candidate materials. Based on all the results obtained graphite, alumina,  $TiO_2$  and  $ZrO_2$  exhibited much greater resistance to attack by the leach solutions than the other materials. Further investigation is needed, however, before any final conclusions can be drawn about the long-term resistance in nuclear waste repositories.

The favourable results for highpurity alumina support the KBS proposal described in chapter 5.3.

### 5.9 Polymeric materials

So far polymers have received little attention as materials for nuclear waste canisters. PNL, however, has tested more than 30 polymers by exposure to deionized water for 7 days at temperatures up to 250°C and in additional tests also to  $\gamma$  radiation (8). After these tests four materials have been selected for further

investigation by simultaneous exposure to the chemical environment, temperature and radiation, expected in the repository. The four selected polymers are:

- ethylene-propylene terpolymer (EPDM) rubber
- polyphenylene sulphide
- poly(ethylene-tetrafluoroethylene) copolymer
- polyfurfuryl alcohol.

Polymers can be applied as coatings, films or sheets, molded or extruded canisters. Such application could be both economically and technically feasible. It might be very difficult, however, to predict the long-term stability of these and other polymers, as they are artificial products of which there is only comparatively short experience.

#### 6. Concluding remark

The development of a technology for nuclear waste disposal is far from completed. The proposals worked out in Sweden by KBS in short time under the hard directives of the "Stipulation Law" seem very conservative with great emphasis on safety. In other countries where less hard time constraints are limiting, more attention is being paid to the economy. In most countries, including Sweden, several years and even decades are available to optimize the disposal technology before it needs to be put into operation. In the development work special attention should be paid to the corrosion resistance of welds and other joints on the canister. With respect to the progress made during this period it might be possible to relax somewhat the extreme precautions in the Swedish proposals. Society, however, will certainly also in the future require a very high safety level in the storage of nuclear wastes.

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#### References

1. "Handling of spent nuclear fuel and final storage of vitrified high level reprocessing waste." KBS, Stockholm, 1978.

2. "Handling and final storage of unprocessed spent nuclear fuel." KBS, Stockholm, 1978.
3. Cameron, D.J., "Fuel isolation research for the Canadian nuclear fuel waste management program." Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, 1981 (in preparation).
4. Braithwaite, J.W. & Molecke, A., "Nuclear waste canister corrosion studies pertinent to geological isolation." Nuclear and Chemical Waste Management 1 (1980).
5. Heath, G.R., "Can we dispose of radioactive waste in the deep-sea floor?" Maritimes 20 (1976), 8.
6. Röthemeyer, H. & Closs, K.-D., "High level waste disposal." 1980 ANS/ENS International Conference.
7. Haijtink, B., "Corrosion of potential materials for containers and repository structures for the disposal of highly radioactive waste in geological formations." European Appl. Res. Rept.-Nucl. Sci. Technol. 2 (1980), 597.
8. Westerman, R.E., "Investigation of metallic, ceramic, and polymeric materials for engineered barrier applications in nuclear-waste packages." Battelle Pacific Northwest Laboratory, report PNL-3484, Richland, Washington, 1980.
9. Molecke, M.A., "Sandia conceptual waste package design guidelines." Sandia National Laboratories, Albuquerque, New Mexico, 1981.
10. Bennecke, "Zusammensetzung von Salzlösungen für Auslaug- und Korrosionsexperimente an verfestigten radioaktiven Abfällen." Physikalisch-Technischen Bundesanstalt, Braunschweig. Protokoll 1981-02-24.
11. "Corrosion resistance of titanium canisters lined with lead for final disposal of reprocessed and vitrified waste from nuclear reactors." (in Swedish). KBS Technical Report 107, Stockholm, 1978.
12. "Copper as canister material for unprocessed nuclear waste - evaluation with respect to corrosion." KBS Technical Report 90, Stockholm, 1978.
13. "Aluminium oxide as an encapsulation material for unprocessed nuclear fuel waste - evaluation from the viewpoint of corrosion." SKBF/KBS Technical Report 80-15, Stockholm, 1980.
14. Molecke, M.A. & Abrego, L., "Status of Sandia HLW canister/overpack program studies." Sandia National Laboratories, Report SAND 80-2191C, Albuquerque, New Mexico, 1980.

15. Johnson Jr., A.B. & Francis, B., "Durability of metals from archeological objects, metal meteorites, and native metals." Battelle Pacific Northwest Laboratory report PNL-3198, Richland, Washington, 1980.
16. Mattsson, E., "Corrosion resistance of canisters for final disposal of spent nuclear fuel." Scientific Basis for Nuclear Waste Management, Plenum Publ. Corp., New York, vol 1, 1979.
17. Abrego, L. & Rack, H.J., "The slow strain rate behaviour of Ticode 12 in aqueous chloride solutions." NACE, Corrosion/81 Toronto, 1981.
18. Mattsson, E., Ekbohm, L., Grenthe, I., Hallberg, R., Hannerz, K. & Vannerberg, N.-G., "Corrosion resistance of copper canisters for final disposal of spent nuclear fuel." Proc. 7th Int. Congr. Metall. Corros., Rio de Janeiro, 1978, 1502.
19. Denison, J.A. & Romanoff, M., "Soil corrosion studies, 1946 and 1948: Copper alloys, lead and zinc." J. Res. NBS 44:259 (1950).
20. Coriou, H., Centre d'Études Nucléaires de Fontenay-aux-Roses, private communication, 1981.
21. Henrikson, S., "Properties of materials in sea-water." Materials in Marine Environment, IVA-rapport 177, Stockholm, 1980.
22. Shreir, L.L., "Corrosion", Newnes-Butterworths, London, 1976.
23. Krysko, W.W., "Blei als Behälterwerkstoff für Atommüll. - Analyse des Korrosionsverhaltens aufgrund archäologischer Funde." Metall 34 (1980), 433.

Table 1. Groundwater composition at the repository site

Analysis	Units	Probable interval	Min. value <sup>x)</sup>	Max. value <sup>x)</sup>
Conductivity	µS/cm	400-600		1100
pH		7.2-8.5		9.0
KMnO <sub>4</sub> cons.	mg/l	20-40		50
COD <sub>Mn</sub>	"	5-10		12.5
Ca <sup>2+</sup>	"	25-50	10	60
Mg <sup>2+</sup>	"	5-20		30
Na <sup>+</sup>	"	10-100		100
K <sup>+</sup>	"	1-5		10
Fe-tot		1-20		30
Fe <sup>2+</sup>	"	0.5-15		30
Mn <sup>2+</sup>	"	0.1-0.5		3
HCO <sub>3</sub> <sup>-</sup>	"	60-400		500
CO <sub>2</sub>	"	0-25		35
Cl <sup>-</sup>	"	5-50		100 <sup>xx)</sup>
SO <sub>4</sub> <sup>2-</sup>	"	1-15		50
NO <sub>3</sub> <sup>-</sup>	"	0.1-0.5		2
PO <sub>4</sub> <sup>3-</sup>	"	0.01-0.1		0.5
F <sup>-</sup>	"	0.5-2		8
SiO <sub>2</sub>	"	5-30		40
HS <sup>-</sup>	"	< 0.1-1		5
NH <sub>4</sub> <sup>+</sup>	"	0.1-0.4		2
NO <sub>2</sub> <sup>-</sup>	"	< 0.01-0.1		0.5
O <sub>2</sub>	"	< 0.01-0.07		0.1

x) The estimated probability that a value will fall between the min. value and the max. value is 95%.

xx) During the phase for drainage and filling, max. 400 mg/l.

TABLE 2

EFFECT OF TEMPERATURE ON THE UNIFORM CORROSION RATE OF TITANIUM ALLOYS IN (O<sub>2</sub> 30 ppb) BRINE A (14)

Alloy	Corrosion Rate (mm/yr)		
	70°C	150°C	250°C
Ti-50A	.00006	.0026	.014
TiCode-12	.00007	.0009	.0032
Ti-Pd	.00009	.0003	.0024

TABLE 3

EFFECT OF DISSOLVED OXYGEN ON THE UNIFORM CORROSION RATE OF TITANIUM ALLOYS AT 250°C (14)

Alloy	Corrosion Rate (mm/yr)			
	Seawater		Brine A	
	30 ppb O <sub>2</sub>	500 ppm O <sub>2</sub>	30 ppb O <sub>2</sub>	450 ppm O <sub>2</sub>
Ti-50A	.0117	.0162	.014	3.2
TiCode-12	.00110	.00060	.0032	.0018
Ti-Pd	.00114	.00062	.0024	.0004



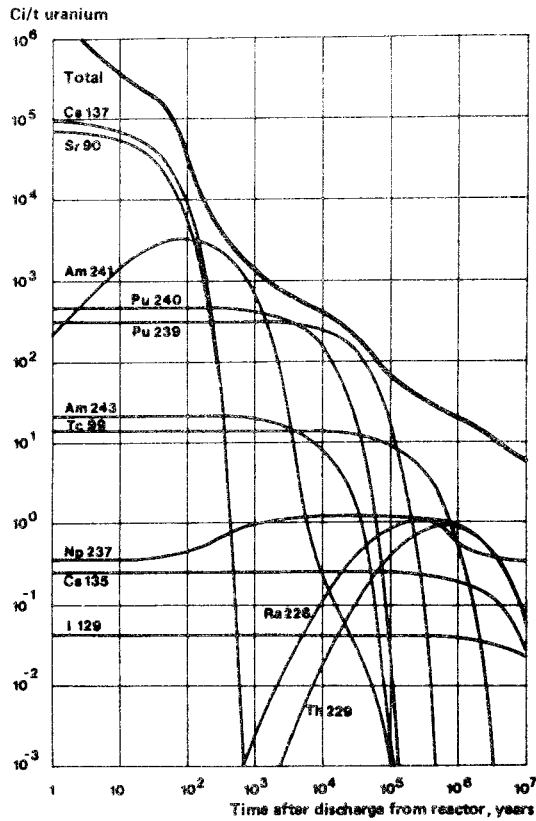


Figure 1. The graph shows how the radioactivity of the radioactive elements in spent PWR fuel declines with time (2).

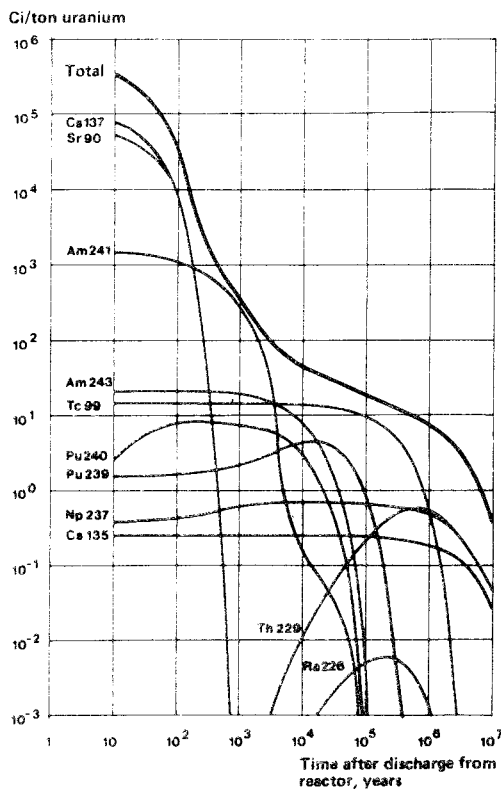


Figure 2. Radioactive elements in high-level waste. It is assumed that reprocessing takes place ten years after discharge of the spent fuel from the reactor (1).

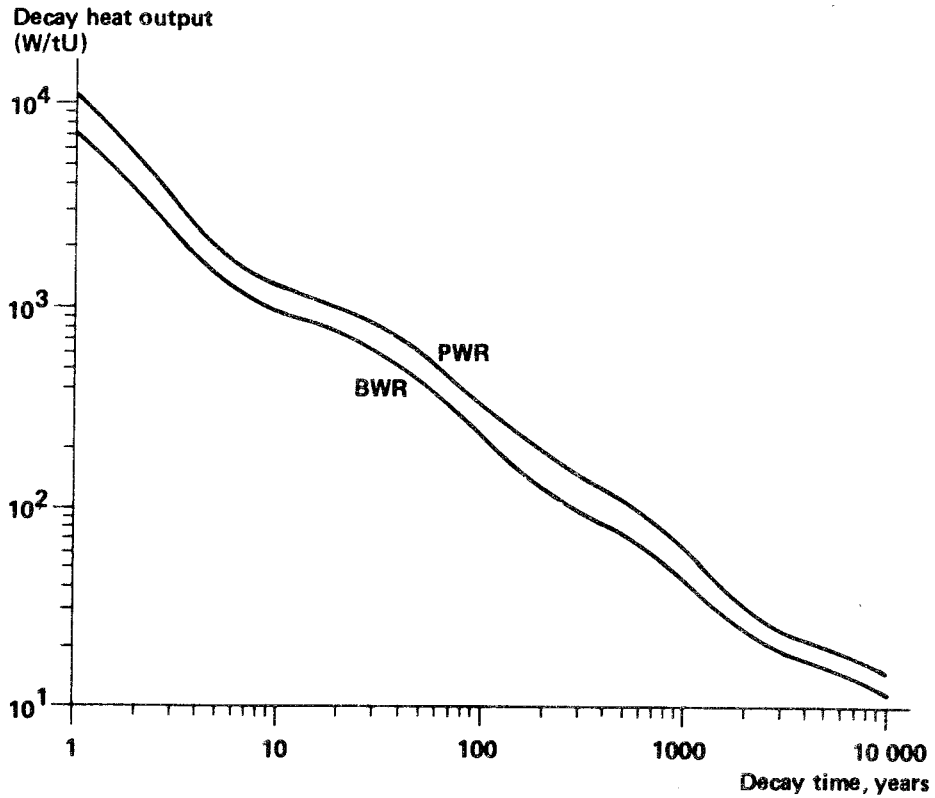


Figure 3. The graph shows how heat generation per tonne of uranium (decay heat output) in spent PWR and BWR fuel declines with time (2).

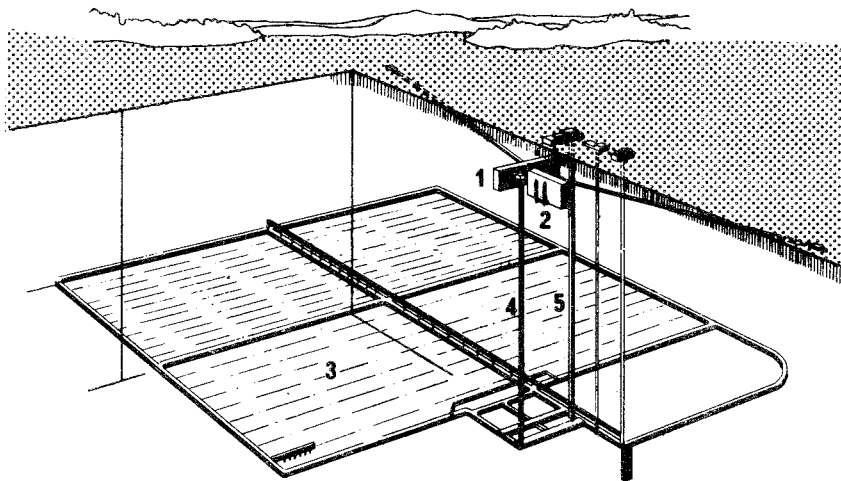


Figure 4. Repository: (1) Receiving and encapsulation station, (2) Intermediate storage, (3) Final repository, (4) Hoist shaft for waste canisters, (5) Main shaft (1, 2).

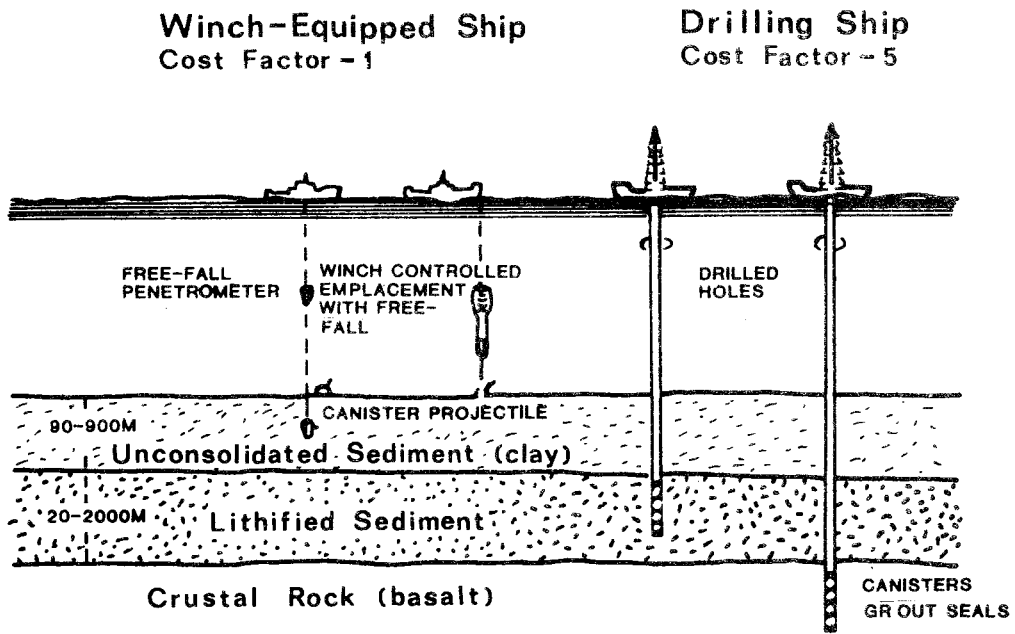


Figure 5. Sub-seabed emplacement concepts (5).

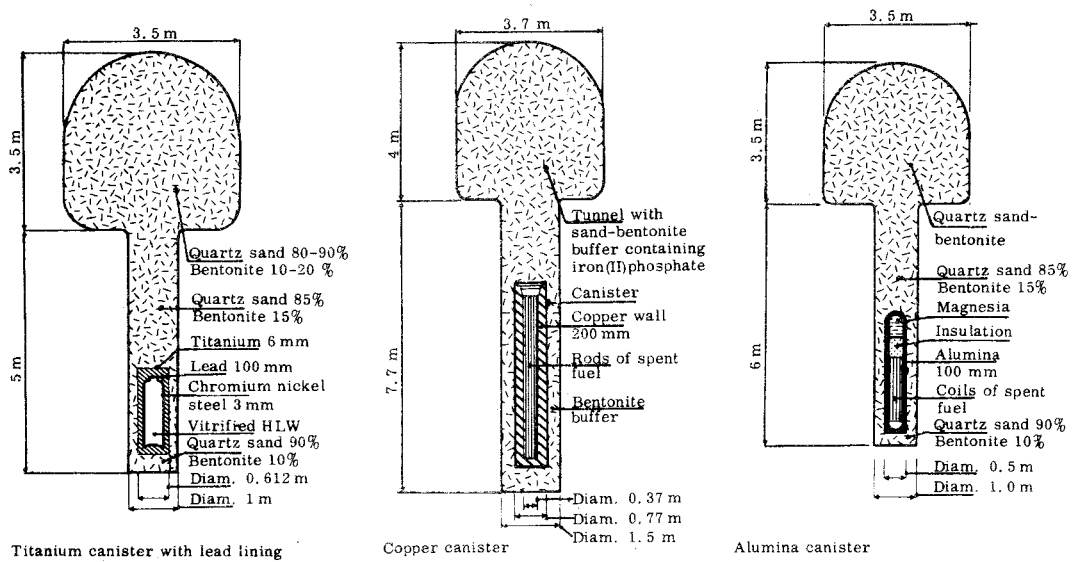


Figure 6. KBS' canister alternatives (16).

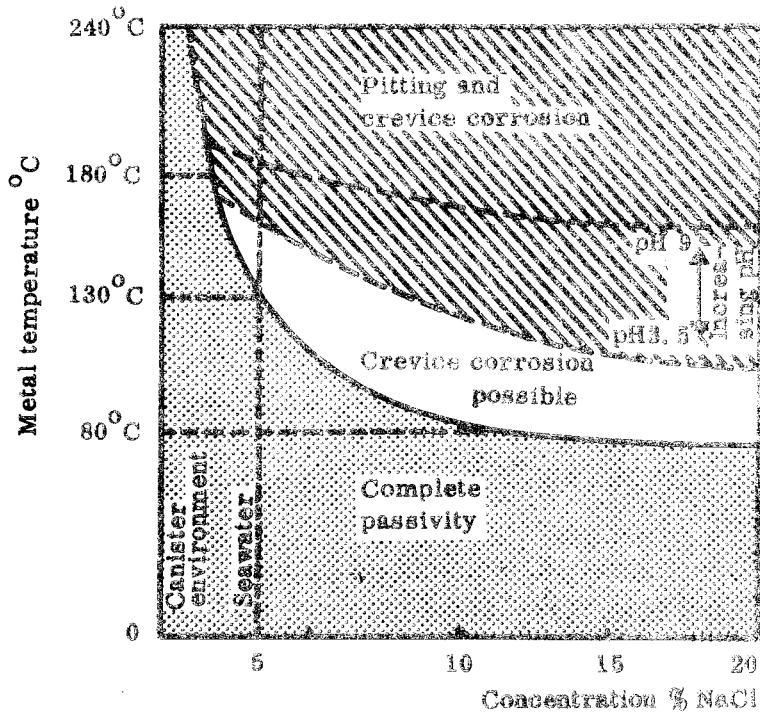


Figure 7. Influence of Temperature, Chloride Content and pH Value on Crevice Corrosion and Pitting of Unalloyed Titanium (IMI) (16).

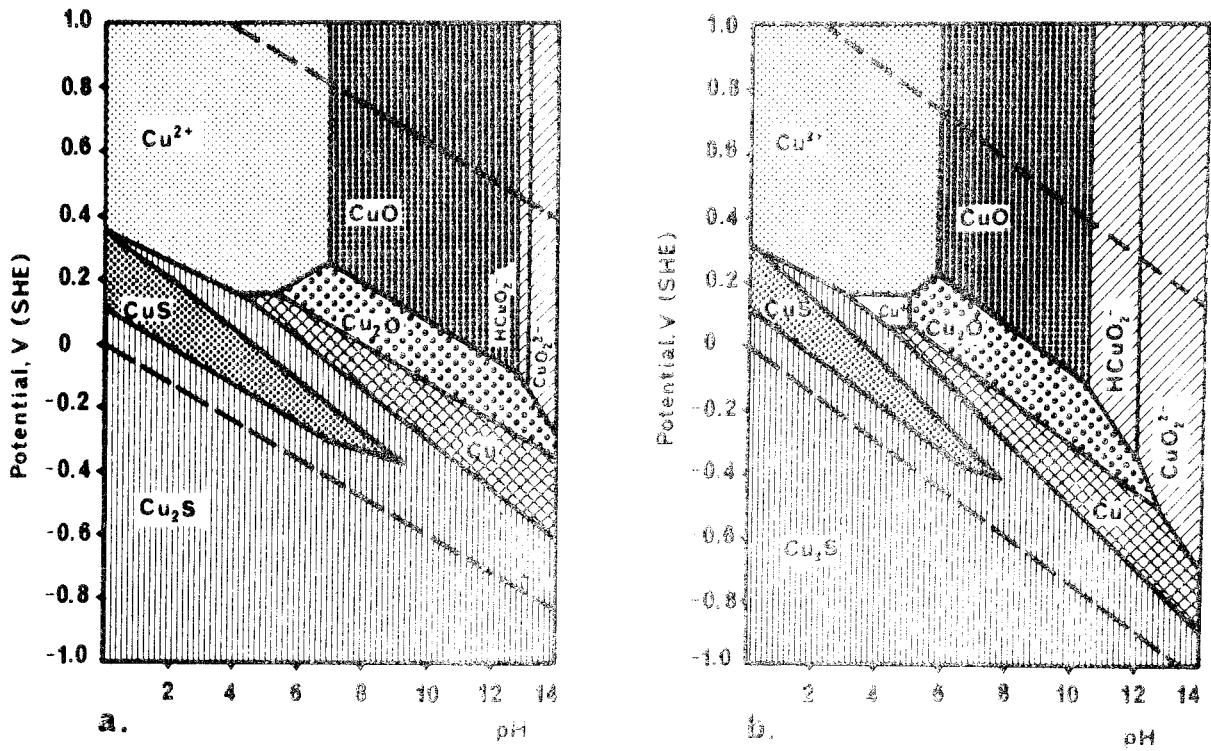


Figure 8. Potential-pH-diagram Cu-H<sub>2</sub>S-H<sub>2</sub>O, 10<sup>-6</sup> M Cu, 10<sup>-4</sup> M S (Ferreira) (16).  
 a. 25°C; b. 100°C.

## FÖRTECKNING ÖVER KBS TEKNISKA RAPPORTER

### 1977-78

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

### 1979

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

### 1980

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

### 1981

- TR 81-01 A note on dispersion mechanisms in the ground  
Ivars Neretnieks  
Royal Institute of Technology, March 1981
- TR 81-02 Radiologisk exponering från strandsediment  
innehållande torium-229  
Karl Anders Edvardsson  
Sverker Evans  
Studsvik Energiteknik AB, 1981-01-27
- TR 81-03 Analysis of the importance for the doses of  
varying parameters in the biopath-program  
Ulla Bergström  
Studsvik Energiteknik AB, 1981-03-06
- TR 81-04 Uranium and radium in Finnsjön - an experimental  
approach for calculation of transfer factors  
Sverker Evans  
Ronny Bergman  
Studsvik Energiteknik AB, 1981-05-07

TR 81-05 Canister materials proposed for final disposal  
of high level nuclear waste - a review with  
respect to corrosion resistance  
Einar Mattsson  
Swedish Corrosion Institute, Stockholm, June 1981