NEED FOR AN ADVANCED HLLW FIXATION MATRIX

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ABSTRACT

As a result of a multitude of safety analyses performed for a variety of repositories, it becomes obvious that only natural geological barriers guarantee the long-term isolation of the disposed wastes and that the waste form is important mainly for waste handling, interim storage, and the operation phase of a repository. Thus, it is common understanding that borosilicate glass is a satisfactory waste form for high-level radioactive wastes. However, its durability at elevated temperatures and high water flow conditions is less satisfactory compared with ceramic matrices. Sol-gel technology offers a promising route to solidify liquid waste and to incorporate fission products and actinides into a dense ceramic matrix. Generic advantages of gel processing are the absence of dust, easy pneumatic transfer and sampling of either liquids or free-flowing solid microspheres, easy sintering to high density, and simple equipment amenable to remote operation and maintenance. Two different gelation methods are being developed for immobilization of high-level liquid waste in crystalline Al_2O_3 ceramics of the spinel type. The products exhibit excellent leaching resistance.

INTRODUCTION

The general approach to radioactive waste management is based upon containing and isolating the source of radioactivity as far as is practicable. The most effective way to put a containment and isolation approach into practice is to contain the radioactive waste in a stable waste form, and to isolate the waste form from the biosphere by additional barriers. In principle, such a so-called multiple barrier concept (1) should ensure that any return of radioactivity to the biosphere, even over very long time periods, will only occur at safe and acceptable levels.

Various waste forms have been proposed to immobilize the high level waste. Vitrification of the fission products and actinide solutions originating from spent fuel reprocessing using borosilicate glass is the only high level waste management strategy which is established commercially. Various advanced waste forms are under investigation with a view to finding a waste form with improved properties over borosilicate glass.

The question arises: does such research still deserve continued support because of the need to apply the best practicable, rather than merely adequate technology in radioactive waste management?

MULTIBARRIER PRINCIPLE

The German strategy in isolating nuclear waste is to impose a series of barriers between the radioactive material and the biosphere as illustrated in Fig. 1 (2). This approach has been adopted by several other countries as well.

For a safety assessment, the whole system of barriers must be considered. The great advantage of this multiple barrier system is that as long as the overall safety objective can be met, a less than optimum good performance of one barrier can be compensated by appropriate performance of others.

It is very probable that either one of the barriers 2, 3, or 4, if appropriately chosen, could by themselves provide the necessary isolation of waste, irrespective of the quality of the waste form.

Thus, the main function of the waste form within the German disposal concept is to contain and safety isolate the radioactive material during handling, interim storage and transportation procedures until proper emplacement in the geological repository. However, it is common understanding that the waste form should be made as chemically resistant as reasonably possible to provide maximum possible protection within an acceptable cost range.

RISK ASSESSMENT OF HIGH LEVEL WASTE DISPOSAL

The assessment of long-term waste confinement requires an identification of the various potential mechanisms, rates and pathways by which radionuclides could leave a repository and migrate through the various barriers to enter finally the human environment and bring about radiation exposure either directly or indirectly. Once these factors have been identified, calculations can be made of the radiation doses that could arise through these mechanisms. The performance assessments consider a set of given scenarios on the basis of the normal evolution of the site.

Once HLW products have been sealed in a geological repository, brine or ground water flow will provide the only transport mechanism of radioactivity between the waste product and the biosphere. The only means for radionuclides to enter the biosphere and thus into drinking water horizons will be as dissolved species or as mobile colloids. The extent to which radioactive nuclei will attain a harmful level in the ground water is a function of the kinetics of their

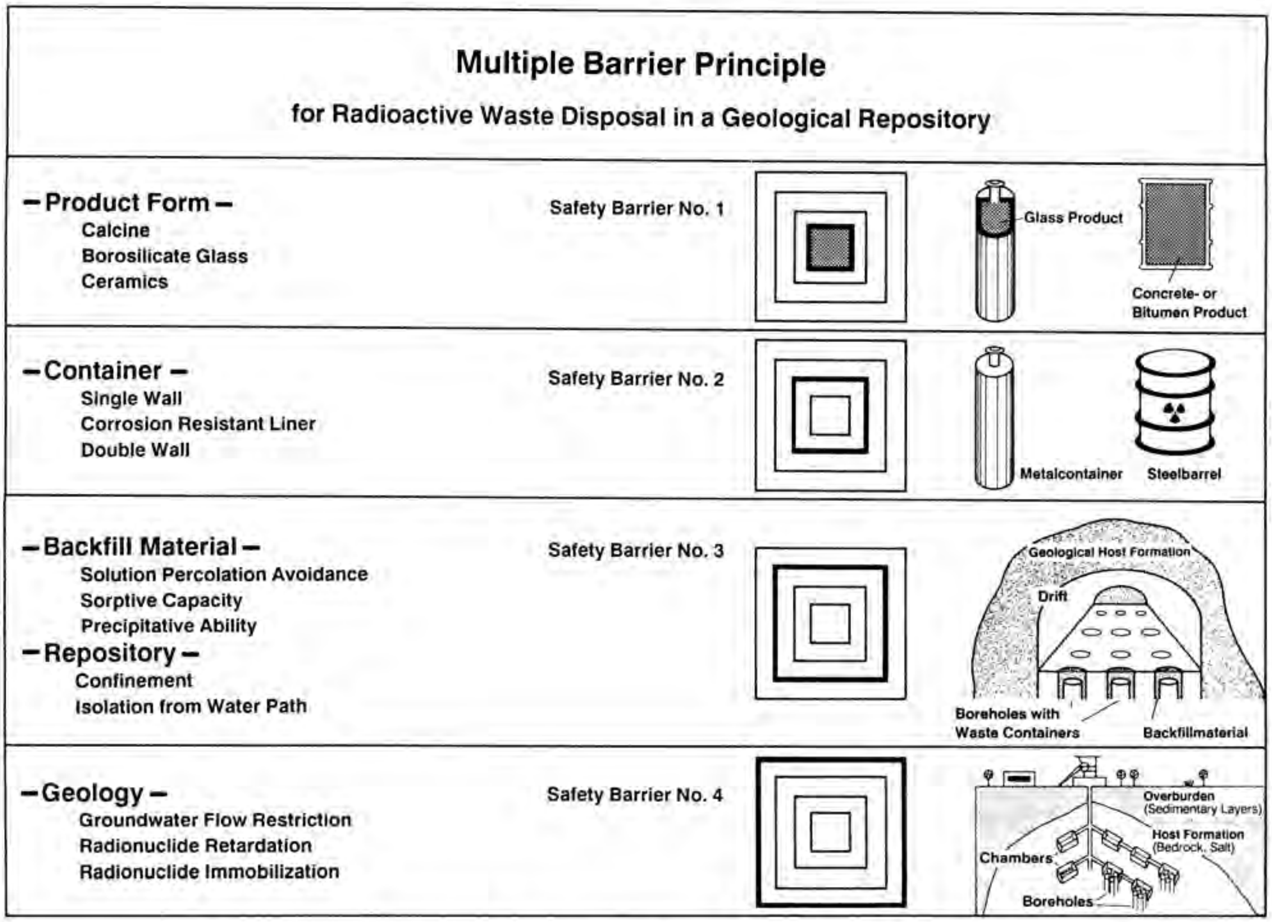

Fig. 1. Multibarrier principle for radioactive waste disposal in a geological repository.

release from the waste form, their solution speciation chemistry and solubilities, diffusion in solution, ground water flow rates, and adsorption behavior on solid surfaces.

The waste form itself is only an element of minor importance in the multibarrier system if one considers long-term safety. Nevertheless, the chemical properties of the HLW form in a specific repository environment establish the initial individual element release rates. A leach rate, specified in terms of fractions leached per day or year, is the input parameter used to characterize the aspects of radionuclide release. The second limiting process is that of solubility.

However, the sensitivity of these two factors in an overall risk analysis is of minor importance. Nevertheless, a good waste form may be able to overcome uncertainties about the characteristics of a site.

In the framework of a joint study by several member states of the Commission of the European Communities a Performance Assessment of Geological Isolation Systems (PAGIS) was performed in which it was shown that regardless of the geological formation chosen as a repository option, a safe disposal of vitrified highly active waste can be achieved. In the study (3) three continental options and various potential sites were analyzed: clay, granite and salt. As a possible alternative to land disposal, the subseabed was included in the study. In all cases radiation doses delivered to populations are acceptable in the short and long range.

Deterministic derived dose rates with "best estimate" values are in all cases and over very long time periods up to 10 million years never greater than 10^{-5} Sv/y. For most scenarios investigated they are in the range between 10^{-6} and 10^{-8} Sv/y. All investigated scenarios show until the time of 10,000 years a similar quality insofar, as no contamination of the biosphere should occur. Different behavior may then take place depending on the geological formation and site characteristics chosen. The German concept of a salt dome repository reveals a high probability of no radionuclide release into the biosphere even in the case of a water intrusion.

For each disposal option the summary report (3) presents the most significant results obtained at specific sites. In addition to dose rates and their expectation values, the

TABLE I

Overview Of Proposed Waste Forms

Category	Waste Loading [max. %]	Product	Remarks		
Low Temperature Process	20	**Bitumen**	production simplicity	lack of thermal stability	radiolysis of hydrocarbons and possibly nitrates
	20	**Cement or concrete composites**	production simplicity	lack of hydrolytical stability	radiolysis of water and nitrates
	80	**Calcines**	production simplicity	lack of chemical stability	dispersable form
Glass	35	**Phosphate**	low viscosity melt	glass melt highly corrosive	devitrification tendency
	25	**Borosilicate**	medium viscosity melt	advanced technology	good radionuclide host, resistancy against radiation and transmutation effects, hydrothermal
	20	**Nepheline-Syenite**	high viscosity melt	high melting temperature	attack at elevated temperature and pressure
Ceramic	25	**Glass ceramic**	largely crystalline	complicated technology	no apparent advantage compared to glass
	60	**Supercalcine**	predominantly crystalline	tolerable technology	thermodynamically stable product particulate form dispersable
	10-20	**Synroc**	purely crystalline	sophisticated technology	thermodynamically stable product waste partitioning required?
Composite	10-20	**Coating (PyC, SiC, Al_2O_3)**	difficult technology	multibarrier effect	
	10-20	**Metal matrix (Cu, Pb,Al) encapsulation**	tolerable technology	improved heat conductivity and mechanical strength, otherwise no essential advantage	
	10-15	**Medium-temperature ceramic**	not seriously considered so far		

predominant radionuclides and pathways to man are identified as well as the most sensitive parameters and phenomena.

It can be assumed that alterations in the product behavior, due to higher or somewhat lower leach resistance, do not cause a significant change of the potential dose to man. The main contribution to isolation capability stems from the natural barrier effectiveness and to a much smaller extent from product quality. However, their essential importance is to be found during the operational phase of a storage and disposal concept.

WASTE FORM

A large variety of candidate waste forms have been proposed and developed in the past 30 years. Table I represents an overview of the most important ones.

Low temperature processes are only suitable for low and intermediate level wastes. For highly radioactive wastes mainly glass structures and ceramics have proved suitable host matrices (4). Composite multibarrier waste forms of different kinds only fulfill the target of advanced performance under idealistic assumptions (5). In practice, their overall behavior is not better than simple glass and ceramic products.

As already mentioned, for the sake of risk evaluation and comparison, a "dose to man" calculation as applied for example in the PAGIS study is a recommendable system approach. The results thus obtained showing that the differences in performance between waste forms did not result in significant differences in the "risk to man" by no means devalue further endeavors towards advanced waste products.

It is worthwhile to note that the importance of simple processing techniques has been greatly undervalued up till now. Existing industrial vitrification plants struggle with troublesome interferences. A technical scale plant for manufacturing ceramic waste products has not been operable so far. Difficulties are obvious and may exclude practical application.

Arguments in favor of further development needs for advanced waste forms in order to improve public acceptance of waste disposal or just to provide more than one waste form do not justify additional efforts under the prevailing circumstances (6). Better vindications are on hand.

FABRICATION AND CHARACTERIZATION OF A SOL-GEL-DERIVED Al_2O_3 WASTE FIXATION MATRIX

The waste form as a critical barrier to radionuclide release is not only beneficial for short term considerations, but also for long range safety support if one uses granite, basalt, etc., as the host formation with its slow flow of water through rock fissures.

SYNROC crystalline ceramic waste forms and Tailored Ceramics represent polyphase ceramics which chemically bind the waste species into known phases (A.E. Ringwood et al., P.E.D. Morgan et al., A. B. Harker in (6)). This research and development work with polyphase ceramics has demonstrated the critical attributes which characterize them as a waste form for future HLW disposal. The crystalline phases in the waste forms offer the potential for demonstrable chemical durability in immobilizing the long-lived radionuclides in a geological environment. With continued experimental research, realistic predictive models for waste form behavior over geologic time scales are feasible.

Up to now, the most important drawback of ceramic host matrices has been the high sintering temperatures of the powders used in the process. This drawback can be overcome by utilizing precipitation processes commonly known as sol-gel processes. One of the advantages of the sol-gel route is that the solution containing the waste and the solution containing the precursor of the matrix are mixed in an early stage of the process. By coprecipitation of waste and matrix precursor, an excellent micro-homogeneity of the ceramic product is achieved. A further advantage of the sol-gel technique is the very small crystallite size of the material precipitated. This results in a relatively low sintering temperature, thus avoiding the volatilization of waste elements. Furthermore, experimental results show that during heat treatment the matrix already becomes so dense at temperatures distinctly below 1000°C that a release of fission products is negligible.

Sols with similar particle sizes and viscosities can be prepared either by hydrolysis of alkoxides or precipitation of hydroxides (7,8).

Production of Al_2O_3-sols by a Dispersal Method

The matrix precursor 1.5 M [$Al(NO_3)_3$]-solution and HLLW are simply mixed and NH_3-gas bubbled through the solution: An incomplete precipitation of $Al(OH)_3$ takes place:

$$Al(NO_3)_3 + 2.7\,NH_3 \rightarrow \{Al(OH)_{2.7}\}^{0.3+}$$
$$0.3\,NO_3^- + 2.7\,NH_4NO_3$$

The peptized sol is then pumped through an orifice to yield small droplets, which in an NH_4OH solution gelate into rigid spheres. Subsequent washing, drying, calcining and sintering yield dense crystalline spheres suitable for direct packaging. It may prove advantageous to pelletize the green particles to larger bodies prior to sintering, applying a suitable compacting technique.

The highly homogeneous distribution of the waste and the extremely small crystallite size of the matrix precursor in the gel lead to dense homogeneous waste products during sintering. Volatilization of fission products is hardly observed since a dense matrix is already formed at temperatures far below 1000°C.

However, a prerequisite for applying the sol-gel technique is usually that the radioactive substances to be fixed are chemically precipitated during gel formation in the same way as the matrix precursor. This requirement is fulfilled for the majority of elements. Ammonia acting on an $Al(OH)_3$ hydrosol causes almost all elements present in the HAW solution to be bound as hydroxides in the $Al(OH)_3$ gel produced. The few exceptions, as for example Sr and Cs, are strongly adsorbed at the Al_2O_3 gel. Cs may cause some problems due to volatilization in the sintering procedure.

Production of Al_2O_3-sols by a Condensation Method

An even simpler procedure is provided through the chemical reaction of a one-phase system to a disperse system, which is called a condensation reaction since particulates are formed due to a condensation of the dispersed molecules present in the system. Of great promise is the application of aluminium alcoholates (alkoxides) via hydrolysis according to the reaction scheme:

$$Al(OR)_3 + H_2O \rightarrow Al(OR)_2OH + ROH$$

$$2\,Al(OR)_2OH + H_2O \rightarrow RO-\underset{\displaystyle |}{\overset{OH}{Al}}-O-\overset{OH}{\underset{\displaystyle |}{Al}}\,OR$$
$$+2\,ROH, etc$$

As the final product, peptized "aluminium oxide" is obtained, which is formed via the interim stage of a linear macromolecule pursuant to

$$x\,Al(OH)_3 + HNO_3 \rightarrow \{Al(OH)_3\}_{x-1}$$
$$Al(OH)_2NO_3 + H_2O$$

The alcoholate usually employed is aluminium-tri-isopropylate $Al[OCH(CH_3)_2]_3$, which is a low-priced commercially available product. The sol is prepared by dissolving the powder in hot water and mixing with the waste solution. The addition of suitable quantities of nitric acid to

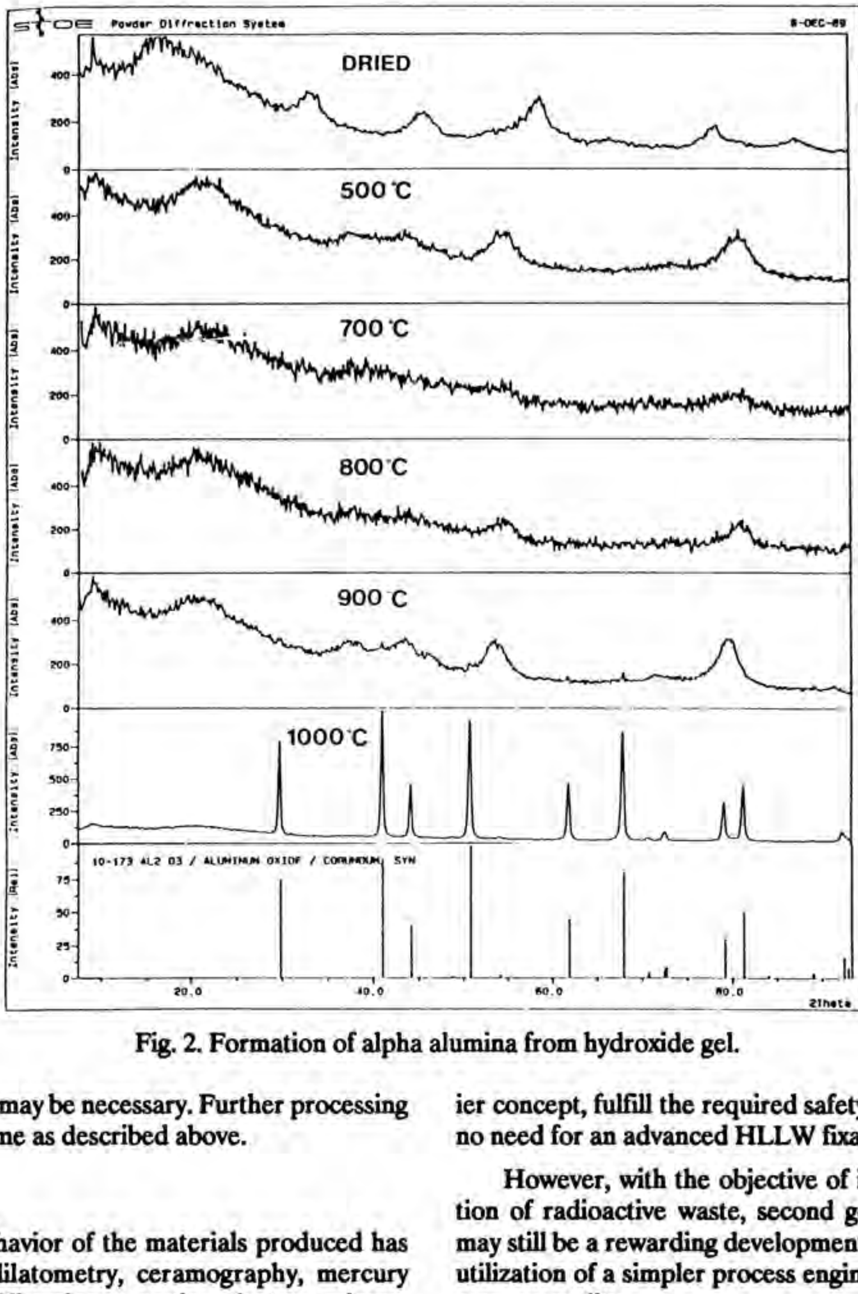

Fig. 2. Formation of alpha alumina from hydroxide gel.

obtain the proper sol may be necessary. Further processing is more or less the same as described above.

Sintering

The sintering behavior of the materials produced has been evaluated by dilatometry, ceramography, mercury pycnometry, X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Until the crystallization temperature has been reached, the samples are X-ray amorphous. Water drainage was complete at about 500°C. The crystallization occurred more or less abruptly at approximately 1000°C for hydroxide gel an 1100°C for alkoxide gel. Figure 2 shows a diffractogram of alumina from hydroxide gel.

CONCLUSIONS

Borosilicate glass products with reasonable quality characteristics, together with a carefully chosen multibarrier concept, fulfill the required safety goal Insofar, there is no need for an advanced HLLW fixation matrix.

However, with the objective of improved immobilization of radioactive waste, second generation alternatives may still be a rewarding development goal, especially if the utilization of a simpler process engineering technology becomes a reality.

Sols with similar particle sizes and viscosities can be prepared either by hydrolysis of alkoxides or precipitation of hydroxides.

The specific surfaces (BET) of the hydroxide and alkoxide gels are 130 and 280 m^2/g, respectively.

The particle size analyses applying photon correlation spectroscopy indicated two distinct diameter distributions for either production route:

35 ± 5 nm (~ 90% frequency)

and

130 ± 10 nm (~ 10% frequency)

TABLE II

Typical Measured Specific Leach Rates.

Element	$g \cdot m^{-2} \cdot d^{-1}$
Mo	$1 \cdot 10^{-3}$
Te	$1 \cdot 10^{-3}$
Sr	$2 \cdot 10^{-3}$
Ba	$9 \cdot 10^{-3}$
La	$2 \cdot 10^{-5}$
Ce	$3 \cdot 10^{-5}$
Gd	$1 \cdot 10^{-5}$
Tc	$4 \cdot 10^{-2}$
U	$2 \cdot 10^{-6}$
Pu	$1 \cdot 10^{-6}$
Am	$3 \cdot 10^{-6}$

Formation of alpha alumina takes place at 1000°C for hydroxide and 1100°C for alkoxide material.

Alkoxide-derived Al_2O_3 shows better sinterability. Formation of compounds, as for instance spinels, already takes place at the crystallization temperature of alpha alumina.

The specific leach rates are in the order of 10^2 better than for borosilicate glasses. Since the spinel type waste ceramics are polyphase materials, there is no single leach rate that can be used to describe the release of the specific waste species. Rather the dissolution mechanisms for the individual waste cations and anions are specific to the waste phases in which they are incorporated.

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