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August 1980

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PRODUCTION AND PROPERTIES OF SOLIDIFIED HIGH-LEVEL WASTE

Knud Brodersen

This report has been worked out according to the agreement between Risø National Laboratory and ELSAM/ELKRAFT concerning advisory assistance from Risø to ELSAM/ELKRAFT's waste management project.

Abstract. Available information on production and properties of solidified high-level waste are presented. The review includes literature up to the end of 1979. The feasibility of production of various types of solidified high-level waste is investigated. The main emphasis is on borosilicate glass but other options are also mentioned. The expected long-term behaviour of the materials are discussed on the basis of available results from laboratory experiments. Examples of the use of the information in safety analysis of disposal in salt formations are given. The work has been made on behalf of the Danish utilities investigation of the possibilities of disposal of high-level waste in salt domes in Jutland.

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1. INTRODUCTION

For more than 30 years, reprocessing of spent nuclear fuel has taken place in various countries. Most high-level wastes from these operations are presently stored in liquid form. Liquid high-level waste will also be produced by future reprocessing of power reactor fuel, but there is a strong tendency to avoid further accumulation as liquid waste. This is because conversion to a solid material is expected to improve the safety of intermediate storage and is regarded as absolutely necessary for safe transportation and final disposal of high-level waste.

Solid materials containing high-level waste should be made in the form of large monolithic blocks having material properties compatible with the surroundings during storage and disposal. The material must be able to resist heat and radiation. The rate of dissolution in water should preferably be low. Production of the material and control of material quality must be possible under the severe circumstances imposed by high activity levels.

Conversion of high-level waste to solid materials have been studied for more than 20 years. The technical feasibility of at least one of the many possible processes has been demonstrated, but further work on process development and characterisation and improvement of materials is going on.

In the following a general review of the state of the art is given with special emphasis on features which are of interest in connection with the Danish utilities investigation of the safety and feasibility of disposal of high-level waste in salt domes in Jutland.

General reviews of production methods and characteristics of solidified high-level waste are available from IAEA (1,2). The development of concepts and technology can be followed in proceedings from American and international conferences (3 to 12).

2. TYPES OF SOLIDIFIED HIGH-LEVEL WASTE

High-level waste is a complicated mixture of a large number of isotopes of many different elements. Some of these are fission products, some actinides, and some simply inactive corrosion products or chemicals added during reprocessing. Many different types of high-level waste exist and are produced according to practice at the reprocessing plants. Mixing of waste from various batches of fuel with, for example, different burnup must be expected.

A composition proportioned as indicated in the three left columns in Table 1 is typical of waste from reprocessing of spent LWR fuel. About 15% by weight are long-lived radioactive isotopes. The rest are stable fission products or corrosion products. A considerable amount of gadolinium can be present if this material is added as a soluble neutron poison to control criticality during reprocessing.

The composition in the table is given as oxides since this is the form in which the isotopes will be incorporated in the solid material. An exception is noble metals which are often present as metallic inclusions. Due to the high activity level only radiation-resistant inorganic materials can be used as additives in the formation of the solidified waste. Various systems have been investigated:

2.1. Glass

Incorporation of oxides from high-level waste as structural members of a glass was proposed in the early fifties and was the topic of many laboratory and pilot plant investigations in subsequent years (2). Glass or more specifically borosilicate glass is still the main alternative for solidification of high-level waste.

Glass has many properties which makes it attractive as a solidification material: Structurally a silicate glass consists of a nearly unordered network of silica tetrahedrons linked at the corners. Some of the silicon atoms are replaced by other network formers of similar size such as boron or aluminum. The resulting imbalance in electrical charge is compensated by network modifiers such as alkali or alkaline earth cations fixed more or less strongly in the relatively large holes in the network. This flexible structure makes glass ideally suited to incorporation of the complicated mixture of high-level waste oxides. The structure is shown schematically in Fig. 1.

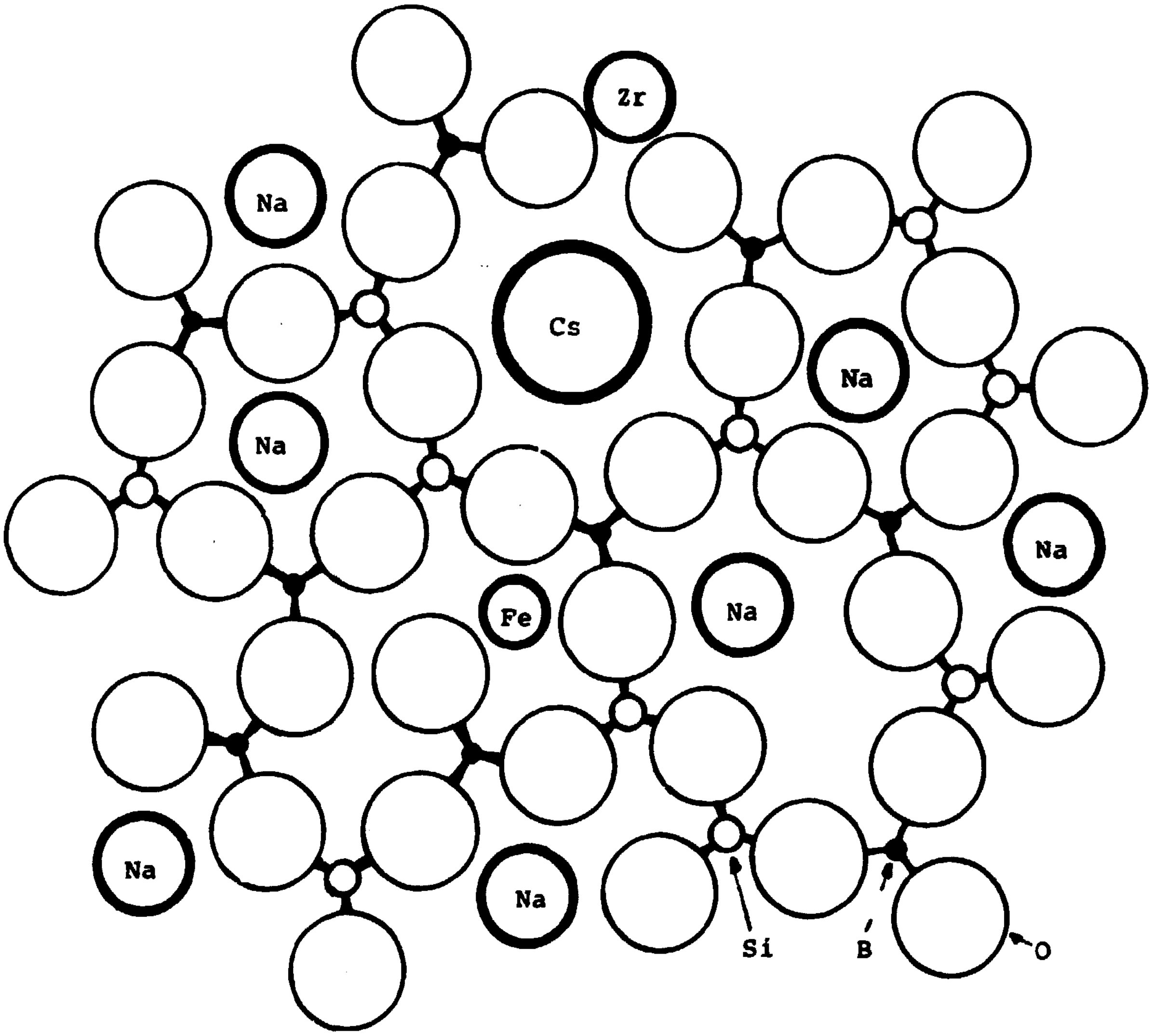


Fig. 1. Schematic structure of high-level borosilicate glass.

The main part of a silicate glass must always be network formers. Structural considerations will therefore place an upper limit on the content of waste oxides, since these act mainly as network modifiers, although some of them may contribute considerably to the quality of the glass. The maximum amount is about 35 weight % waste oxides depending on the composition of the waste.

A high content of waste oxides is desirable when liquid waste with high concentrations of inactive materials is solidified. This is typical of some older types of waste, but modern reprocessing of LWR fuel does not introduce much foreign material into the high-level liquid. To avoid high peak temperatures in the waste units during storage and disposal a considerably lower content of waste oxides must therefore be used in practice. Low values, about 9% fission products and actinide oxides, were proposed by the Swedish KBS study (33) and is also used in the work of the Danish utilities (18). The German reference glass with the composition given in Table 1 contains about twice as much waste oxides and is more typical of the international work going on. Although there is a general tendency to prefer disposal of glasses with relatively low fission product content most of the presently available experimental results have been obtained from glasses with higher fission product content. This is probably mostly because of the considerable time lag in such experiments.

The optimum content of waste oxides in the high-level glass depends on many safety-, resource-, and economy-related parameters, but in general the safety documentation is made easier by decreasing waste concentration. This is an argument for a relatively low waste content at least in the initial phase of the production of such materials where practical experiences with disposal are lacking.

2.1.1. Types of glass

Borosilicate glass of the type given in Table 1 is the most promising of the various glass systems. It combines reasonable production temperatures with good to excellent properties.

A glass composition can be divided into a SiO_2 fraction, a B_2O_3+Al_2O_3 fraction, and a network modifier fraction consisting of Na_2O, CaO, and most of the waste oxides. The composition can then be presented as a point in a triangular diagram as shown in Fig. 2. This is done for the three types of glass discussed in connection with Table 1.

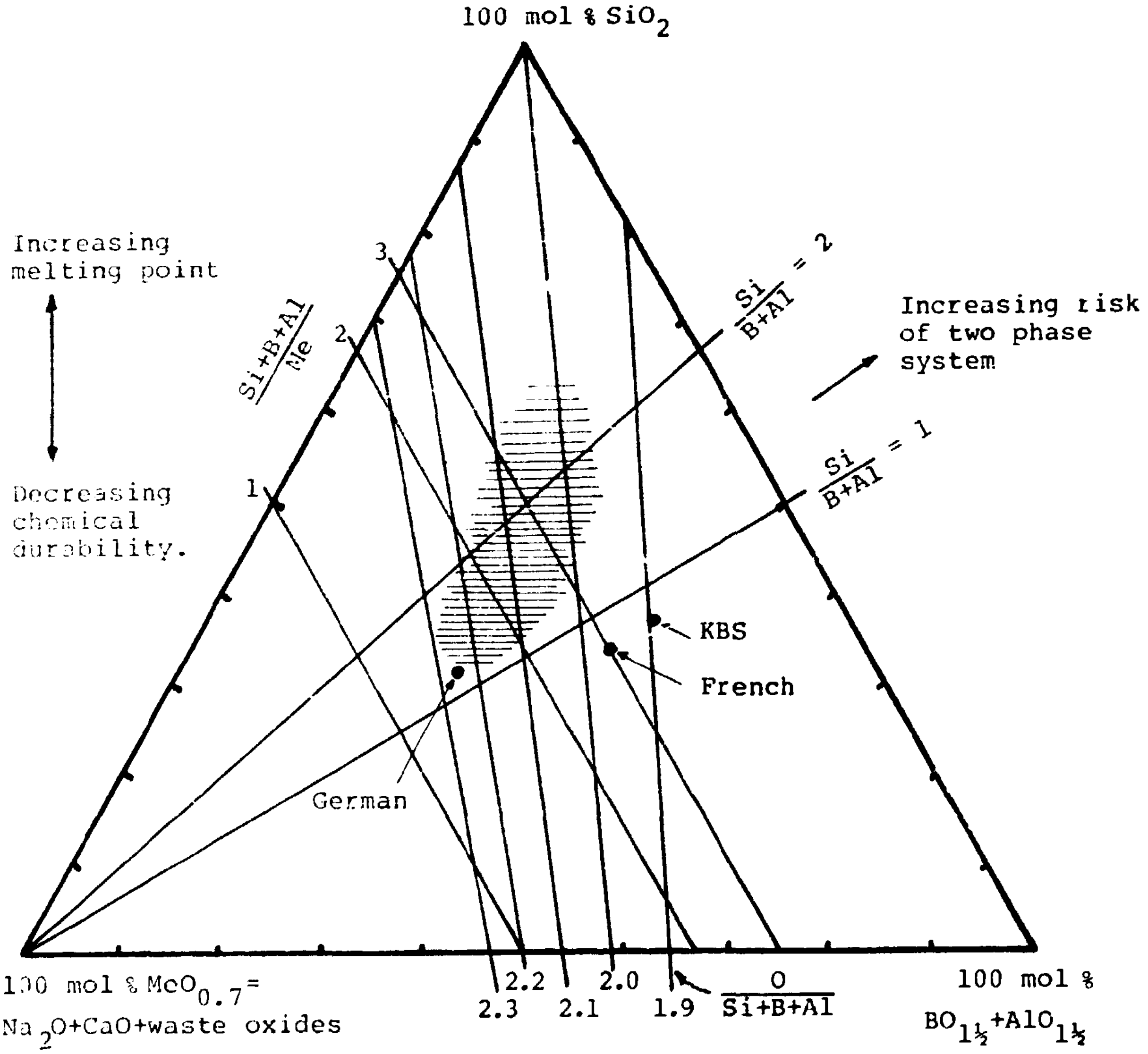


Fig. 2. Triangular diagram of glass compositions. Some general trends in change of properties with composition are indicated.

Table 1. Example of high-level waste composition.

Weight % oxides in glass.

active fission products		active+inactive fission products	
$^{79}SeO_2$	0.004	SeO_2	0.03
		Rb_2O	0.18
^{90}SrO	0.30	SrO	0.50
		Y_2O_3	0.28
$^{93}ZrO_2$	0.47	ZrO_2	2.36
		MoO_3	2.47
$^{99}TcO_2$	0.53	TcO_2	0.53
^{106}Ru	0.04	Ru	1.06
		Rh	0.19
^{107}Pd	0.11	Pd	0.64
		Ag	0.03
		CdO	0.05
^{126}SnO	0.01	SnO	0.03
$^{125}Sb_2O_3$	0.004	Sb_2O_3	0.01
134 135		TeO_2	0.35
$^{137}Cs_2O$	0.85	Cs_2O	1.36
		BaO	0.76
		La_2O_3	0.71
$^{144}Ce_2O_3$	0.08	Ce_2O_3	1.60
		Pr_2O_3	0.67
		Nd_2O_3	2.23
$^{151}Sm_2O_3$	0.02	Sm_2O_3	0.46
		Pm_2O_3	0.05
154 $^{155}Eu_2O_3$	0.03	Eu_2O_3	0.10
		Gd_2O_3	0.06
Total:	2.34%	Total:	16.62%

inactive corrosion products	
Fe_2O_3	1.87
Cr_2O_3	0.53
NiO	0.29
Total	2.69

reference borosilicate glass	
SiO_2	40.2
TiO_2	3.3
Al_2O_3	1.1
B_2O_3	10.8
CaO	2.2
Na_2O	21.9
Corrosion product ox.	2.7
Actinide oxides	1.1
Fission product ox.	16.7
Total:	100.0%

actinides	
234 235 236 $^{238}UO_2$	0.52
$^{237}NpO_2$	0.41
238 239 240 241 $^{242}PuO_2$	0.015
241 $^{243}AmO_2$	0.10
242 $^{244}CmO_2$	0.015
Total:	1.06%

Comments on Table 1:

The table shows a typical composition of high-level waste from reprocessing of LWR fuel with burnup: 33000 MWd/t after a cooling time of one year.
The plutonium losses to waste is supposed to be 0.3% and the uranium losses 0.1% (recalculated from (24) supplemented with additional information about a few long-lived isotopes).

The composition is given in weight % oxides after solidification in a typical borosilicate glass used as reference glass in German studies. The glass contains about 15 weight % fission products + actinides calculated as elements, or 17.7 weight % calculated as oxides. 0.5% of the atoms in the glass are radioactive and will decay to other elements.

The density of the glass is 2.76 g/cm^3.

One t of glass contains waste from 4.8 t of spent fuel.

After only a one-year cooling time the activity per t glass will be about 11 MCi and the heat production about 50 kW.
With a cooling time of 10 years the activity per t glass is reduced to about 1.5 MCi and the heat production to 5 kW.

If glasses with lower waste oxide concentrations are used the activity and heat production per t glass are reduced proportionally.

A typical French glass intended for use in glass production from waste from reprocessing of LWR fuel at LaHague has the composition:

47.6% SiO_2, 18.6% B_2O_3, 12.4% Na_2O, 6.4% Fe_2O_3, 15% fission product and actinide oxides.

Vitrification is supposed to take place about 4 years after removal of the fuel from the reactor. The heat production is then 10 kW/t glass in agreement with calculations given in (19b).
Final selection of glass compositions for use in the vitrification plants at LaHague is first expected in 1984-85 (9d).

A maximum of 13% fission product and actinide oxides is indicated in (19). Of this 0.8% is expected to be UO_2 and 0.4% transuranium oxides, mainly NpO_2.

In the KBS study (33) the following glass composition is given:

54.9% SiO_2, 20.0% B_2O_3, 2.0% Al_2O_3, 11.7% Na_2O, 1.1% Fe_2O_3, 9.1% fission product and actinide oxides.

It is an example of a glass with low waste concentration. The background for the selection of the chemical composition is not given (see also Fig. 2).

Based on classical glass formation theory it is possible to formulate some simple rules for the range of molar ratios of Si/(Al+B), O/(Si+Al+B) and (Si+Al+B)/(Na+Ca+waste) which can be expected to result in glasses of reasonable quality (41). The area of 'good' glasses defined by the molar ratios is shown hatched in the figure. This is not very exact, so the quality of the glasses with compositions indicated by the points, may still be quite acceptable although they fall somewhat outside the area. The French glasses must contain a considerable amount of 3-coordinated boron.

Extensive ranges of compositions have been investigated experimentally (5c,22,31,32,50,61). Besides variations in the relative amounts of the main components SiO_2, B_2O_3, Na_2O, and waste oxides the effects of various additives such as Al_2O_3, TiO_2, ZnO, CaO, and Li_2O have been investigated. Improved leach resistance has been demonstrated for glasses containing such additives, but some of them seem to increase the tendency to devitrification (5c,5f,27).

Decreasing the content of waste oxides from about 20 to 9% introduces some possibilities for improving the glass. A simple dilution with a proportionate amount of the inactive glass components may not be optimal. The various options should be investigated systematically (39).

A theoretical interpretation of observed variations in properties with composition is difficult in these very complex systems. The selection of new compositions of high-level glasses must therefore always be based on laboratory studies using the large body of experimental investigations of other glass compositions as guidance.

Other glass systems have also been worked on. Some of the earliest experiments with high-level glass were made in Canada in 1955-60. They made active samples of silicate glasses containing aluminum instead of boron. A typical composition was 50% SiO_2, 20% Al_2O_3, 16% CaO, 9% Na_2O, 4% K_2O, and 1% Fe_2O_3 (3a). Melting such glasses requires high temperatures, but they can probable be produced in ceramic joule-heated meters now under development. They can be very leach resistant and that can be part of the explanation of the low leach rates found in the Canadian burial experiment (5d, see also section 4.3.2.8).

A completely different approach is represented by the phosphate glasses, where the silica network is replaced entirely by phosphate. Attractive production features with this system are a completely liquid feed, relatively low operating temperatures, low viscosity of the melt, and compatibility with sulphate; the melt is extremely corrosive, however (8e).

2.1.2. Glass as a material

Glasses, which are attacked only relatively slowly by water, can easily be prepared. Some compromises between leach restistance, melting range, evaporation of volatile components, corrosion of equipment and other process-related parameters will have to be made, but these will normally not present serious difficulties. Leach resistance and the relatively high tolerance of the flexible glass structure against radiation will be discussed in detail later, but a few phenomena associated with glass as a material will be mentioned below:

2.1.2.1. Devitrification. Glass is an undercooled liquid and is therefore not a system in thermodynamic equilibrium. It has a tendency to devitrify: forming crystals of defined composition in a matrix of glass which will be depleted or enriched accordingly in some elements. The change in composition may result in inferior leach properties compared with the original glass, and the mechanical stress from volume changes during formation of large crystals may crack the glass and increase the external surface of the unit. This possibility of devitrification is the principal disadvantage associated with solidification of high-level waste in the form of glass. Although it may not represent any real safety problem it makes the material properties difficult to document over long time periods.

The tendency to devitrify is a function of the composition of the glass and the temperature of the system.

By measurement of, for example, thermal expansion or other semilar properties of a glass it is easy to show that there is a fundamental change in this and related properties at the so-called glass transition temperature, T_g, where a large increase in the thermal expansion coefficient is found (8f,30). Above this temperature, which has a value of 500-550°C in typical borosilicate glass, devitrification can be expected to proceed rapidly due to an opening up of the glass structure and the resulting large increase in mobility of the ions in the glass.

In principle, devitrification is a two-stage process consisting of nucleation and crystal growth. In high-level glass small inclusions of noble metals or undissolved refractory oxides, which can act as seeds in nucleation of crystals, will probably always be present. This facilitates nucleation although primarily at relatively high temperatures (6b).

It has been shown experimentally that devitrification can take place if borosilicate glass is heated to temperatures between 500 and 800°C for relatively short periods (12a,27). It is more difficult to show that nothing happens during very long periods of storage at lower temperatures. Theoretical studies indicate, however, that the diffusion-controlled growth of crystals will be exceedingly slow, involving periods of billions of years. The presence of water is likely to accelerate devitrification, but it is still a very slow process if only the temperature is reasonably low (8a).

Investigations of the influence on the material properties of devitrification artificially induced at higher temperatures provide the additional information that devitrification, even if it takes place, normally is of minor importance for the relevant properties (12a).

That glass can persist as material for a very long time is shown by samples containing glass spheres billions of years old, which have been collected from the surface of the moon, where they are preserved by the completely dry environment. Tektites and vulcanic obsidian glasses up to 35 million years old have been found on the earth's surface and at the bottom of the ocean. Remineralisation due to the presence of water is thought to be the determining factor for the lifetime of these materials as amorphous solids (6b,8a,57).

2.1.2.2. Immicibility. Close examination of a glass sample may sometimes show that in reality it consists of two immicible undercooled liquids with different compositions. One phase may be completely embedded as inclusions within the other or they may form interconnectiong networks. The scale of the inclusions of the single phases may typically be from 0.001 to 0.01 μm (6b, 9k). Immicibility on the microscale can be expected in borosilicate systems with a low content of modifiers. It should be looked for when characterising such glasses since it may influence the leach rate and also other properties. Immicibility on the macroscale is well known from laboratory and pilot-plant experiments with high-level glass. If the glass together with sodium contains much molybdenum and especially if there is sulphate present, a so-called 'yellow phase', mainly consisting of Na_2MoO_4 and Na_2SO_4, may separate entirely from the melt. This type of phase separation cannot be tolerated, since the yellow phase is easily soluble and contains much Cs and Sr. The formation of the yellow phase can be controlled by selection of glass composition. A high concentration of B_2O_3 or substitution of sodium with lithium diminishes the tendency to yellow phase formation (27) and is probably one of the reasons why so much boron is used in French glasses. Another possibility is melting under slightly reducing conditions obtained by adding silicon or carbon to the melt (9k).

The formation of yellow phase should not be a problem with glasses containing low concentrations of fission products and therefore small amounts of fission product molybdenum. This is the case with the glass used in the Danish utilities study. A further condition is, however, that there be no sulphate present in the waste and in the additives used in the glass production. This is a question of quality control at the reprocessing plant.

Phase separation of a material containing technetium has been noticed in some American experiments (62,11a).

Other types of phase-separated materials may also occur when limits of solubility of specific components in the glass are exceeded. The small spherical inclusions of noble metal fission products have already been mentioned. The solubilities of actinide oxides in typical borosilicate glass have been investigated. In general a weight % above 3-4 can be kept in solution, but plutonium solubility is influenced by the rare earths and is decreased to about 1% if much gadolinium is present (29). It follows from Table 1 that the solubility limits for actinides in molten glass are not exceeded by actual waste compositions. This does not prevent particles of actinide oxides from being incompletely dissolved in the glass if the melting time is too short or the temperature too low.

As already mentioned small inclusions of undissolved material may influence devitrification. Otherwise they are probably of minor importance. Since the particles often are of considerably higher density than the glass there is a theoretical possibility of settling, but this does not seem to be a very pronounced effect. This is probably due to the small particle size and the relatively high viscosity of the molten glasses even at the refining temperatures. Small gas bubbles is another type of inclusion which often appears in the glass. They are probably of no importance.

2.2. Crystalline materials

The obvious method of avoiding possible deleterious effects from uncontrolled crystallisation of solidified high-level waste is to produce materials which are designed for crystallisation and for general chemical equilibrium with the surroundings. Research related to this possibility is going on in many countries, but the state of the knowledge and especially the practical experience is not sufficiently advanced to decide whether or not crystalline materials represent feasible future alternatives which can compete with glass. The concept has received considerable - and maybe not quite unbiased - support as a theoretically sound solution of the problem of material stability (59), but it has also been pointed out that radiation and transmutation damage in the crystals make the concept of a long-time equilibrium system somewhat doubtful and that many practical problems have to be solved (8a,9c).

The possibility remains that research and development may result in solidification methods which are easier to work with than glass making and/or which produce materials with more suitable characteristics as seen from a long-term safety point of view. Such schemes may be adopted by future reprocessing centres and may result in production of waste units having properties and dimensions different from the borosilicate glass units which are the most probable products now.

2.2.1. Types of crystalline materials

The following types of systems are under investigation:

2.2.1.1. Calcinates. Simple calcination by drying of liquid high-level waste followed by thermal destruction of the resulting nitrates by heating to 500-800°C is the initial step in glass-making and has also been carried out on a technical scale as a separate operation. The resulting materials are dusty powders from which activity is easily leached. The leaching properties can be greatly improved by adding soluble silica and other suitable compounds to the liquid waste before calcination. In the resulting so-called 'Super-calcine' most of the activity is fixed in well-defined crystalline minerals of low solubility: cesium, for example, in pollucite, strontium in sodalite or apatite, and so on. The composition of the mixture must be carefully adjusted so that mutually compatible minerals are produced and easily soluble minerals such as Cs_2MoO_4 are avoided.

It has been demonstrated that this is possible even with very high waste loadings: up to 80% (48.8 g).

Super-calcine as produced is a powder, but it is also possible to make granulated materials as it is done, for example, in the LOTES Process developed at Eurochemic (8e). Here the main component of the calcinate is aluminum phosphate.

2.2.1.2. Ceramics. Dense monolithic crystalline ceramic materials can be made from calcinates in the following ways: as fusion-cast, by hot-pressing, by sintering, and as a glass-ceramic.

The original 'Synrock' process (16) is an example of a fusion-cast crystalline material proposed for solidification of high-level waste. Other mixtures of oxides forming mutually compatible minerals may in principle also be usable. Synrock A, which has to be made at about 1350°C, is composed as a nearly eutectic mixture of perovskite $CaTiO_3$, hollandite $KAlTi_3O_8$, barium felspar $BaAl_2Si_2O_8$, and zirconia ZrO_2. On cooling the melt forms well-developed crystals of the minerals although substantial substitutions of elements take place. Fission products and actinides added in moderate amounts (< 10%) will mainly be present in solid solution in the minerals. Slightly reducing conditions are necessary to avoid formation of water soluble K_2MoO_4. The high melt temperature and the possibility of formation of residual phases with inferior properties are main drawbacks with this Synrock concept.

Large scale hot isostatic pressing of precalcined powders are technically feasible using equipment developed by ASEA, Sweden (9i). Hot isostatic pressing has been proposed as a method for production of Synrock B ceramics at lower temperatures (9j,16a), and for consolidation of Super-calcine (8g). The production of dense rutile, TiO_2-based materials by hot pressing of titanate ion exchangers loaded with high-level waste has been demonstrated at Sandia, USA (10b) and in Sweden where work is continuing in cooperation with Kjeller, Norway, using waste stored from the early reprocessing studies at that place (40).

The production of materials by hot isostatic pressing is not without problems. The need for a relatively tight control of composition can be a special difficulty, but the main drawback is the use of large-scale high-pressure and high-temperature equipment in active areas (9c).

The consolidation of oxide powders by sintering is conventional ceramic technology using simple furnace equipment. In principle it is possible to make dense materials by careful firing of well-defined powders, but considerable residual porosity will probably be the norm. Votalization of isotopes can be a problem.

By careful heat treatment, glasses with suitable compositions can be converted to glass ceramics in which the size and composition of the crystals are controlled. This possibility has been investigated in Germany (28). The products seem to be excellent, but the need for exact temperature control is a disadvantage and may put limitations on the size and shape of the blocks of waste materials.

2.2.2. Properties of crystalline materials

The consolidated crystalline materials described above are often strong, dense, and heavier than glass. Their radiation resistance has not been studied sufficiently, although it recently has been shown by study of old uranium containing natural samples that the two main actinide-containing minerals in the new Synrock B,C and C compositions: zirconolite, $CaZrTi_2O_7$, and perovskite, $Ca,SrTiO_3$, are not very susceptible to damage by α-radiation and can be expected to accommodate, for example, the decay of Sr-atoms to Zr-atoms quite well (16a).

The crystalline materials can be expected to resist high temperatures and especially the combination of high temperature, high pressure, and the presence of water better than glasses. The resistance of Synrock materials under hydrothermal conditions in water as well as brine has been demonstrated (9j). The crystalline materials are therefore interesting candidates for disposal systems with high thermal loadings, but the use of the materials may not result in special safety advantages compared with glass where only moderate temperatures are involved.

On the other hand, a safety analysis of a disposal system based on glass should not be made invalid by substitution of glass with a consolidated ceramic material of equal or better quality, provided the content of active material is approximately the same. Possible future changes in solidification processes at the reprocessing centres are therefore of minor importance in connection with the Danish utilities study of disposal of waste in salt domes.

2.3. Composite materials

Various systems for consolidating granulated calcined waste have been proposed. The general idea is to convert granulated waste materials into monolithic blocks and at the same time provide each particle with a separate micro-encapsulation of an impermeable material.

2.3.1. Types of composite materials

Glass or ceramics can be used as matrix material, but metals are generally regarded as more suitable. Cast copper, lead, and aluminum alloys and hot-pressed aluminum and titanium have been proposed for the matrix (8e,55). Complicated systems involving combinations of layers of pyrolytically deposited graphite and alumina on the waste particles have also been made (9e,48). A cermet consisting of waste oxides dispersed in an iron-nickel alloy produced by hydrogen reduction is also under development (9h). The use of composite materials provides a method for low temperature consolidation of super-calcine or similar products. In the PAMELA process developed by Eurochemic, Belgium, specially prepared beads of phosphate glass or granulated calcine from the LOTES process are embedded in a lead-antimony alloy matrix (8e).

2.3.2. Properties of composite materials

Composite materials based on metals are strong and have excellent heat conductivities. The low temperature difference between centre and surface of the units is valuable in intermediate storage and in the initial period of final storage (8c). The leach rate will depend on the corrosion rate of the metal and on whether or not the individual waste particles are in contact with each other.

The availability of some of the metals (lead, copper) for waste conditioning may be limited in the future. The economic value of such materials and the chemical toxicity of lead may be undesirable factors. The substitution of glass with a composite material may require some modification of a safety analysis, mainly due to the greater emphasis which must be placed on metal corrosion problems.

3. PRODUCTION METHOD FOR SOLIDIFICATION OF HIGH-LEVEL WASTE

The following description of the state of the art is mainly restricted to production methods for high-level borosilicate glass.

3.1. The French AVM and AVH systems

Two years of smooth active operation of the French AVM plant in Marcoule has proved beyond doubt that full-scale technical production of high-level borosilicate glass is feasible. About 70 t of active glass have been produced in these two years without any serious operational troubles (12, panel discussion).

Construction of the plant in Marcoule was initiated in 1974. Cool testing began in '77 and active operation in June '78. The plant is intended only for processing of the types of French waste stored at Marcoule, but similar and somewhat larger plants, the AVH system, are being designed for use at the reprocessing centre at LaHague. These plants could be available for solidification of reprocessing waste from a future Danish nuclear power programme. Typical borosilicate glass units produced at such a plant are therefore used as a design basis in the Danish utilities study of the feasibility of disposal in salt domes in Jutland. French glass was also used as a design basis in the Swedish KBS study (33).

3.1.1. Production system

A diagram of the AVM system is shown in Fig. 3. The layout of the hot cells in which the equipment is placed is shown in Fig. 4. The figures and the following description of the operation of the plant are taken mainly from (5a,8b,21).

A batch of high-level liquid is placed in the feeding tank. A sample is analysed and adjustments to the chemical composition made, if necessary. The liquid then flows at a rate of about 40 l/h through a metering device to the calciner. This is a rotary kiln consisting of a slightly inclined and slowly rotating metallic tube heated electrically from the outside. The tube is closed with specially designed seals at the ends. The calcined material (8-9 kg/h) flows directly from the kiln into the melter which is also fed at regular intervals with measured amounts of previously prepared glass frit (9-12 kg/h).

The melter consists of an inconel vessel heated by induction. The through-put is about 15 kg/h of glass melted at 1100-1150°C. Steam and off-gas from the reactions are treated and decontaminated in the associated off-gas system. Some evaporation of cesium and ruthenium takes place, but most can be reintroduced into the feed. 120 kg glass is emptied from the system every 8 hours by melting a solid glass plug formed inside a cooled drain tube in the bottom of the melter. The glass is cast into thin-walled stainless steel cylinders with diameter 35 cm and height 180 cm (19). A different type of cylinder with diameter 50 cm and height 100 cm is mentioned in (8b). The maximum diameter of

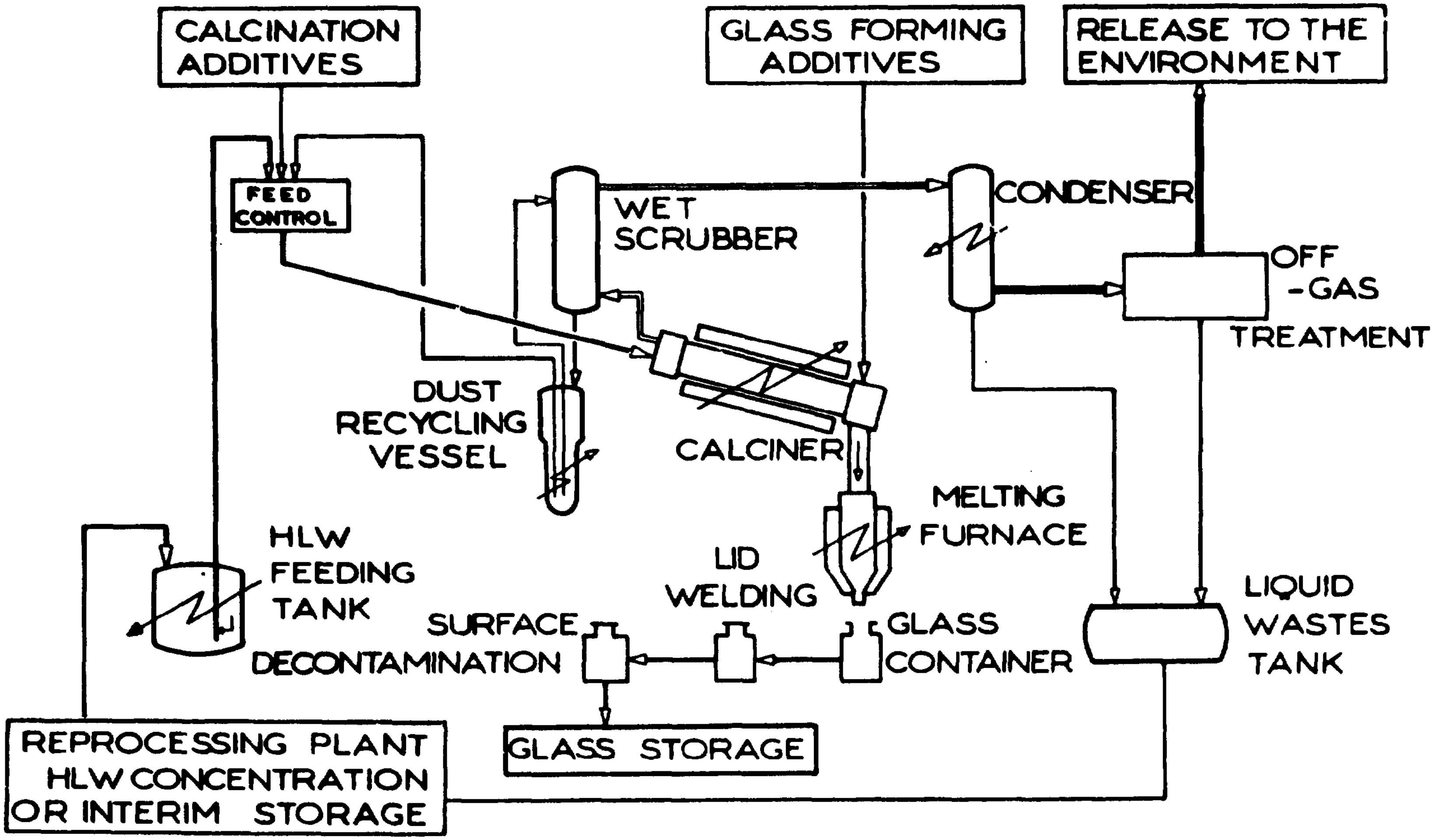


Fig. 3. Diagram of the Marcoule vitrification facility. (8a)

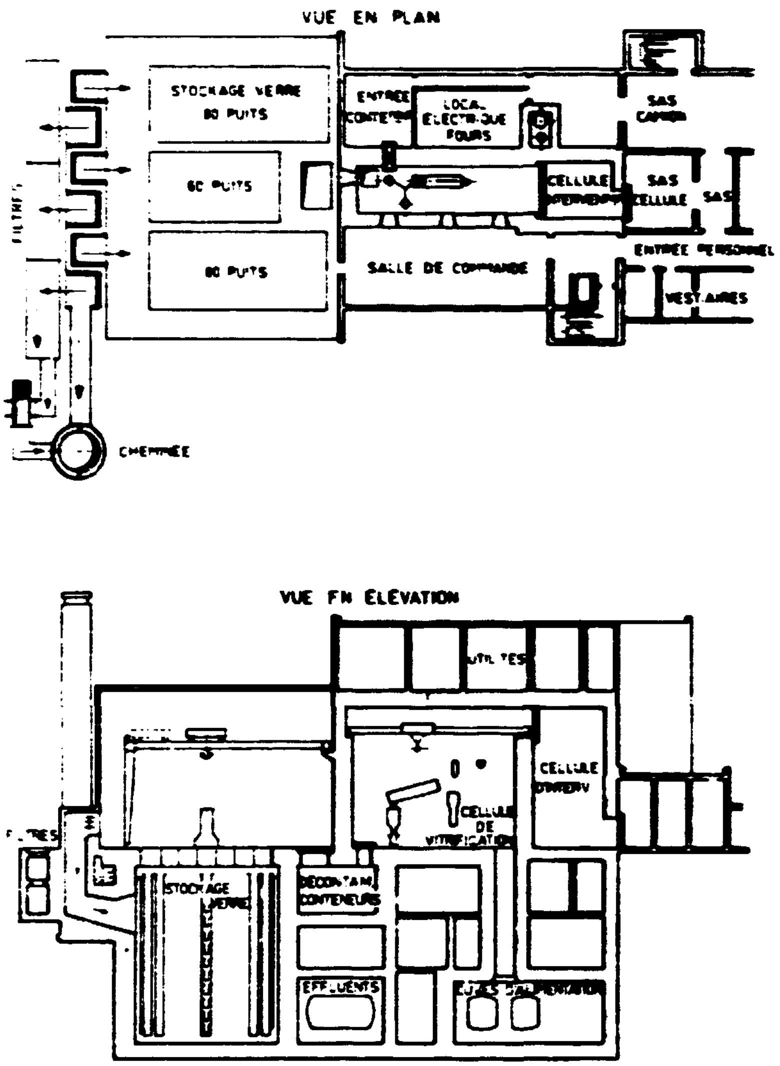


Fig. 4. Layout of the hot cells and the intermediate storage area at the Marcoule vitrification facility. (5a)

the cylinder is limited by transmission of decay heat but can otherwise be selected independently of the glass production equipment if only the necessary handling facilities are available in the cell. The unit used in the Swedish KBS study had an external diameter of 40 cm (33).

Three batches of 120 kg each are cast into a cylinder. It is equal to about 150 l glass. An empty space is left at the top to secure sufficient space for the last batch. After a few hours cooling a lid is welded on top of the cylinder. On the following day the outer surface of the steel container is decontaminated with a high-pressure water spray, and finally the unit is placed in the air-cooled intermediate storage area.

3.1.2. Quality assurance

Documentation of the agreement between the specified composition and the composition of the actual glass produced depends on the feed analysis and precision of the various metering devices. Considerable deviation from the specified composition can probably be tolerated without significant decline in the quality of the glass.

The weight of the cylinder is recorded continuously during the casting operation. The viscosity of the molten glass is an important operational parameter. It influences the homogeneity of the melt and governs the rate of emptying of the melter. Normally this operation takes 10-15 minutes. The viscosity of molten borosilicate glass at 1000°C typically decreases by about a factor 2 for each 30°C increase in temperature (30), but when the temperature is known, a deviation from the expected emptying time is an indication of a change in composition (63b). The rate of emptying could therefore be used as an indirect control of the process.

Homogeneity of the solidified glass, the presence of inclusions of only partially melted calcine or phase-separated material, and the degree of cracking of the cast glass can be estimated on the basis of investigations of glass units produced in inactive experimental runs or possibly by inspecting selected active units. Only limited information is available for the French system. Chemical homogeneity has been demonstrated by sectioning a glass unit produced in an early discontinuous pilot plant (4b). American experiments indicate that extensive cracking due to stresses developed by rapid cooling of glass units must be expected (8f). Cracking was also found in French glass units coiled rapidly in water. The surface increase was estimated to a maximum factor of 10. An insulated glass unit that was cooled very slowly also developed some cracks (7a).

Measurements of heat production and radiation properties are obvious non-destructive tests which can be used to characterize the final glass units. The γ-radiation spectrum has, for example, been measured as a function of height on an American experimentally produced glass cylinder (63a).

Contact with the French glass producers indicates that there will be no problems in getting glass made with prespecified fission product concentrations in the range between 9 and 13 weight % (19). Very low concentrations may require too much of available melting capacity. Future research may result in changes in the selected chemical composition of the glass.

The isotopic composition of the solidified waste will not be identical with the fuel sent for reprocessing but will reflect something like the mean value for the types of fuel reprocessed at the plant. Specification of the isotopic composition of the glass product must be expected to be available before the units are returned.

3.2. Other systems

Technical full-scale or nearly full-scale glass production plants are under development or construction at various other places (1). The important systems seen from a practical point of view are probably the British HARVEST process, the German VERA process, modifications of Eurochemics PAMELA process, and somewhat more remote processes from the USA, Japan, India, and the USSR. It will be of interest to survey whether or not the expected products from these plants could serve as substitutes for the French glass. The important parameters will be the size of the units, especially the outer diameter, the heat production rate per unit length and the technical possibilities of making quality assurance measurements.

The British HARVEST process is discontinuous and based on the early FINGAL experiments at Harwell (2,9a,14). In this process calcination and melting of a borosilicate glass take place in the stainless steel container itself. An industrial size plant is scheduled for hot operation at Windscale in 1988. The design has not been fixed, but will be based on experience with small active and inactive plants and with a full-scale inactive facility. To reach large through-put capacity in such a system calls for large diameter (0.5-0.6 m) cylinders as containers. Possibly an annular shape with outer diameter 1.3 m will be used. HARVEST will probably be a high-cost system for production of glasses with low fission product concentration. Direct or indirect control of the quality of the product seems to be difficult.

The German VERA process exists in various pilot scale versions. The major difference from other systems is in the calcination step, where reducing conditions are maintained to limit volatilization of ruthenium (5b). The process is continuous like the French one, and should give a very similar product. Casting is made in separate containers without process-related limitations on dimensions. A metallic melter as well as a ceramic one with so-called 'joule heating' by electrodes sending current through the glass have been investigated. Information about development to an industrial scale is unavailable at the moment, but some of the features seem to be included in the following system (9f).

The PAMELA process has been mentioned before. It produces a phosphate glass in the form of small beads which are later enclosed in a metal matrix (8e). Work on the use of the principle on borosilicate glass is continuing. The size and shape of the final storage units are unimportant in this process. It has the inherent advantage of easy control of samples of the produced glass and easy remelting of products outside specifications. There should be no practical problems associated with the use of this type of product as a substitute for French glass. A low heat rating per unit length can be obtained by diluting the glass beads in more metal. Investigations of alternatives to lead as matrix would be desirable. DWK, Germany, supports the building of a full-scale plant at Eurochemic, Belgium. It should be in operation in 1985. It will produce borosilicate glass and should be able to do it as well in the form of beads in a metal matrix as in form of ordinary cylindrical glass units (9f).

The work in Japan, India, and USSR will not be commented on. A full-scale plant should soon be operating at Tarapur in India (2).

In the USA many different options have been investigated and many basic investigations are being performed. As far as glass production technology is concerned the ceramic melter under development at PNL is of special interest (9g). Joule-heated ceramic melters, which by the way were used first at Risø in experimental work with simulated radioactive borosilicate glass (17), seem to be a common feature in many of the continuous glass production plants under development. They are well known on a large scale from the ordinary glass production industry and permit the melting and pouring of glasses with considerably higher melting range than is possible in metallic melters. Operational problems due to phase-separation of a heavy bottom layer have recently been noticed at PNL (63a).

Most of the technological efforts in the USA are directed against old military waste. As long as reprocessing of power reactor fuel is 'deferred indefinitely', development of technology specifically designed for waste from this type of fuel must be expected to be given secondary priority.

In general, it can be concluded that at least the continuous glass production systems under development should be able to make waste units having properties compatible with a disposal system for French glass cylinders. Some degree of flexibility regarding reprocessing options is therefore maintained.

4. PROPERTIES REQUIRED BY HANDLING AND DISPOSAL

Glass units, in the following exemplified by French borosilicate glass cylinders having diameters of about 0.4 m and heights about 1.5 m, should be able to withstand interactions with three different types of environment: 1) at the intermediate storage area, 2) during transportation, and 3) in final disposal. Each of these types of environment in combination with the time history of the waste places emphasises on special material properties of the units:

4.1. Intermediate storage

Storage of new glass units for periods from 5 to 50 years or even longer in engineered structures above or below the ground surface is expected to be normal practice in the future. The purpose is to permit decay of short-lived and some of the long-lived isotopes so that heat generation is reduced. The storage area will be cooled artificially by water or air. Besides physical integrity of the units, the most important single material property in this period is the heat conductivity, which, together with the heat generation rate, the geometrical dimensions of the unit, and the surface temperature, determines the temperature at the units centerline.

4.1.1. Heat conductivity

The temperature along the centerline of a cylindrical unit of a homogeneous material in which heat production takes place evenly distributed is, as a first approximation

$$T_{center} = T_{surface} + \frac{d^2 \times q}{16 \times k} \quad {}^{o}C$$

where the heat generation per unit volume, q watt/cm^3, is determined by the fission product concentration and decreases as a function of time according to the decay of the activity.

The heat conductivity of typical borosilicate waste glass increases slightly and nearly linearly with temperature from $k = 0.008$ watt/cm·°C at 20°C to 0.012 at 500°C (1). The variation with temperature is disregarded in the formula.

Inserting $d = 40$ cm, a typical value of $k = 0.01$ watt/cm·°C and the heat production given in the comments to Table 1: 10 kW/t or $q = 0.027$ watt/cm^3 glass containing 15% fission product and actinide oxides from 4-year-old waste results in a calculated temperature difference between centerline and surface of 270°C.

Similar glass units produced from 1-year-old fuel would have a temperature difference above 1000°C which is unacceptably high. Postponing the glass production until the waste is 10 years old will reduce the temperature difference to 120°C.

A glass with lower fission product concentration will have a proportionately lower temperature difference. The centerline temperature increases rapidly with increasing unit diameter.

The selection of unit diameter, solidification time, and fission product concentration is therefore important and may influence the properties of the material since centerline temperatures in the neighbourhood of or above the glass transition temperature $T_g \cong 500$°C may result in devitrification.

Maximum permissible centerline temperatures well below the glass transition temperature should be agreed upon and the earliest acceptable solidification time regulated accordingly.

The efficiency of the artificial cooling will also influence the centerline temperature somewhat: The surface temperature and theserefore also the centerline temperature of the units can be expected to be higher in an air-cooled system than in a water-cooled one, but another phenomenon is probably more important in this connection:

4.1.2. Thermal contraction

When the hot glass-filled containers are cooled rapidly, decontaminated with water spray or placed in a cooling basin, the more rapid temperature declines in the surface layer than in the centre of the glass results in higher contraction and considerable strain and cracking in this layer. This problem can be minimized although not eliminated completely by slow cooling and careful handling of the units. Selection of an air-cooled storage system may, for example, be preferable.

Another thermal mechanism, which on a somewhat longer time scale might lead to cracking, is the fall in centerline temperature which is a result of the steady decrease in decay heat. Below 400°C a typical value of the linear thermal expansion coefficient for borosilicate glass is: $9 \times 10^{-6}\ {}^{o}C^{-1}$ (1,30). A reduction in centerline temperature from say 400°C to 100°C will therefore result in a volume contraction of about $3 \cdot 9 \cdot 10^{-6} \cdot 300 \cdot 100 = 0.8\%$ of the central part of the glass unit relative to the surface layer.

These phenomena have been investigated in the USA, theoretically as well as experimentally (8f). Some results are summarized in Fig. 5. They show the relative increase in surface areas due

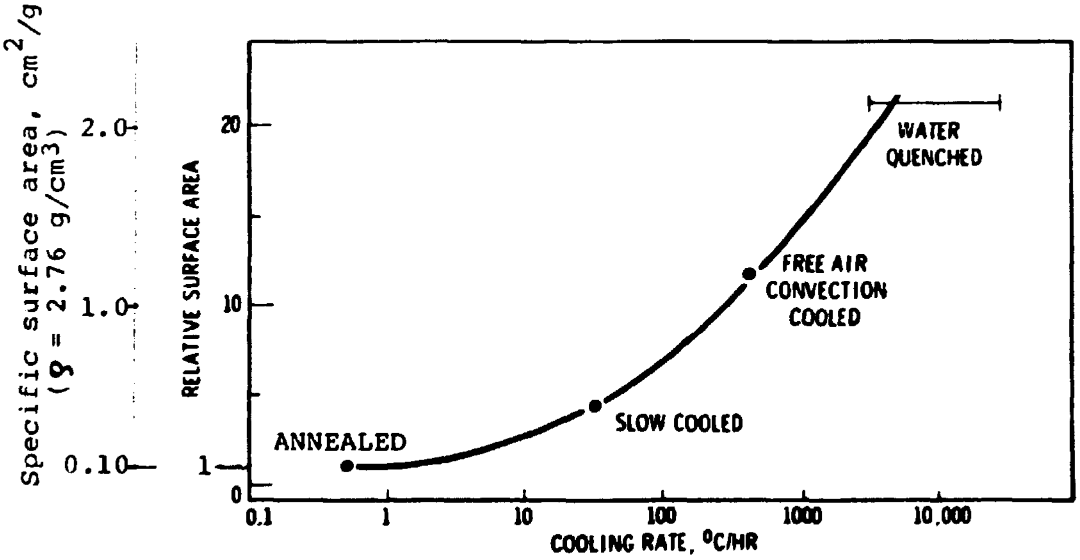


Fig. 5. Effect of cooling rate on the generation of increased surface area in 15-cm diameter and 150-cm long glass castings (8f).

to cracking of 15-cm diameter glass cylinders as a function of cooling rate. Even slow-cooled units develop some crackings. This is in agreement with observations made in France (7a). The specific surface area of monolithic glass cylinders decreases proportionally with increase in diameter. In the case of cracked glass, the specific surface area was found to be nearly independent of cylinder dimensions. The value for free air convection-cooled cylinders of a glass with density 2.8 g/cm^3 will be about 1 cm^2/g glass.

The cracking is most pronounced in the outer layers. The fragments of cracked glass are kept tightly together as a form of three-dimensional jig-saw puzzle by the stainless steel container, which will be under considerable strain after cooling due to the higher thermal expansion of steel relative to glass.

It has been proposed that stress, cracks and other imperfections should be removed by annealing - heating to about 500°C - or even remelting of the glass blocks after the period of prolonged intermediate storage, but before they are placed in final disposal. The processing time for annealing will be long - some weeks for each unit due to the necessarily slow cooling rate.

A facility for annealing or remelting of glass might also be useful for the reconditioning of units which have been damaged, for example, in transportation accidents.

The question whether the necessary furnace systems for such operations should be available at the disposal site has not been resolved, but the improvements in safety and in the documentation of safety associated with the somewhat better known material which can be obtained by such a treatment, must be balanced against the difficulties and hazards involved in an additional process step.

If intermediate storage in water pools is used there must be some kind of assurance against the possibility that water has penetrated the stainless steel container through cracks, pittings or defective welded lids, and filled, for example, an empty void at the top of the unit.

4.2. Transportation

Transportation of the glass units from the reprocessing plant to the country where the waste materials originated may take place either before or after a period of prolonged intermediate storage. During transportation through public areas units of solidified high-level waste will always be protected by specially designed transport containers similar to those used in the transport of spent fuel elements. Such a container in itself will prevent dispersal of activity in all reasonable forms of accidents in which it might get involved. The high physical integrity of the glass blocks, their low leachability and high resistance, therefore, mainly serves as desirable additional safety factors. Accidents, for example, in the form of a fall from a crane, may also take place with the unprotected units during handling at the solidification plant, at the intermediate storage area, and in the final disposal operation. In such cases high physical integrity of the unit is important.

Impact strength of full-scale glass units have been investigated in the USA using standard fall tests, for example, in the form of 9-m free fall onto an unyielding surface. The stainless steel containers with inactive glass used in the experiments were not breached by the impact so there were no releases. Some quantities of fine materials were produced inside the containers, but most of the glass was undamaged. Correlations between fractions of fines and impact velocity were established and are shown in Fig. 6 (8f).

It is the fraction below 10 μm in size which represents the main inhalation hazard in accidental releases. The consequence of mechanical damage which does not involve breaching of the container is simply an increased specific surface of the material in the container. Values of up to 20 cm^2/g have been measured. The result is increased leaching of material from the unit in the initial phase of contact with water.

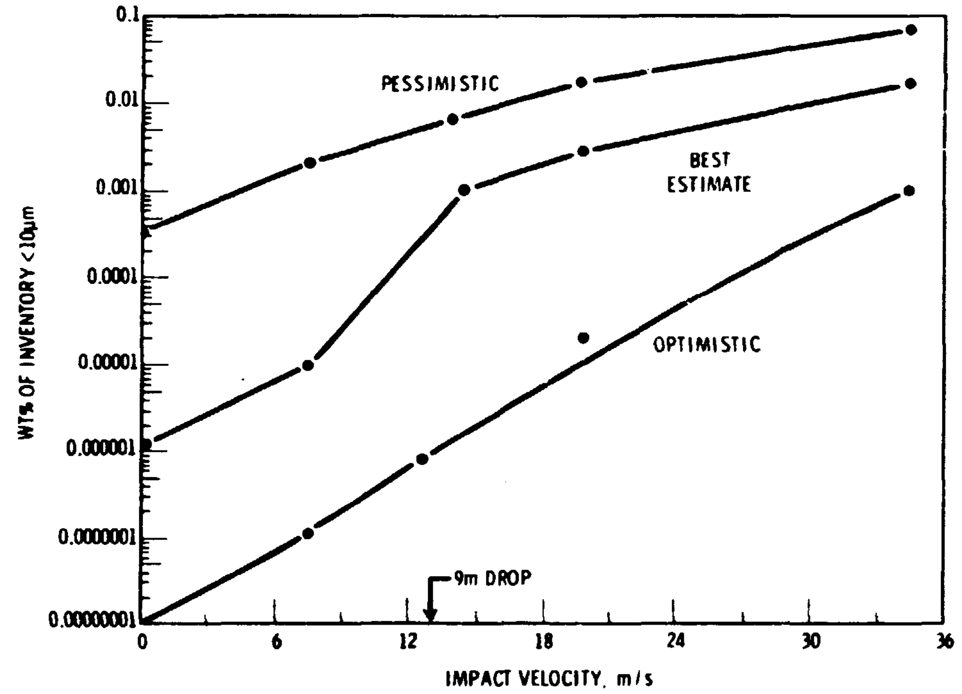


Fig. 6. Prediction curves for sub-10 µm fines generation (15- and 5-cm diameter glass cylinders in stainless steel containers after impact on unyielding target) (8f).

Mechanical properties as, for example, bulk strength of typical borosilicate high-level waste glass are similar to industrial glass. A bulk strength of 38±7 MPa has been measured (8f). The strength is very much dependent on defects in the surface of the glass. Due to stress corrosion it can be expected to decrease slowly with time if water is present (6d). The contribution of a cracked glass to the overall strength of a waste container is a complicated matter.

4.3. Final disposal

The most characteristic feature of the final disposal phase of waste management is the long-time periods involved. Safety studies extended over millions of years have been attempted, for example, in the KBS study (34). Such studies - also on a less ambitious scale - must be backed by a reasonably secure knowledge of the probable behaviour of the waste as material. The fundamental problem in this connection is the necessity to extrapolate measurements from relatively short-time experiments over very long periods. Wherever possible, such extrapolations should be based on a theoretical understanding of the mechanisms involved. Additional supporting information can be derived from the study of old natural materials which can serve as model substances over the long-time behaviour of the waste (8c). Unavoidable uncertainties must be covered by other safety factors in the overall disposal system.

The main phenomena associated with long-term behaviour of high-level waste, for example, in the form of borosilicate glass, are alterations due to the radioactivity of the material and to interactions between the material and the surroundings, with leaching by water as the most important example.

4.3.1. Radiation and other decay effects

High radiation doses will be received by the glass during storage and disposal.

Beta- and gamma-radiation is mainly the result of fission-product decay. The accumulative dose over infinite time increases with the concentration of active fission products in the glass at the time of vitrification and is therefore dependent on the cooling time of the waste before this operation. The accumulative dose of β- and γ-radiation to a typical high-level glass will be about 10^{12} rad of which most is delivered during the first few hundred years of storage. The effect of this type of radiation on the material is insignificant compared with the effect of α-radiation (1).

Alpha-radiation is produced by decay of actinides in the waste. The accumulative dose depends on which type of fuel the waste has been produced from, the fraction of plutonium and uranium left in the waste, and the time of cooling before reprocessing which determines the fraction of ^{241}Pu converted to ^{241}Am. Long cooling times before reprocessing result in higher α-doses in the glass. Due to the long half-lives of most of the actinides the α-dose rate will be relatively low but the accumulation of dose continues over very long periods: from about 10^{17} α's per g glass at 10 years storage to about 10^{19} α's per g glass at 10^6 years (5c).

The effect of α-radiation in glass is mainly displacement of atoms: about 130-200 from the α-particle itself and 1500-2000 from the recoil of the decayed nucleus (1,13). About half of the number of atoms in high active waste is expected to be displaced by α-decay (13), but the saturation value of the resulting defects in the material will be much lower due to slow annealing by diffusion.

The effect of α-radiation on glass has been studied by increasing the concentration of short-lived α-emitters such as ^{242}Cm or ^{238}Pu in the glass. This makes it possible in a five-year experiment to simulate α-doses equal to storage of a normal high-level glass in about 10 000 years. The dose rate is of course increased proportionally. This may lead to measurements of saturation values which are too high for the effects compared with real waste which will receive the same dose over a much longer period.

The observed effects are:

4.3.1.1. Change in dimensions. Alpha-radiation may result in dilations as well as contractions of the glass depending on composition and heat treatment. Volume increases or decreases of up to 1% have been measured and may result in stresses in the glass units. Volume contraction is most common in glass. Large dilations in some crystalline materials have been observed (6a,9c,12c,15).

4.3.1.2. Stored energy. The energy stored in the form of defects in the glass can be released by heating. It is, however, a characteristic of glass compared with crystalline materials that this release takes place relatively slowly over a large temperature range from 70° to about 600°C. A self-sustained sudden release of stored energy is therefore improbable.

The largest amount of stored energy has been measured in a German study using glasses of a composition similar to the one given in Table 1. The values were about 350 J/g glass. Saturation was reached after about 10^{18} α's/g glass. The samples were irradiated at room temperature (24).

Other experiments (5c,6a,12c,15,45) have given results in the range 80-100 J/g glass. In some of the experiments at least the lower values can be ascribed to higher storage temperatures during irradiation: 50° and 170°C (5c).

A maximum energy content of 100 J/g seems probable for glasses stored at 50°C or above. With a typical heat capacity of 1 J/g•°C, this is equal to a maximum temperature increase of 100°C if the stored energy should be released adiabatically. This is of low probability and the possible consequences are small.

4.3.1.3. Helium generation. An α-particle is the nucleus of a helium atom. A dosage of 10^{18} α's/g glass accumulated after 10 000 years storage is therefore associated with the formation of an equal number of atoms or molecules of helium gas. If the gas is released at normal pressure this is equal to about $22\ 400 \cdot 10^{18}/6.02 \cdot 10^{23} = 0.037$ Ncm^3/g glass or about 13 Nl helium in a typical French glass cylinder with 360 kg glass. Some of this helium will be kept in solution in the glass. This is typical in the experiments mentioned above with increased α-dose rate at room temperature. High helium concentrations are also known from old natural glasses of vulcanic origin (7a). If the temperature is increased some of the helium may diffuse to the surface of the glass and result in considerable pressurization of the container if the gas is not able to escape and there is insufficient free volume inside the container.

The diffusion behaviour and the solubility of helium in borosilicate glass have been studied at increased temperatures (1, 5c,5e,46). A sample heated to 50°C in 1 year did not lose any helium, but 12% of the helium diffused out of a sample held at 170°C (5c). The diffusion coefficient as a function of temperature for helium in a typical borosilicate glass has been measured in the USA. An initial value of

$$D = 0.0021 \exp - \frac{15000}{R \times T} \text{ cm}^2/\text{sec}$$

was found. This value decreases by about a factor 10 at high α-doses probably due to trapping of helium atoms in radiation defects. Release rates for helium at various temperatures and at different degrees of cracking of the glass were calculated. It was found that if 10% free volume is allowed in the containers significant pressurization is improbable with waste from LWR fuel (46).

4.3.1.4. Other effects. No significant changes in mechanical properties of irradiated samples have been observed. The change in leach rate with irradiation seems to be small and lies within experimental uncertainties (1).

Another phenomenon, which might influence the properties of the waste, is the decay of radioactive isotopes of elements to other elements with different properties and valency. It has been calculated that this will result in something like an excess of 10^{20} electrons/cm^3 glass or about 0.5% of the total number of valency electrons in the material (1). This means that the valency of some of the components in the glass is uncertain, but the phenomenon is probably of minor importance.

The unordered structure of glass is well suited for the accommodation of changing elements. The same might not be the case with crystalline materials which can be expected to be much less tolerant of change in size and valency of the atoms in their ordered structure. Large differences in behaviour of various types of crystals can be expected, and it seems to be possible to find crystalline materials which can tolerate such changes (16a).

4.3.2. Leaching and other interactions with surrounding materials

Transport by water is the main mechanism by which activity can move from waste to the biosphere after geological disposal. The initial phase in such transport is the solubilization of active material from the waste units. This process is called leaching. It is a complex phenomenon involving many physical and chemical properties of the waste material and its surroundings.

Leaching requires water to be present and in contact with the waste.

Transportation of activity by diffusion from high-level glass into dry surrounding material may also take place but is such a slow process that it normally can be disregarded. A typical diffusion distance in rock salt at 100°C will be some few cm in millions of years (22).

The quantity of interest in connection with safety evaluation of leaching from waste units is the rate of release of the various radio nuclides from a given amount of waste. Ideally the rate of release of isotope i at time t can be calculated from the formula:

$$x_i = M \cdot O \cdot S_i \cdot \rho \cdot a_i \text{ Ci/day}$$

where

M	g	is the amount of waste present,
O	cm^2/g	is the specific surface of the waste material,
S_i	cm/day	is the leach rate for isotope i,
ρ	g/cm^3	is the density of the solidified waste, and
a_i	Ci/g	is the concentration of isotope i in the material.

To some extent all the quantities in this formula are functions of time and treatment of the waste.

4.3.2.1. Quantity of waste. The original quantity of waste stored, M_0, must be expected to be known with certainty. The quantity of waste, M, may then decline with time at a rate depending on the rate of solution of bulk materials from the glass.

If the bulk leach rate, S_b, is a constant and the original waste blocks have a uniform size, b cm, equal to an initial specific surface, $O_0 = 6/(\rho \cdot b)$ cm^2/g, and if the leaching proceeds without further subdivision of grains, then it can be shown that the fraction of M_0 which has gone into solution at time t, is:

$$r = 1-(1 - \frac{2 \cdot S}{b} \cdot t)^3 = 1-(1 - \frac{S \cdot O_0 \cdot \rho}{3} \cdot t)^3 \cong S \cdot O_0 \cdot \rho \cdot t$$

$$\text{if } t < 1/(2 \cdot S \cdot O_0 \cdot \rho)$$

This means that the declining size of waste particles, which is one result of leaching, is of importance for the rate of release only when more than half of the material has been leached away. It is a condition that the waste particles are of a reasonably uniform size. This is not normally the case.

4.3.2.2. Specific surface. The original specific surface, O_0 cm^2/g, of the glass in the waste units may depend on the size and shape of the cylinders but is mainly a function of the degree of cracking due to thermal contraction of the glass or to mechanical damage during handling. Helium generation, devitrification, and interaction with water may, at least theoretically, result in further cracking during storage.

Most of these phenomena have already been discussed. American investigations indicate that values of O_0 between 0.5 and 1 cm^2/g independent of cylinder size may be expected due to thermal contraction (8f). This is equal to a typical mean lump size b from 2 to 4 cm since $O = 6/(\rho \cdot b)$ for reasonably proportioned shapes. The surface will, of course, be distributed over lumps of different sizes. This is especially typical of mechanical damage, which is likely to produce a small amount of nearly pulverized glass at the point of impact, while the rest of the glass lumps in the unit are more or less unchanged. A unit of this type may have an initially high rate of release while the small particles with large specific surface are leached away, but after this period it will return to the situation that is normal for undamaged containers.

It is improbable that helium generation should result in much further cracking of the glass (46).

Devitrification will probably not take place if the material is stored dry at temperatures much below the glass transition point. If devitrification takes place, cracking will result only if large size crystals with volumetric properties much different from the glass are produced. This is not typical for the glass compositions under investigation now. The tendency to form large crystals of $ZnSiO_4$ was one of the reasons why the Americans dropped the use of high ZnO concentrations from their glass formulations.

The risk of devitrification is higher if water is present, but the process is still very slow at low storage temperatures: 150°C or most probably lower, since use of corrosion-resistant containers makes access of water to the glass extremely unlikely in the first many years of disposal where the temperature is highest.

The presence of water may also result in further cracking of the glass due to stress release by stress corrosion. That moisture, especially acid moisture, is likely to reduce the strength of glass is well known from investigations of normal glasses (64,65). How this phenomenon may effect large lumps of active glasses under internal stress during storage has not yet been investigated. An introduction to the phenomena is given in (6d).

In an undisturbed disposal situation the lumps of cracked glass are kept tightly together by the container or by the surrounding geological formation. Restrictions in flow rate and the chemistry of the concentrated solution developing in the cracks is likely to diminish the effect of the increased specific surface on the rate of release from such a unit. Partial closing of the cracks by swelling of hydrated surface layers in them is a possibility.

4.3.2.3. Leach rate expressions. In the formula on p. 39 the leach rate, S, has the unit cm/day. This is the most easily visualized presentation of leaching indicating simply the thickness of a layer of material removed per unit time from the surface of the sample. It may, however, lead to the misconception that leaching is a simple surface corrosion phenomenon.

In the literature the leach rate is often given in leach units: $R = S \cdot \rho$ g/cm$^2 \cdot$day, where the density ρ g/cm^3 normally can be regarded as a constant.

In older UK literature, the measurement of leach rate is given as a leach factor: $F = 1/(7 \cdot S)$ week/cm.

Instead of the leach rate, S, the accumulative fractional amount of leached material as a function of time is often reported. The fraction of material removed by leaching from a sample at time t is:

$$z = \int_0^t M \cdot O \cdot S \cdot \rho \cdot a \, dt / M_0 \cdot a_0 \cong O \cdot S \cdot \rho \cdot t$$

if variations in the parameters with time are disregarded. Corrections for decay of tracer activity are normally made. It is convenient to measure z since no knowledge of surface area of the samples is necessary, but z is not of much general use if this information is unavailable.

Another measure of accumulative release is the equivalent leached thickness:

$$L = \int_0^t S \, dt = S \cdot t \text{ cm},$$

if S is a constant.

L is not a real thickness of a removed layer but the equivalent of the amount of partially removed material from a somewhat thicker layer.

The same material will often have different L and S values for the different elements in the material. Leaching is therefore not the same as surface corrosion, which would give identical leach rates for all elements. Diffusion and probably also adsorption phenomena, which depend on the chemical properties of the various leached species, are also involved.

An expression of the form:

$$L = A\sqrt{t} + B \cdot t \text{ cm}$$

has been proposed for the description of leaching phenomena. A and B are constants determined from experiments. The first term is dominant in an initial diffusion-controlled phase, and the second term is dominant in a later phase when a simple solution process is supposed to take over. The formula seems to fit experimental results quite well, but should not be regarded as representing an exact model of the reactions that take place (4a,9k).

The shift from mainly diffusion- to mainly solution-controlled leaching takes place at a time $t = A^2/B^2$. The experimental determination of this time of transition is interesting since it is a measure of the ability of the glass to form a protective coating in the leaching environment under investigation. Values of t greater than one year have been found in some experiments (9k) while other systems seem to have very short diffusion-controlled phases (15,43).

A mathematical expression for the equivalent leached thickness L has been derived assuming a constant corrosion rate u for the glass combined with diffusion of individual active isotopes out of the glass (see Fig. 7) (10a,59). The expression is:

$$L = \frac{1}{2}ut + \left(\frac{1}{2}ut + \frac{D}{u}\right) \operatorname{erf} \sqrt{\frac{u^2 t}{4 \cdot D}} + \sqrt{\frac{t \cdot D}{\pi}} \exp\left(-\frac{u^2 t}{4 \cdot D}\right) \text{ cm}$$

This expression has the same general properties as the simple

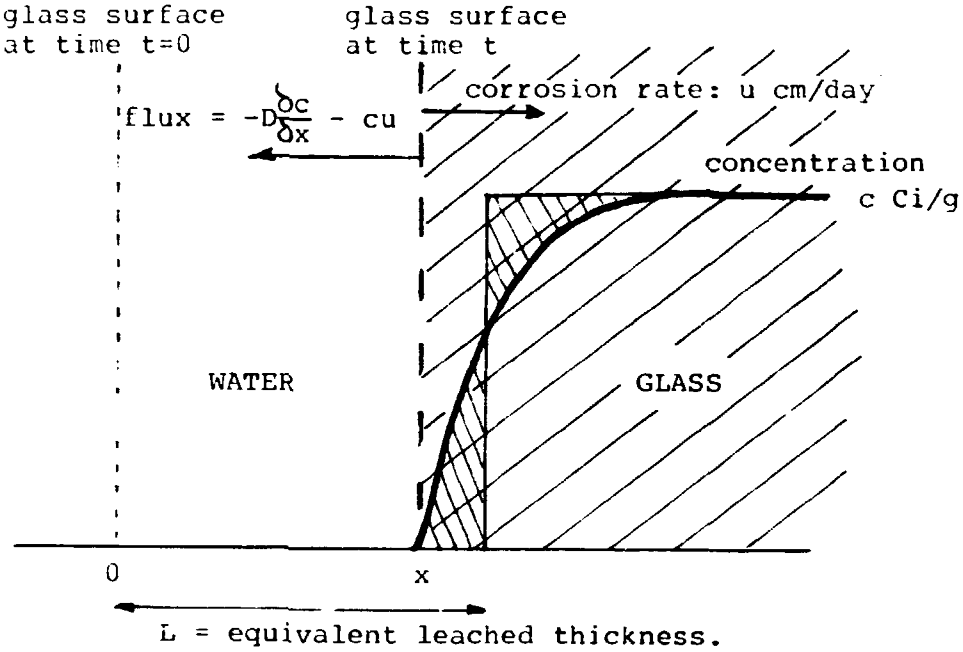


Fig. 7.

formula above and can be fitted to single experiments, but it has recently been shown to be insufficient for the explanation of leaching of a mixture of actinides (62). The concept of a constant corrosion rate, u, may therefore be invalid or the chemical interactions cannot be described by a single diffusion coefficient for each isotope. This will be the case if, for example, absorption in the surface layer on the glass is involved.

In practical safety analyses of geological disposal it is often assumed that the leach rate S is a constant independent of time, so that L = S•t cm (33). This simplifies the calculations very much. The assumption is probably always conservative - possibly in some cases too conservative. Values of S measured in leaching experiments after more or less steady-state conditions are reached and used in such calculations. See also section 4.3.2.6.

4.3.2.4. The leaching phenomena. The behaviour of ordinary glasses in contact with water have been studied for many years. The theory for the interaction is as follows (6c,67):

The initial step is thought to be indiffusion of water or a proton into the glass where it reacts with the silica structure according to:

$$\equiv\mathrm{Si{-}OMe} + \mathrm{H}^+ \rightleftarrows \equiv\mathrm{Si{-}OH} + \mathrm{Me}^+ \quad \text{or}$$

$$\equiv\mathrm{Si{-}OMe} + \mathrm{H_2O} \rightleftarrows \equiv\mathrm{Si{-}OH} + \mathrm{Me}^+ + \mathrm{OH}^- \ .$$

The observation of an isotopic effect when heavy water is used indicates that diffusion of water is the rate-limiting step (66). If Me^+ is sodium it will diffuse relatively fast out of the glass while the hydroxyle ion reacts and disrupts the oxygen bond in the silica network:

$$\equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{OH}^- \rightleftarrows \equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}O}^- \ .$$

The nonbridging oxygen formed reacts with more water forming a new hydroxyl ion which may repeat the previous reaction:

$$\equiv\mathrm{Si{-}O}^- + \mathrm{H_2O} \rightleftarrows \equiv\mathrm{Si{-}OH} + \mathrm{OH}^- \ .$$

The overall result is the formation of a gel-layer of hydrated silica at the surface of the glass and the diffusion of Me^+ and OH^- out in the surrounding water. The pH and the concentration of cations in the water will therefore increase at a rate depending on the diluting capacity of the system which mainly is determined by the ratio between the area of the exposed glass surface and the volume or flow rate of the leach water. In a static or nearly static system with only little water present the pH will increase to high values which at pH > 9 will result in solubilisation of silica from the gel-layer.

It follows from the reaction schemes and can be shown from thermodynamic data that the presence of high concentrations of cations in the leach water will decrease the tendency to hydrolysis of the glass (67). This is in agreement with the normally somewhat lower leach rates observed in sea water or in brine compared with leach rates in deionized water.

In a closed system with only little water present two opposing trends can therefore be expected: Increasing leaching due to solubilisation of silica at high pH and decreasing leaching due to increasing cation concentration in the water. Which one will be dominant depends on the type of glass, the initial composition of the water, interaction with surrounding materials, and the temperature.

The thickness and properties of the gel-layer on the surface of the glass determine the rate of leaching of elements from the interior of the glass. The thickness of the layer increases until the rate of formation and removal are equal. A typical thickness seems to be about 1 μm.

In some types of leach-rate measurements a mechanical removal of the gel-layer takes place. Removal of the gel-layer by flaking due to swelling resulting from water uptake seems also to be rather typical. This is seen as a cyclic increase in the rate of leaching when new glass surface is exposed (26,56).

Preferential leaching of boron from gel-layers on borosilicate glass may leave the hydrated silica as a low-density material with poor strength and high permeability. This may explain why glasses with high boron content tend to have a leach rate where the solution is dominant (43).

A uniform removal by dissolution of the gel-layer may also take place governed by the solubility of amorphous silica in water, which at pH < 9 is about 100 ppm at 25°C, increasing to 400 ppm at 100°C. The solubility of crystalline silica, which determines the concentration of silica in natural waters, is considerably lower: less than 10 ppm at 25°C. At high pH the solubility increases rapidly due to the formation of $H_3SiO_4^-$ and $H_2SiO_4^{--}$ ions.

The resistance against alkaline corrosion can, in agreement with thermodynamic data, be improved by glass additives such as ZnO, Al_2O_3 or ZrO_2, which will remain as more alkali-resistant compounds in the gel-layer (67).

The resistance against leaching by acids depends mostly on the stability of the silica network in such an environment and on the low diffusibility of especially the di- and tri-valent network modifiers in the glass. Glasses with high contents of sodium or boron and low silica content can therefore be expected to have relatively low acid corrosion resistance.

Glasses containing a complex mixture of modifiers will be more leach resistant than glasses with only a single modifier. A part of the explanation is that cations of different size and valency probably do not cooperate well in diffusion. A classical example is the so-called mixed alkali effect of much lower leach rates from glasses containing mixtures of alkali metals than from glasses containing equal amounts of either Na or K. It is interesting to note that a similar although slighter effect is observed if the mixture of ions is present in the leach water and not in the glass (68).

It has been shown by electron microprobe analysis (69) that Ca has a tendency to concentrate in a specific zone in the gel-layer thereby probably acting as a migration barrier against Na diffusion. This may be the mechanism preventing deterioration of ordinary window glass.

Similar layers of increased concentrations of adsorbed elements in the gel-layer have also been observed for uranium and can be expected for the other actinides as well (8c,56). This may result in complicated release mechanisms for these elements. For example, it has been demonstrated that plutonium is leached from the sample surface as part of colloid particles of hydrated silica with a size about 0.01 μm (26).

Deposition of protective compounds in the gel-layer from reactions with ions in the water is also a possibility. For example, the presence of aluminum ions in concentrations above 25 ppm in the leach water will tend to decrease the leach rate due to precipitation of aluminum hydroxide in the gel (6c). The presence of magnesium ions in the water has the opposite effect. The reason is probably that the small Mg^{++} ion removes more valuable di- or tri-valent cations from the gel by ion exchange.

4.3.2.5. Temperature effects and hydrothermal reactions. Leaching proceeds at a rate at least partially determined by diffusion of various species in the gel-layer and in the glass. It is reasonable with such a reaction to expect a doubling of the rate for each 10°C increase in temperature, or about a factor 10 increase in leach rate for each 30° temperature increase. A temperature dependence of this general order of magnitude has been found in many experimental determinations of leach rate (15,43).

The logarithm of leach rates measured at various temperatures plotted against 1/T, where T is the temperature in °K, can often be approximated by a straight line (42,43, see also Fig. 12). This means that leaching follows normal Arrhenius behaviour at least approximately, dominated by a single rate-determining reaction. The dependence of leach rate on temperature can be written:

$$S = S^{*} \cdot \exp - \frac{A}{R \cdot T} \text{ cm/day}$$

where A is the activation energy in cal/mol and R = 1.986 cal/mol·°K is the gas constant. Values of A have been measured from 11 000 to 19 000 cal/mol (15,43).

A temperature dependence of the Arrhenius type can be expected only if the system as such and the mechanism of leaching are unaffected by the change in temperature. An example of a possible reason for deviation could be that the thickness or structure of the gel-layer is changed by the temperature variation of the solubility of silica in water. To be observable the change must, however, be rather large due to the not very high reproducibility of leach rate measurements.

If glass is heated with water in a closed system to temperatures of about 250-350°C at the associated pressures of 40-165 bar rapid reactions take place. It has been demonstrated that samples of simulated high-level glass are converted to a mixture of various crystalline materials after a few days under such hydrothermal conditions (52,53). The reactions can be regarded as an extreme case of water-catalysed devitrification. Although the glass is transformed to other materials it does not follow that much of the activity will remain in solution. On the contrary, most of the long-lived radioactive isotopes will be built into the new minerals produced. It is interesting to observe that study of the thickness of reacted layers on cylindrical glass samples kept under hydrothermal conditions indicate that a temperature dependence of the Arrhenius type with an activation energy of 8 kcal/mol can be extrapolated from leaching at lower temperatures to even such extreme conditions (54). The rate-determining reactions may therefore be rather similar over a large temperature interval indicating a gradual transition from ordinary leaching to hydrothermal reactions. However, this is probably an oversimplification. Further studies would be valuable, especially in the transition range 150-250°C, and some are in progress (11b).

An interesting study of brine chemistry effects on durability of simulated waste glass held 28 days at 250°C in various solutions has been made at Sandia, USA (57). Some general results may also be valid at lower temperatures: a) When the ratio between water volume and sample surface area is small, build-up of reaction products retards the reaction rate. b) Corrosion is higher in originally deionised water than in brine with unsaturated salt solutions having an intermediate position. c) The presence of Mg^{++} ions accelerates corrosion, probably due to ion exchange with Ca^{++} and other divalent cations resulting in a more permeable gel-layer. d) Saturation of the leach solution with silica (~ 2 g/l at 250°C) retards the corrosion but, and this effect was unexpected, the addition of clay minerals to the solution accelerate the corrosion. This indicates that the type of backfill material around the canisters with high-level glass can have a somewhat unpredictable influence on leach behaviour.

Hydrothermal reactions may not be important in practical disposal since the temperature of the units probably is below 100°C before contact with water can be expected. This is the case at least when thick-walled corrosion-resistant canisters are used as protection.

What will always be present also at low temperatures is high pressure on the units from the lithostatic pressure in the disposal formation. Reactions and reaction rates are known to change with pressure. Some theoretical considerations are given in (8d). Experimental investigations of, for example, leaching in high pressure systems at low temperatures have not been made, but the effects are probably not very pronounced.

<u>4.3.2.6. Leach-rate measurements</u>. Leaching experiments have been performed with two purposes in mind: One is simply the use of leach-rate measurements as a screening test in selecting optimum glass compositions. The other is more ambitious: To try to understand the various chemical mechanisms involved in the leaching phenomenon so that credible extrapolations over long periods and variable external conditions can be made.

Leach rate depends on the following parameters:

1. Chemical composition and homogeneity of the glass.
2. Chemical composition of the leach water.
3. Temperature and pressure of the system.

The second point is especially complicated since the composition of leach water is a function of: a) initial water composition, b) leach rate of the various components combined with time of contact and the ratio between exposed glass surface area and water volume, c) solubility limitations which normally are dependent on temperature and pH, d) degree of mixing of the water which determines the tendency to form local high concentrations near the glass, e) radiation effects on chemistry, and, at least in systems simulating real disposal, f) interaction with other materials in the surroundings.

The methods used in many leaching experiments to simplify this bewildering system have been to operate with high flow rates and large water volumes compared with the sample surface areas. Unfortunately, this is the opposite of what can be expected in most real disposal situations, where low flow rates and small water volumes will be normal, and where - and this is probably important - the water chemistry to a large degree will be determined by the surrounding material. Experimental leach rate measurements taken from the literature must therefore be treated with considerable reservation when used in safety analysis.

In general an experimental set-up for measuring leach rate consists of a thermostated cell in which a known volume of water is in contact with a sample of waste material with known surface area. Two different well-defined modes of operation are possible:

1) In systems with a continuous flow of relatively large amounts of water, the chemistry of the water is independent of the glass sample and the leach rate is determined by kinetic phenomena like diffusion in and corrosion of the gel-layer on the surface of the glass.

2) In systems with a final amount of water the leaching results in a build-up of leached materials in the water. This may, as described in section 4.3.2.4, influence the kinetics of the leaching of the glass in various ways. One likely possibility is that the system more and more slowly approaches a pseudo-equilibrium situation determined by the solubilities of the leached materials.

Effects of limitations in solubility may of course also influence continuous flow systems, especially if the flow rate is low. A system with a final amount of water can be regarded as a system with zero flow rate.

<u>Static systems</u>

In experimental systems without water change, a volume of water is left undisturbed in contact with the glass sample for the selected time period of the experiment. Analysis of water composition and changes in the glass are made only after the experiment is finished. The principle has been used to study the influence of the ratio between water volume and exposed glass surface area on the durability of normal glasses (67,68).

The methods used in the studies mentioned in section 4.3.2.4 of hydrothermal reactions of simulated high-level glass are also of the type without water change. This is simply because the method is easy to combine with high pressure work in autoclaves.

Otherwise the principle has not been used very much in connection with radioactive glasses, although it should be very suitable for the study of reactions involving small amounts of water or the interaction of glass with water and surrounding materials. An experimental method and some preliminary results are described in (8c). A model of the development of concentrations or pH in water in such a system is given in (9b).

Another experimental possibility is the burial of glass samples in cells filled with water-saturated porous materials. After some time the amount of activity leached out of the glass is measured. Back-diffusion of leached ions into the gel-layer may be important under such conditions.

Although the behaviour of the complicated borosilicate waste glasses have not yet been studied systematically under static conditions, it is indicated by other available information that the accumulation of corrosion products in the water has a considerable retarding effect on the leach rate. The increase in pH which is the dominant factor in the corrosion of ordinary glasses in closed static systems does not seem to be so important in connection with the borosilicate waste glasses.

Dynamic once-through systems

Experimental systems using continuous flow of leach water exist in various versions:

The Soxhlet leach system is one of them. The principle is that water in a collection vessel is purified by distillation, refluxed into the sample cell and siphoned back into the collection vessel. This takes place at such short time intervals, about 3 minutes, that the system can be regarded as continuous. The Soxhlet test can be used only for leaching in distilled water at $100^{\circ}C$ or lower temperature if the system is operated under reduced pressure. The flow rate is high, so there is probably no influence on pH, which can be regarded as 7. The water is always unsaturated in silica, which has a considerable solubility at $100^{\circ}C$. This is likely to result in accelerated dissolution of the gel-layer. Soxhlet leaching must therefore be regarded as a severe test. It is used extensively in the UK (43,15) and USA (63a,63b) as an easily operated screening test, but the result should not be used to predict long-time behaviour of disposed waste materials. Even relative ranking of quality of materials based on the test should be regarded with some reservation, since material properties, which result in a low leach rate in a Soxhlet test, may contribute less to leach quality under other circumstances.

An example (63b) of the use of the test is given in Fig. 8, which show the influence of Soxhlet leach rate of systematic variations of the various components in an American glass. A positive slope of the lines indicates decreasing leach quality with increasing concentration of the component in the glass. The addition of NiO, MgO, Na_2O, CaO, and B_2O_3 has a negative effect while adding SiO_2, TiO_2, ZnO, Al_2O_3, Fe_2O_3, and Cr_2O_3 has a positive effect.

In another study (63a), the Soxhlet test has been used to investigate whether or not high melting glasses containing 62-68% SiO_2, and with Al_2O_3 instead of B_2O_3, are more leach resistant than the normally produced lower melting borosilicate glasses. This is often supposed to be the case and follows to some degree from the tendencies given in Fig. 8. It was found that the weight loss for the high melting glasses after 24 hours leaching in a Soxhlet apparatus at $100^{\circ}C$ were from 0.3 to 0.7%. Corresponding values are 1.4 to 1.6% for the usual American glasses. Typical weight losses for some durable natural materials under similar conditions are: quartz: 0.14%, corundum: 0.26%, and

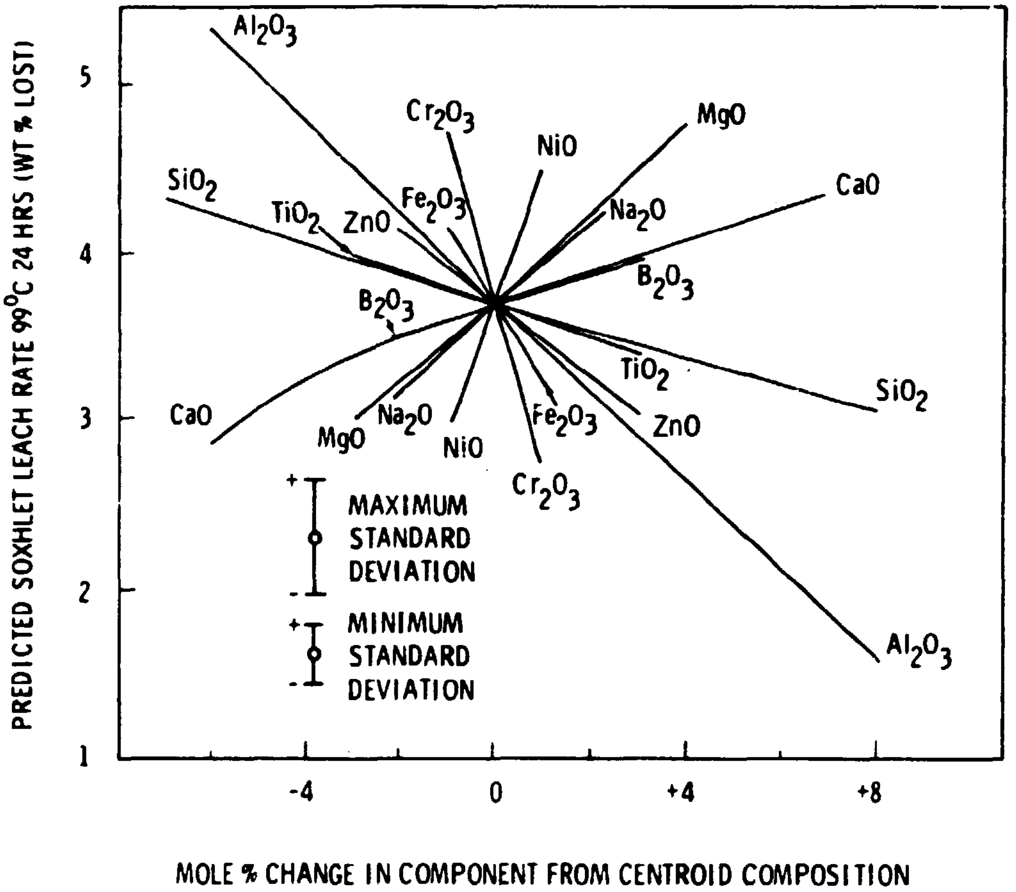


Fig. 8. Effects of change in composition on Soxhlet leach rate (63b).

granite: 0.37%. It was concluded that no significant improvement was obtained by use of the high melting glasses, and that the not very much lower values for very resistant natural materials indicate that no significant improvement of the corrosion resistance of glasses can be expected by a change in composition. But this conclusion may be incorrect as considerable differences in leach resistance under other circumstances are quite possible.

The Soxhlet test and also other once-through leaching experiments are sometimes made on a size fraction of a pulverized glass, for example, the fraction with grains from 0.25 to 0.4 mm. This principle was used in the two American experiments mentioned above. It increases the sensitivity of the test due to the large specific surface area of a pulverized sample, but it is generally not regarded as suitable for studies of leaching mechanisms due to difficulties in exact measurement of the surface area and the risk of local high concentrations of leached material in water between the grains or in possible cracks in the grains.

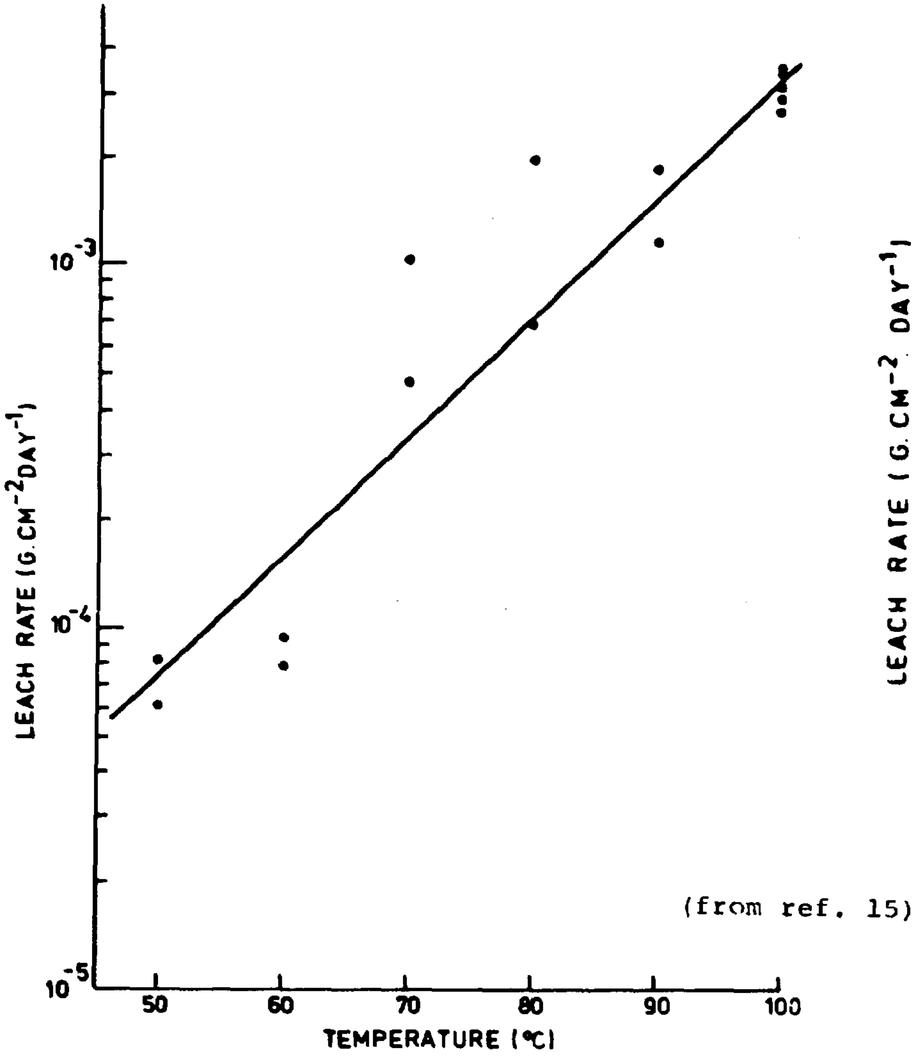
Since the Soxhlet method gives information only about leaching in nearly pure distilled water, some other type of once-through system must be used to study the influence of pH and the general chemical composition of leach water on the leach rate.

In the UK a simple system has been developed, where a prepared water solution or a solution equilibrated by contact with various solid materials flows through the thermostated sample cell (43). Some results based on weight loss measurements from an Inter-European comparative study using this method among others (15) are shown in Figs. 9 and 10, mainly for a French glass with the composition 43.6% SiO_2, 19.0% B_2O_3, 9.4% Na_2O, and 28.0% waste oxides (22.7% fission-product oxides).

The variation in leach rate with temperature (which actually was measured using the Soxhlet technique) shows the typical increase in leach rate of about a factor 10 for an increase in temperature of 30^oC.

The variation in leach rate with pH is also in agreement with expectations showing increased leach rates in acid as well as basic solutions. Experiments have not been performed at $pH > 9$ but the leach rate would probably have increased steadily due to solubilisation of silica. However, somewhat better resistance against alkaline than against acid attack seems to be typical of these glasses.

Figure 10 also shows the variation of leach rate with pH for the French glass at 90^oC together with the leach rates measured at that temperature by the Soxhlet technique, in synthetic sea water and in water prepared by equilibration with granite or clay. In general similar relative positions for the leach rates in these types of water were obtained for the other glasses as well. The greater aggressiveness of Soxhlet leaching compared



(from ref. 15)

Fig.9. Soxhlet leach rate of the French glass SON 58.30.20.U2.

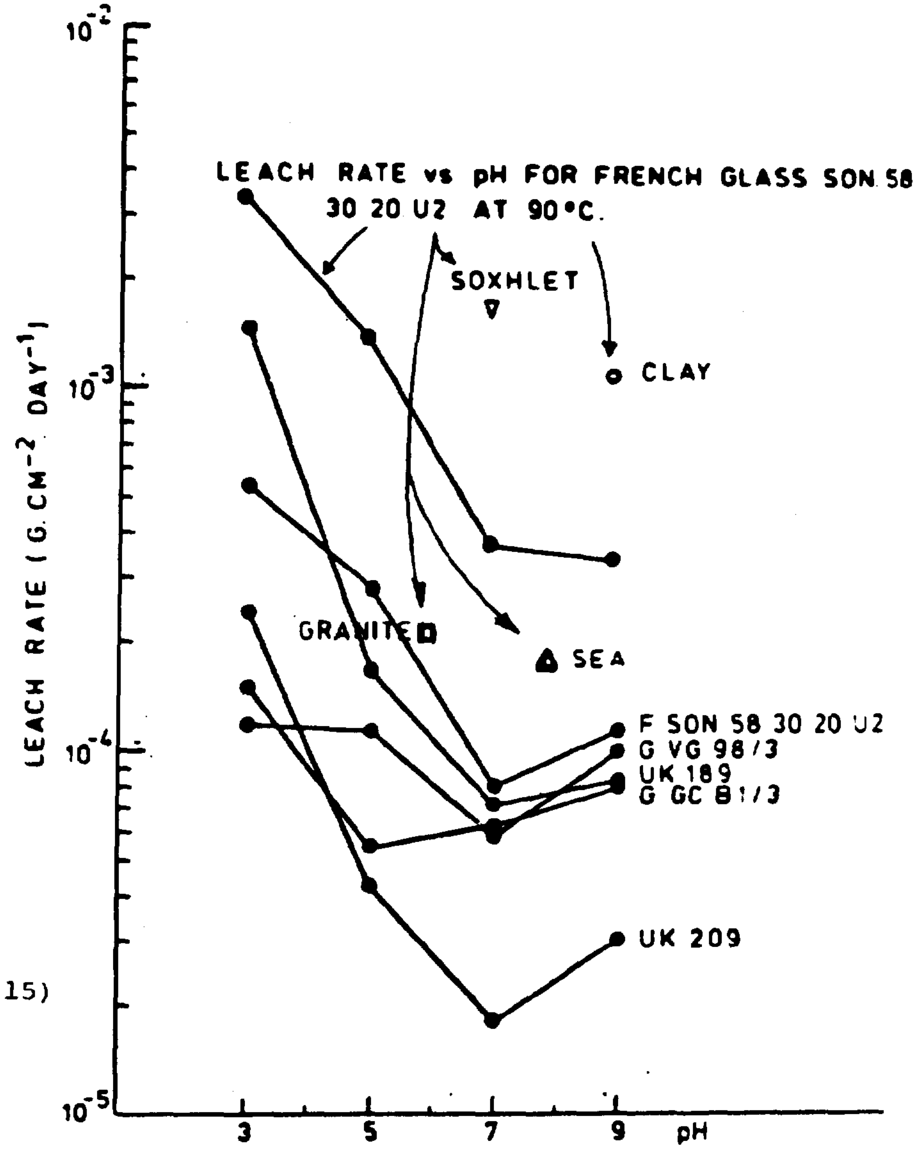


Fig.10. Leach rate in flow system at 60°C versus pH for all the glasses. Results at 90°C for a French glass are also shown.

with leaching in granite water or sea water can be explained from theory, but the behaviour of clay water is curious and cannot be explained from the composition of the water (15). It might be worthwhile to recall that aggressive behaviour of clay was also observed in hydrothermal leaching experiments at Sandia (57).

A study of the influence of flow rate and chemical composition of leach water on leaching of actinides and technetium from beads of an American glass with the composition: 40% SiO_2, 9.5% B_2O_3, 12.5% Na_2O, 5.0% ZnO, 2.0% CaO, 3.0% TiO_2, 9.6% Fe_2O_3, 4.2% UO_2, 0.5% plutonium or neptunium oxide, and 13% fission product oxides is under way at LLL in the USA as part of the WISAP Task 2 program (11e). Three flow rates are used in the once-through system: 10, 43, and 300 cm^3/day, two temperatures: 25^o and 75^oC and three types of water: distilled water, a sodium bicarbonate solution (2.5 g $NaHCO_3$/l), and a salt brine solution (287 g NaCl/l,some $CaCl_2$ and minor components, but very little Mg^{++}).

Some preliminary results for leaching of Pu and Np in salt brine are produced in Figs. 11 and 12. The leach rate is normally highest in the fast flow system but the effect is not very pronounced at the low temperatures. The behaviour of plutonium will be discussed later.

<u>Semi-static systems</u>

A system in which the water in the leach cell is removed for analysis and replaced by new solution at relatively long-time intervals is designated here as semi-static.

A system of this type was recommended by IAEA as a standard method in 1971. It has been used extensively for leach rate measurements, since it is an experimentally easy system to work with, but the water chemistry in the system develops in a discontinuous manner due to the sampling. This complicates the interpretation of the measured leach rates. A decrease in leach rate with decreasing frequency of water replacements has often been noticed.

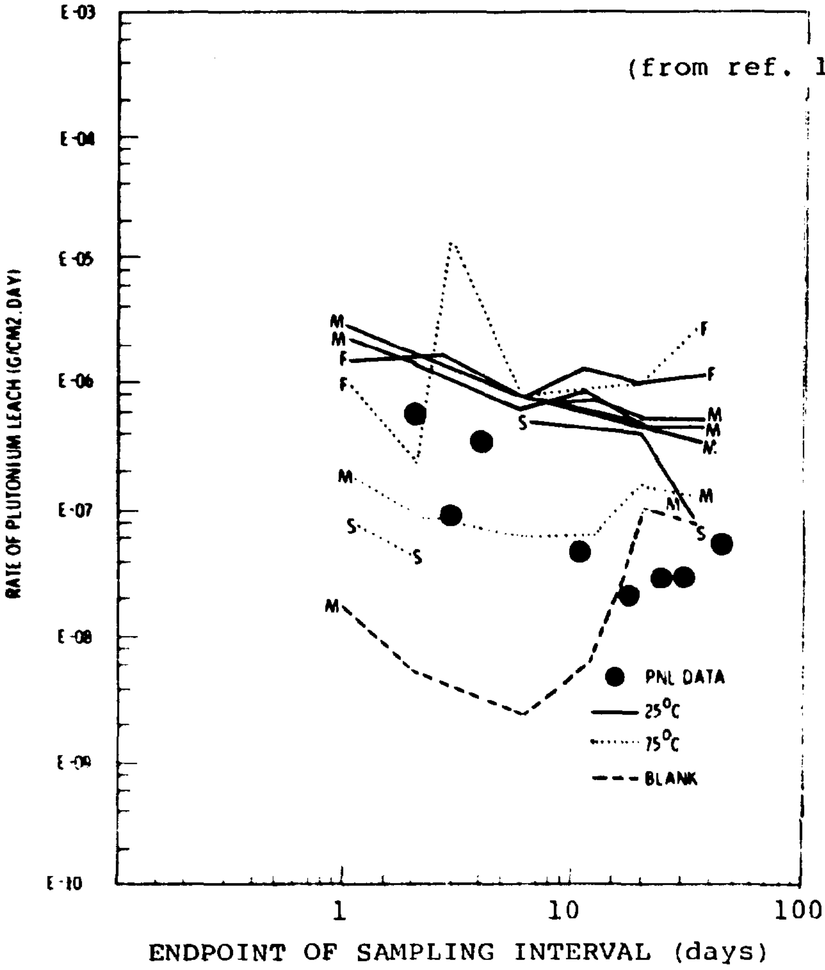


Fig. 11. Leaching of plutonium samples in flow and semi-static system with brine.

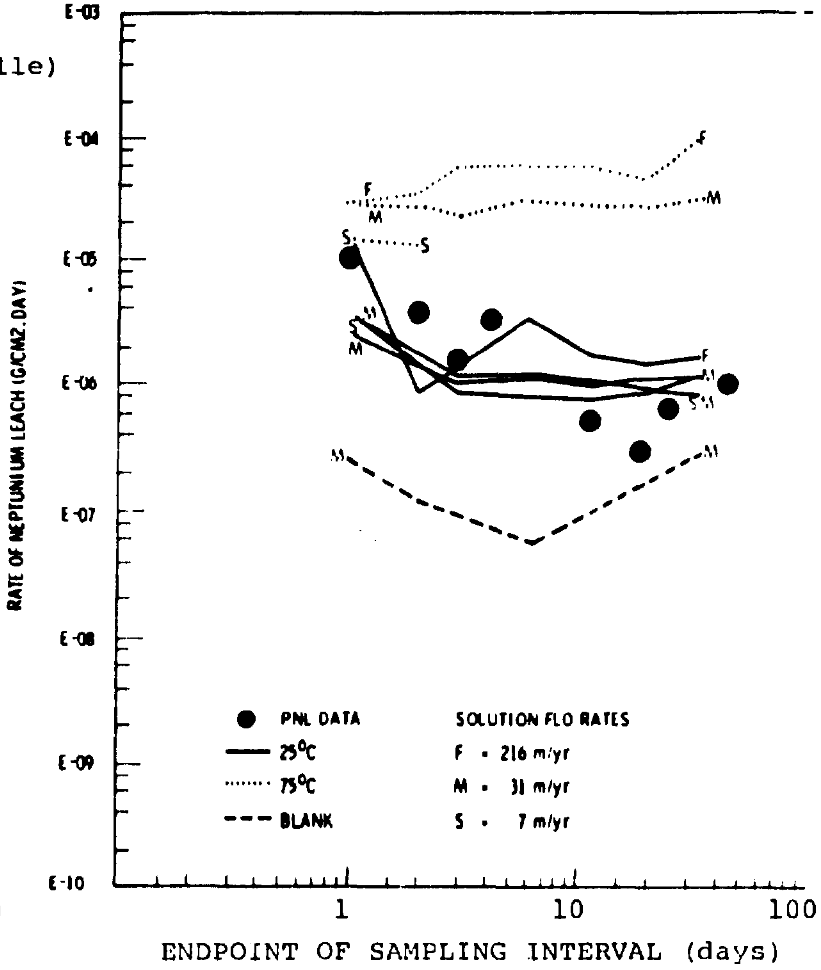


Fig. 12. Leaching of neptunium samples in flow and semi-static system with brine.

The method is still widely used, for example, for comparative purposes in the American study of leaching of actinides from glass in various solutions (11a). Examples of the results are shown together with the results of the continuous flow leach tests in Figs. 11 and 12 (indicated as PNL data with black dots).

One problem with the simple semi-static system is the undefined degree of mixing of the water in the sample cell in the periods between the replacements. Some slow mixing due to thermal gradients will probably take place, but areas with uncontrolled high concentrations of leached materials may easily develop at the surface of the sample. This is especially the case if pulverized samples are used. An example is given in (11c) where the leach rate of a glass was found to be about a factor 100 higher for a cylindrical sample than for the same material as a powder.

This is interesting in itself, since it shows that leaching is not necessarily proportional to the surface area of the sample. It follows that the degree of cracking of a glass may influence the amount of leached material from a unit considerably less than that calculated from the increase in specific surface. A condition is of course that the grains of waste material are kept together in one way or other.

On the other hand, it is also demonstrated by the example that a possibility exists of systematic errors in semi-static leach rate measurements.

Semi-dynamic systems

The problem of undefined mixing is overcome in a semi-dynamic system developed in France for the leaching of large (~ 2 kg) blocks of fully radioactive glass (20). A similar system was installed in Sweden in connection with the KBS study (36,38). The principle is that a relatively large volume of water is circulated through the sample cell in such a manner that the cell is alternately drained and filled with water. The sample surface is never dry since the cycle takes only a few minutes. The circulating water is changed or partially sampled for analysis at suitable intervals. The system is therefore not truly dynamic like a once-through system, but the influence of leached materials on water chemistry is probably low, since the ratio between water volume and sample surface is high.

Results

A collection of results from experimental measurements of leach rate is shown in Fig. 13. The values indicated are the more or less constant corrosion-controlled leach rates reached after some leaching time. The values are taken from Ref. 11a, 11e, 15, 26, 42, 43, 51, and 54 and replotted in the unit cm/day against 1/T $(^{o}K)^{-1}$. More than 10 different borosilicate glass compositions produced in France, Germany, the UK, and USA are represented. The values are mostly from continuous once-through systems using water with a pH of about 7. Some of the results have been obtained using semi-static or semi-dynamic leaching. The ratios between water volume and sample surface areas varies but are in most cases high. Leaching in deionised water as well as tap water, sea water, and even brine are included. Values from Soxhlet tests have not been used.

In such a plot the finer details associated with differences in glass compositions and leaching conditions disappear and only the typical tendency of increasing leach rate with temperature is retained. However, the figure demonstrates that the scatter of leach rate results obtained at the same temperature lie within one decade. It therefore seems reasonable to estimate that the leach rate for a glass of reasonable quality but with unknown composition can be given by:

$$S = S^{*} \cdot \exp - \frac{11\ 000}{R \cdot T} \text{ cm/day}$$

where $R = 1.987$ cal/mol·^{o}K and S^{*} has a value between 40 and 400 cm/day. The formula can probably be used with reasonable confidence only up to 150^{o}C, although the few available experimental results at higher temperatures fit reasonably well into the system.

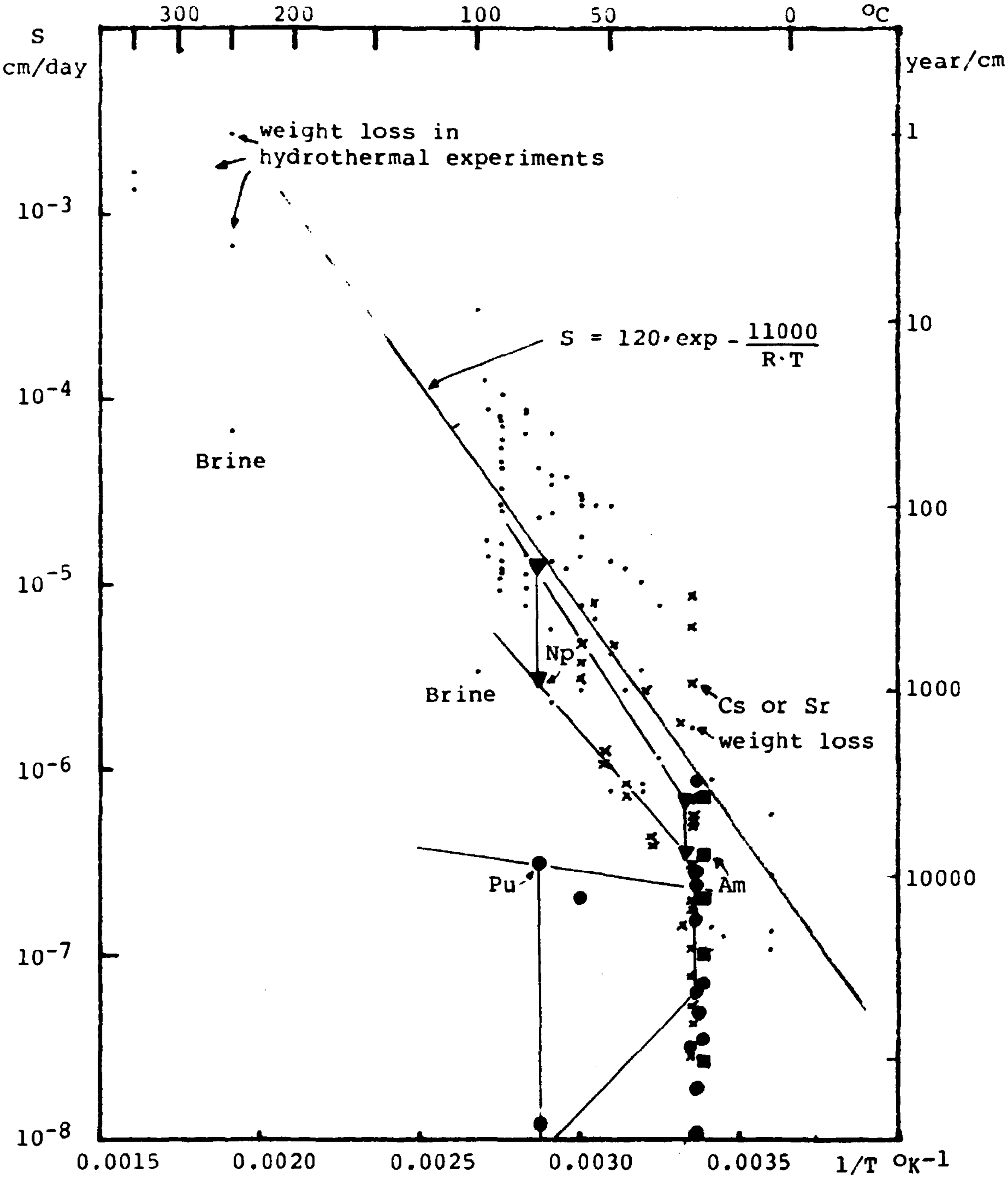


Fig. 13. Arrhenius plot of steady-state leach rates for about 10 different glasses under different conditions.

Most of the leach rate measurements especially at higher temperatures are based on weight loss of the glass samples (indicated as points in the figure). When leach rates based on measurements of leached activity of fission products such as Sr and Cs are plotted (indicated as crosses in the figure) a general trend towards somewhat lower values can be observed. (The three crosses above the line at 25°C is for a single American type of glass which may not be typical.) The use of a value S* = 120 cm/day as indicated by the line in the figure is therefore thought to be conservative as far as leaching of Sr and Cs are concerned.

These results are valid only at a pH of about 7. An approximation to the variation of leach rate with pH, as indicated in Fig. 10, would be to use the formula:

$$S = S^{*} \cdot \left(1 + \frac{(pH-7)^{2}}{pH^{1.5}}\right) \cdot \exp - \frac{11\ 000}{R \cdot T} \text{ cm/day}$$

This will give an increase in leach rate of a factor 10 going from pH 7 to pH 4 and a factor 3 going from pH 7 to 10. This is in agreement with the relatively high resistance against alkaline corrosion which has been observed for these types of borosilicate glasses.

The formula with a value of S* = 120 can be used for calculating leaching of Ca and Sr in ordinary ground water or dilute salt solutions such as sea water. In strong salt brines without Mg^{++} it seems reasonable to use the value S* = 40, while leaching in Mg^{++} containing brine and in water in contact with clay could be approximated by S* = 400. The experimental evidence for these assumptions is admittedly sparse especially as far as combined variations in temperature and pH are concerned. The mechanism of the effect of clay is not even understood.

The glass may be altered in various ways before leaching takes place: The effect of artificially induced devitrification has been studied, but the effect of devitrification on leach rate is generally low and equal to an increase of a factor 2 to a maximum factor of 5 (15).

The influence of irradiation on leach rate has also been investigated, but no effect or correlation with dose can be observed (5e,1).

If irradiation takes place during leaching the effects may be different since the water chemistry may change. Only preliminary experimental results using static systems are available. In one case no effects were found (57), while the other indicates some increase in leach rate at radiation dose rates typical of relatively fresh high-level glass (11d).

Significant γ-radiation as well as storage temperatures above the ambient in the geological formation are present only in the first few hundred years after the disposal of high-level waste. After 500 years the leach rate for Cs and Sr are not very significant since most of the activity from isotopes of these elements have decayed.

The fission product of most interest after this period is technetium. The only available experimental measurement of the Tc leach rate (11a) indicates values above the same as for Sr and Cs, but with a higher leach rate in brine than in deionised water. (Is this an effect of leaching as technate anion?) The glass investigated contained the Tc as a component in phase-separated spherical inclusions. Tc leaching is probably dependent on the oxidation state of the system, with less leaching taking place when Tc^{++++} is formed in a reducing environment.

In general, the leach rates decrease with increasing valency of the cations: The leaching of Cs^{+} is normally somewhat higher than that of Sr^{++} which again is considerably higher than the leach rates for trivalent rare earth isotopes (15,51).

<u>4.3.2.7. Leaching of actinides</u>. In connection with an evaluation of the contribution of leach rate to the long-term safety of radioactive waste disposal, the most important is the behaviour

of the actinides.

Leaching of Am and Cm will normally take place as trivalent cations and the isotopes can be expected to behave quite similarly to the rare earths. Some results for leaching of Am^{+++} at 25°C are given in Fig. 13 (indicated as black squares). The use of the formula for fission-product leaching with a value of $S^* = 40$ may be permissible and can probably also be used in the cases of leaching of Pu, Np, and to some degree U under reducing circumstances. Experimental evidence is lacking since leach rate measurements normally have been made under oxidizing condiditions.

Even under oxidizing conditions the leaching of neptunium, probably as NpO_2^+, seems to follow the same trend with temperature (11e, indicated as black triangles in Fig. 13). The use of the value $S^* = 40$ is a reasonable approximation in this case also.

The leaching of plutonium under oxidizing conditions appears to be different. The leach rate at 25°C is one or two decades lower than the bulk leach rate of the glass and does not rise with temperature in the typical manner. Even decreases with temperature have been observed (9d,11e). In French experiments slow increases in plutonium leach rate with time were found (5e,9d). In an experiment in Sweden, using the same type of equipment as in France, a sudden release of quite large amounts of Pu was encountered when semi-dynamic leaching was started on a sample which had been kept under semi-static leaching conditions for some months (38).

These phenomena can probably be explained by a leach rate governed by an extremely low solubility of plutonium possibly combined with a tendency to formation of complexes with hydrated silica. Plutonium from the glass is therefore deposited in the gel layer. The leach rate increases slowly with increased concentration of plutonium in the gel, and there is a risk of a sudden release of large quantities if changes in the outer circumstances remove some of the gel layer. The released plutonium is probably absorbed in colloid particles of hydrated silica, as demonstrated in a German experiment (26).

If leaching of plutonium is limited by solubility, a tendency to variation with water flow rate can be expected. This was also observed in the American experiments (11e, see Figs. 11 and 13), but the effect is not as strong as could be expected especially at low temperatures.

From experimental results in general, it can be concluded that the leach rate of plutonium is considerably lower than the bulk leach rate for the glass as long as the gel layer is retained on the surface. If the gel layer is unstable, short discontinuous releases at relatively high rates can be expected. When leaching takes place in very large amounts of water, or if the colloid Pu-containing particles can be carried away, the conservative approach is to use the same leach rate for plutonium as for the other isotopes, for example, corresponding to a value of $S^* = 40$.

If leaching takes place in a limited amount of water and especially if the gel particles are retained by filter effects in the surroundings near the glass, a release rate based on solubility of Pu-oxides in the available water volume is more reasonable. The effects of pH, complexing agents, and oxidation state for the plutonium must be taken into account using data as given, for example, in (19a).

A simplified model for leaching of Pu^{VI} under oxidizing conditions can be represented as in Fig. 14.

The Pu-concentration in the water is supposed to be determined by the solubility product for the reaction:

$$PuO_2^{++} + 2 \cdot OH^- \rightleftarrows PuO_2(OH)_2$$

$$[PuO_2^{++}] \cdot [OH^-]^2 = L = 10^{-23} \qquad (19a)$$

$$[PuO_2^{++}] = \frac{10^{-23}}{10^{2(pH-14)}} = 10^{5-2 \cdot pH}$$

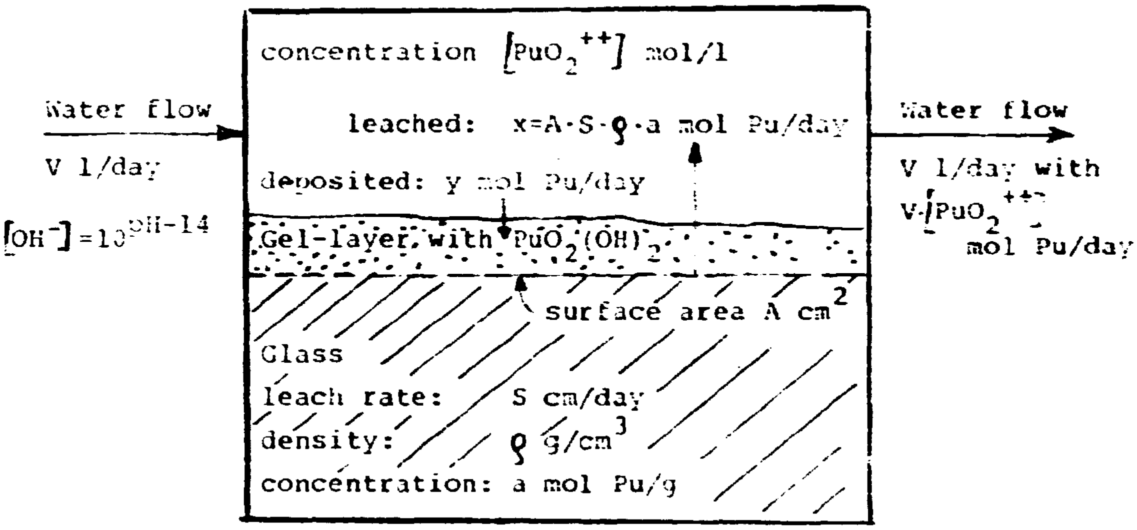


Fig. 14. System for solubility-limited leaching of plutonium from a glass surface out in flowing water.

The apparent leach rate, provided only soluble PuO_2^{++} is measured in the water from the system, should then be:

$$S_{app.} = \frac{V\cdot[PuO_2^{++}]}{A\cdot\rho\cdot a} = \frac{V\cdot 10^{5-2\cdot pH}}{A\cdot\rho\cdot a} \text{ cm/day} \quad .$$

and the increase in the Pu-content in the gel layer can be calculated from the mass balance:

$$y = x - V\cdot[PuO_2^{++}] = A\cdot S\cdot\rho\cdot a - V\cdot 10^{5-2\cdot pH} \text{ mol/day}$$

where S is the rate of leaching from the glass as such.

Inserting, as an example, the values: $V = 0.01$ l/day, $A = 100$ cm^2, pH = 7, $\rho = 3.0$ g/cm^3, and $a = 2\cdot 10^{-5}$ mol/g $\approxeq$ 0.5% Pu, which may represent the low flow alternative in (lle), gives an apparent leach rate:

$$S_{app.} = \frac{0.01\cdot 10^{5-14}}{100\cdot 3.0\cdot 2\cdot 10^{-5}} = 1.3\cdot 10^{-9} \text{ cm/day}$$

This is of the order of magnitude expected.

However, the model is much too simple. Besides pH, the effects of complex chemistry, Pu-oxidation state and temperature influence on the solubility product (which in itself is rather uncertain) will have to be taken into account. Formation of mixed compounds with hydrated silica may be important, so that the concept of well-defined $PuO_2(OH)_2$ as a precipitate is invalid. The strong tendency to polymerisation makes the system very complicated, but at least somewhat better models of the transition from solubility-limited leaching to glass corrosion rate-limited leaching can probably be developed.

Solubility limitations may of course also be of importance in leaching of other elements at low flow rates.

<u>4.3.2.8. The Canadian burial experiment</u>. The model developed on the basis of the leach rate measurements in Fig. 13 presumes that a constant steady-state leach rate is reached in a relatively short time. This may be correct with some types of glass and for leaching of unprotected glass surfaces with large amounts of water. But if the water flow is small, if the glass has a tendency to form a dense protective gel layer, if the water is at least partially saturated with silica, and if the surface is protected against mechanical removal of the gel layer, then the duration of the diffusion-controlled period of leaching may be extended over many years resulting in greatly reduced leach rates for all the isotopes. The experience from the Canadian burial experiment may support this theory:

In the experiment, glass blocks containing mixed fission products were buried in a sand formation in flowing ground water. The burial took place in 1960 and the leached amounts of ^{90}Sr calculated from the analyses of water and soil samples from the surroundings have been followed since that time. The release in the first year was equal to a leach rate of $4 \cdot 10^{-8}$ g/cm^2 day or about $1.5 \cdot 10^{-8}$ cm/day. In the following years, the leach rate dropped rapidly to a more or less constant value of about $5 \cdot 10^{-11}$ g/cm^2 day in the period from 1967 to 1974 (5d).

Leach rates about a factor 10^5 lower than the typical values given in Fig. 13 can therefore in principle be obtained by a combination of suitable glass composition and disposal conditions.

Some of the explanation of the low leach rates can, as previously mentioned, be related to the alumina content of the glass, which is expected to assist in the formation of a durable surface gel layer (8c). Some may, however, also be attributed to the specific storage conditions, and may therefore be destroyed if the storage is physically disturbed. Further studies of the various types of interaction between glass types and surroundings would be valuable. Such studies are necessary before the Canadian experience can be used in safety analyses of other systems.

<u>4.3.2.9. Decay of activity</u>. Returning to the formula on p. 39 for release of activity from waste units:

$$x_i = M \cdot O \cdot S_i \cdot \rho \cdot a_i \text{ Ci/day}$$

the only factor which has not been commented on is the concentration of activity in the waste: a_i Ci/g for isotope i.

The distribution of the initial concentration a_{0_i} are supposed to be available as information from the reprocessing plant. (See also section 3.1.2, quality assurance). The concentration at a later stage can then be calculated with great certainty over extremely long periods (if it is assumed that no preferential leaching of some of the isotopes takes place).

For simple decay the well-known formula is:

$$a_i = a_{0_i} \cdot \exp - \lambda t \text{ Ci/g} ,$$

where $\lambda = \ln 2/t_{1/2}$ yr^{-1} is the decay constant and $t_{1/2}$ yr is the half-life If decay to radioactive daughter products takes place the mathematics is somewhat more complicated, but the predictions are just as exact.

The heat production and β- and γ-radiation are mainly due to the presence of ^{90}Sr and ^{137}Cs in the waste. The problems associated with increased temperature and influence of radiation chemistry on leaching are therefore limited to the first few hundred years of disposal during which most of these isotopes disappear.

The prevention of access of water to the glass in the relatively short period can be secured with great certainty in almost any reasonable environment by selection of suitable corrosion-resistant overpack containers.

The unavoidably increased uncertainty about the possibility of contact with water at longer periods is compensated by the decay of strontium and cesium, which results in a decrease in toxicity of the waste and in higher durability of the glass due to lower temperatures in the disposal area.

After some hundred years the content of actinides is the dominant factor in toxicity of the waste. In the first few thousand years, the decay of ^{241}Am results in a further decline in toxicity by an order of magnitude. But after this time the long half-lives of some of the actinides such as ^{239}Pu, $t_{\frac{1}{2}}$ = 24 000 years, and ^{237}Np, $t_{\frac{1}{2}}$ = 2 140 000 years result in such a slow decline in activity that it hardly is of any interest measured on a human time scale. However, even this slow decline may compensate for some types of uncertainties associated with slow changes in the waste material, such as devitrification, or some types of change in the geological environment, which also can be extremely slow.

Since access of water to the glass can be prevented while significant amounts of ^{90}Sr and ^{137}Cs are present, it follows that the leaching behaviour of the actinides and of the few very long-lived fission products such as ^{99}Tc, $t_{\frac{1}{2}}$ = 210 000 years are of the greatest importance in connection with safety analysis of disposal of high-level waste. The American experimental study of leaching of these materials under various conditions is therefore of special interest (11a,b,c,d and e).

4.3.3. Use of leach rates in safety analysis

No generally accepted model of the leaching phenomenon is available for use in safety analysis (11c).

Calculations based on a leach rate formula which takes the diffusion- as well as the corrosion-controlled part of the leaching into account have been recommended (49), but sufficient experimental information obtained under reasonably realistic circumstances are not yet available for this type of calculation. Some further simplifications will have to be made:

The most obvious of these is to use a leach rate which does not change with time. This approach was, for example, taken in the KBS study (34.35).

The KBS study analysis was made in the form of a parameter variation study by calculation of doses resulting from transport of activity by water from the buried waste to the biosphere. After an initial period of delay determined by the quality of the containers used as overpack, a long period of constant release rate from the waste was assumed. Only a correction for decay was made. The model used in the calculation of doses is based on a constant environment. This may not be very probable when extended over long periods. However, in the case of disposal in granite, contact between waste and slowly flowing water will almost certainly take place at some time in the future. No physical movement of the waste or change in the properties of the surrounding rock is necessary for the release to take place or for the transport of the leached activity. It is therefore reasonable that the main case in the documentation of safety of the disposal system is a parameter study demonstrating long delays and low doses from more or less certain releases which are assumed to arise from the waste units in a relatively unchanged storage environment.

In the case of disposal in salt it may be more appropriate to look at some specific examples. This is because the presence of flowing water in this system is a highly abnormal occurrence which is possible only if the disposal area is disturbed seriously. The definition of senarios for contact with water is therefore important and to some degree the details of the scenarios will determine the rate of leaching.

In the following a list of calculation examples is given to illustrate the use of the information on leach rate in safety analyses of disposal in salt formations. No attitude towards the actual probabilities of the occurrence of the various scenarios is implied.

The use of the formula:

$$x_i = M \cdot O \cdot f_{(t)} \cdot S^* \cdot \left(1 + \frac{8(pH-7)^2}{pH^{1.5}}\right) \cdot \exp\left(-\frac{11\ 000}{R \cdot T}\right) \cdot \rho \cdot a_{0_i} \cdot \exp - \lambda_i t \quad \text{Ci/day}$$

is proposed for the calculation of release rates from the units.

This is essentially the same formula as given on p. 39 with the specifications of S* and a_{0_i} introduced on pgs. 60 and 68. It follows that a constant leach rate independent of time is assumed. This is probably conservative and may under some circumstances be very conservative as demonstrated by the Canadian burial experiment.

The leach rate of fission products and actinides is supposed to be the same. It means that S* is a function only of glass quality and water chemistry but not of the chemical properties of the individually leached isotopes. This is conservative if values of S* equal to the bulk leach rate in high-flow systems are used. In low-flow systems and in the case of plutonium and other materials with very low solubilities the assumption is probably very conservative. If a release in the form of colloids is not possible it might be more appropriate to base the calculations of the release rate on a combination of solubility and water flow. However, the use of bulk leach rate measured in high-flow systems does also cover the possibility of colloidal release.

As long as the exact chemical composition of the glass is unknown the typical bulk leach rate for borosilicate glass as obtained from Fig. 13 should be used. When experimental evidence for the leach rate from the actual glass can be obtained, the value of S* should be regulated accordingly.

The factor $M \cdot O \cdot f_{(t)}$ is an expression for the area of the exposed glass surface. M is simply the amount of glass present and a suitable value for the specific surface O is 1 cm^2/g in a glass unit which has been prepared without special precautions (see pgs. 32 and 40). The fraction of the surface which actually is exposed to the leaching water is given as $f_{(t)}$. How the value of this function changes with time is important and somewhat difficult to estimate. As long as the container is intact, $f_{(t)} = 0$. When a leak in the container has developed a part or all of the internal glass is exposed to water, but flow restrictions and the chemical protection that the individual particles in a fractured glass give to each other (pgs. 41 and 53) would not make it reasonable to calculate the release on the basis of the total area. A value of $f_{(t)} = 0.1$ for this situation is proposed and thought to be conservative for reasonably large cylinders containing fractured glass with a specific surface of about 1 cm^2/g. If the container is destroyed completely and the glass fragments are dispersed the value of $f_{(t)}$ is 1.

The specific surface O may also be a function of time if further subdivision of grains takes place due to stress corrosion, devitrification, or other phenomena. However, the tendency towards preferential disappearance of small particles during leaching may compensate somewhat for a tendency toward subdivision. A constant value for the product $M \cdot O$ is therefore proposed for the entire lifetime of the waste as glass material.

Examples:
(Proposed values for $f_{(t)}$, S*, pH are given. In all cases O is presumed to be 1 cm^2/g and ρ is 2.7 g/cm^3).

A) Reaction with water from brine inclusions

A restricted volume of water from brine inclusions in the salt may collect around each cylinder due to thermo-diffusion. The water will probably be used in reaction with the container, but if some of it should come into contact with the glass it may react and form a thickness of hydrated glass determined by the available amount of water.

The reaction rate can be estimated from the formula above using, for example: $f_{(t)} = 0.1$, $S^* = 400$, pH = 10, and $T = 30\text{-}70^{\circ}C$ depending on the disposal level in the geological formation and assuming that elevated temperatures from the waste itself have disappeared, i.e. $t > 200$ years. A relatively high value of S^* must be used due to high Mg^{++} concentrations in this type of brine. Initially the pH may be low but will rise to high values in a restricted water volume in contact with glass.

At $T = 70^{\circ}C$ the rate of reaction is then:

$$x = M \cdot 1 \cdot 0.1 \cdot 400 \cdot \left(\frac{8(10-7)^2}{10^{1.5}}\right) \cdot \exp \frac{-11\ 000}{1.987 \cdot 343} \cdot 2.7 = M \cdot 3.5 \cdot 10^{-5}$$

g/day

Since hydrolysis of 1 g of glass requires about 0.5 g water, and, by using $M = 3.4 \cdot 10^5$ g/m disposed glass cylinder with diameter 40 cm, this is equal to a water consumption rate of $3.5 \cdot 10^{-5} \cdot 3.4 \cdot 10^5 \cdot 0.5 = 6$ g water/day/m disposed glass cylinder. As the temperature gradient has disappeared at the time of contact between glass and water, no further influx of brine takes place. If the available amount of water per m of cylinder length is known, the thickness of the reacted layer of glass is easily calculated.

No actual release takes place since this is not a flow system: The leached material remains around the unit.

B) Reaction with water in a flooded repository

One possible accident condition is flooding of the mine or the bore holes with water from above. This again is not a flow system since the tendency toward circulation in the resulting high density brine is slight. The flooding accident is associated with the filling operation. Some remedial action may be possible, but also in this case considerable amounts of water must be expected to remain around the canisters when the system is closed. The water will be in the form of an almost pure sodium chloride brine.

As in the example above the corrosion of the canister will take a long time so that the temperatures will have returned to the levels normal for the geological formation before contact between water and glass is possible. The following values of the parameters are proposed: $f_{(t)} = 0.1$ at $t > 200$ years, $S^* = 40$, $pH = 10$, $T = 30^{\circ}C$ in case of a mine relatively near the surface. The relatively low value of S^* is due to the lower leach rate in pure sodium chloride brine. The rate of reaction calculated as in example A is $M \cdot 1.9 \cdot 10^{-7}$ g/day. This is equal to a water consumption rate of 0.03 g water/day/m disposed cylinder.

C) Water flowing through a crack or a permeable zone in the salt formation

This may not be a realistic possibility, but here at least a mechanism of movement of the leached activity is available. The leaching medium will be an almost pure sodium chloride brine and also the other conditions are more or less the same as in case B. Therefore: $f_{(t)} = 0.1$ at $t > 200$ years, $S^* = 40$, $pH = 10$, and $T = 30\text{-}70^{\circ}C$ depending on the depth of disposal.

D) Intrusion

If the knowledge about the disposed waste for some reason or another is lost, there is a theoretical possibility for future contact with some of the waste units, if, for example, a cavern is built in the salt formation. It seems rather improbable that the knowledge about the waste should be lost in less than 200 years. If a salt cavern is built by solution mining after this time the temperatures will be the normal for the salt formation. Metallic containers exposed by the solution mining will probably corrode rapidly in the large amounts of circulating brine so that the integrity of the glass units is lost. The following values of the parameters are proposed: $f_{(t)} = 1$, $S^* = 40$. $pH = 7$, and $T = 20^{o}C$.

The number of waste units involved in an intrusion accident will probably be a small fraction of the total stored in the formation. If a previously corroded layer of glass is present in the glass units (case A or B) the activity contained in this layer will probably be released immediately on contact with large amounts of water.

5. CONCLUSIONS

Many different methods for solidification of high-level waste have been investigated, and a variety of materials are probably usable for the purpose.

So far it is only the production of high-level borosilicate glass which has been demonstrated on a technical scale. This and the many available studies of properties of glass makes it the obvious material to select as a basis for the Danish utilities present investigation of the safety of disposal in salt domes in Jutland.

Future research and development may show that other materials are even better than glass. Such materials can then, probably without difficulty, be used as substitutes for the glass in more or less the same disposal concept.

The selection of the most suitable glass composition has not yet been made and there seem to be some possibilities for improvement of the quality. Some advantages may also be associated with modification of the environment in which the glass is placed.

At temperatures below 2-300°C the inherent thermodynamic in-stability of glass is of little consequence. Contact with water should be avoided above 100-150°C. This can be secured by the use of containers which are made to resist corrosion, at least for the few hundred years of increased temperatures in the disposal area. At 30-70°C, which are the normal temperatures in the disposal formations, contact with water is of lesser influence and a very long duration of the material as glass can be expected.

Leaching of activity from glass by flowing water is not a probable incident after disposal in salt, but the consequences of various accidental situations should be investigated.

The leach rate as a function of temperature for typical borosilicate glasses is known from experiments. The leach rate and the exposed surface area of the glass determine together the rate of release of activity from a glass unit in contact with water. It is easy to see from typical values of these parameters that the leach rate of borosilicate glass is not low enough to serve as the only barrier against dispersal of activity. The relatively low leach rates may, however, serve as partial protection against high individual doses, for example, in an intrusion accident, since the complete leaching of activity from typical glass lumps is likely to take from 1000 to 10 000 years (see Fig. 13).

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