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ULTIMATE STORAGE OF RADIOACTIVE
WASTES IN TERRESTRIAL ENVIRONMENTS

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WASTES IN TERRESTRIAL ENVIRONMENTS

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August 1972

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ULTIMATE STORAGE OF RADIOACTIVE WASTES IN TERRESTRIAL ENVIRONMENTS

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ABSTRACT

New avenues are opened for the ultimate storage of radioactive wastes via the "STOPPER" and "Thermalt" processes. STOPPER is the Stone Process for Permanent Encapsulation of Radionuclides, a hydrothermal process. Thermalt is a pyrochemical process for fixing radionuclides in a basalt-like product. The products contain analogs of silicate and aluminosilicate minerals such as pollucite, strontium feldspar and "plutonite"--a structural analog of zircon. Ultimate storage will have been effected if these product forms are secured in geochemically compatible media where the authigenic precipitation of cation aluminosilicates will provide additional protection from transport by ground-water movements.

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INTRODUCTION

The ultimate storage of radioactive wastes in terrestrial environments is a major consideration of the nuclear industry. The most satisfactory procedure to be used has not been affirmed by all concerned. As expediciencies, interim storage modes presently are being used in many countries that are producing significant quantities of highly radioactive waste. These materials will be produced by nuclear power reactors at accelerating rates. The primary concern in the management of radionuclide waste is safety. Radionuclides are processed and used in the biosphere with safety in the nuclear industry. This safety is provided in part by adequate monitoring, shielding, isolation, precautions against accidental release, and confinement and transport in suitable containers of high integrity. All containers, no matter how complete, have a finite life which is small compared to the half-life of ^{239}Pu (24,390 years). Wastes with radionuclides must be isolated until radioactive decay reduces the radioactivity to a non-hazardous level. During decay, there must be assurance that hazardous quantities of radionuclides will not be transported by air or groundwater before surveillance can be discontinued. Transport of waste could be minimized by conversion of the waste into non-volatile, virtually insoluble, stable, solid forms. If wastes are to be stored in geological formations the potential for hydrological transport must be negligible.

In the earlier days of managing high-level radioactive wastes, the fission products ^{90}Sr and ^{137}Cs were considered to be the major initial hazards because of their radioactivity and high initial concentrations in the original fission products. But after about 20 half-lives, or about 600 years, initial concentrations of these isotopes decrease by a factor of about one million as they decay to stable daughters. The actinides such as americium and plutonium are initially present in small amounts, but, in time, they become the primary hazard, if present in sufficiently large quantities, because of their longer half-lives. Figure 1 shows the hazard index for ^{241}Am . The hazard of ^{241}Am and its daughter products does not decrease significantly in more than ten million years.[1] As a result, wastes containing significant amounts of actinides must be isolated from the biosphere for millions of years. Removal of actinides from wastes will reduce the required isolation period for the bulk of the wastes; however, further development of waste processing technology is required. With present technology one method that has potential for isolating radioactive wastes that contain actinides is to utilize a geological environment that will be predictable for geologic periods (tens of millions of years).

FIGURE 1. ^{241}Am HAZARD INDEX- after M.J. Szulinski^[1]

Suitable sites for ultimate isolation of radioactive waste, that may be stable for geologic periods, include deep geological formations such as salt deposits, potash mines, dense basalt, gabbro and possibly granitic rock. The hydrology and the groundwater chemistry for any potential storage site requires definition for a site safety evaluation. The importance of groundwater movement in the transport of radionuclides is the subject of a subsequent paper.

SIGNIFICANCE OF WASTE PRODUCT FORM

The advantages and disadvantages of the alternative storage sites are influenced by the product form of the waste. For example, borosilicate glasses containing the radioactive wastes have relatively low solubility (Table 1) and volatility but are unsatisfactory for some environments.^[2] Based on the Hanford studies, the concept of conversion of radionuclide waste into silicates or aluminosilicates in the form of rock-like solids, has become increasingly promising as more is learned about the unique ability of the silicate and aluminosilicate lattices to immobilize all radionuclide cations.^[3,4] Except for a few gaseous radionuclides including tritium, krypton, iodine, and xenon, the fission products such as cesium, strontium, ruthenium, etc., form metallic ions. All of the cations form virtually insoluble silicates or insoluble silicate complexes such as aluminosilicates. The three radionuclides that usually are given primary attention when considering long-term storage needs, are ^{137}Cs , ^{90}Sr and ^{239}Pu . Both strontium and plutonium will form virtually insoluble silicates, Sr_2SiO_4 and PuSiO_4 . Plutonium silicate is a structural analog of zircon, ZrSiO_4 , with the same crystal lattice and extremely low solubility. Strontium also forms a number of aluminosilicates, one of which is a strontium feldspar. Both the strontium silicate and the strontium aluminosilicates have very low solubilities and all are stable at high temperatures. At Oak Ridge National Laboratory ^{90}Sr silicate beads have been prepared by fusion of precipitated strontium silicate for use as high-activity, beta-particle radiation heat sources. The upper temperature limit was not established but the beads were chemically stable when fused at a furnace temperature of about 2000°C .^[5] The silicate and aluminosilicate product forms are essentially inert and unreactive with most geologic materials. Exceptions would include hydrothermal solutions and low pH subsurface waters. Cesium, for example, is highly soluble and volatile in most of its chemical forms; however, pollucite ($\text{Cs}_{20}\cdot\text{Al}_{20}\cdot\text{O}_{34}\cdot\text{SiO}_2$) is highly stable in neutral or basic chemical environments.

The selection of the most suitable environmental site for ultimate storage of a radioactive waste depends on the

characteristics of the waste. If the waste is in the form of a solution, a salt cake or a calcine, it should be stored where it is isolated from natural water percolation because of its high solubility and toxicity. Such wastes have been kept in storage tanks on an interim storage basis. If the waste is a separated and concentrated fission product such as cesium chloride and contained, the container must be protected from corrosion because of the high solubility of cesium chloride in water. Consideration has been given to storing cesium chloride in dry vaults, dry caves and salt deposits with safety dependent upon the integrity of the container or immobility of cesium chloride in salt. Cesium compounds also tend to be volatile at elevated temperatures. Because the cesium ion is the most difficult of the cations to immobilize, the theory of cesium immobilization is briefly discussed.

CONTROL OF CESIUM BY POLLUCITE LATTICE

Cesium is the principal fission product of concern that belongs to the Group I cations in the periodic table of elements. Ions of these metals are characterized by a +1 valence, high elemental volatility and relatively high solubility of their compounds. The solubility of cesium can be minimized by forming a cesium "clathrate" in which each cesium ion is "caged" by a highly insoluble aluminosilicate lattice. Cesium aluminosilicate is found naturally as the mineral pollucite.^[6] In pollucite the cesium ion is enclosed by the 12 oxygen atoms (see Figure 2) of the aluminosilicate lattice according to Newnham.^[7] Once formed in this crystalline lattice, the cesium ion is locked in and cannot be exchanged.^[8] The solubility of the cesium essentially is reduced to that of the aluminosilicate lattice which is virtually insoluble in neutral or alkaline water. The caging of the cesium atoms in the aluminosilicate lattice also prevents volatilization of cesium from the compounds. Pollucite can be dissolved in silicate melts such as fused basalts without apparent loss of cesium.^[9] The melts may have fluid temperatures of 600 °C to 1350 °C or more depending upon the composition involved.^[10,11] Cesium in elemental cesium, cesium oxide, cesium chloride and other salts is considerably more volatile than in pollucite at much lower temperatures.

CONVERSION OF WASTES TO ALUMINOSILICATES

Two general types of processes are being studied at Hanford for conversion of radioactive wastes to silicates and/or silicate complexes. One type is a hydrothermal process in which rearrangement of the ions occurs in an aqueous system at temperatures from 90 °C to 500 °C and at or above atmospheric pressures. The STOPPER and Gel

processes are examples. [12,13] The second type is the hot melt system in which rearrangement of the ions occurs in a hot melt of liquid silicates. The heat for the Thermalt or hot melt may be supplied by an exothermic thermite-type reaction by the components in the premix, [4,14,15,16] from an external heat source as a glass or basalt melt in a furnace [16,17] or by a combination of methods. The choice between these processes depends in part upon the form of the radionuclides that are to be immobilized. Most investigations have been made with the exothermic process using simulated dry salt cakes. Initial studies indicate the process is effective for both low-level and high-level radionuclide wastes in the form of essentially dry nitrate salt cake or in the form of calcined wastes; i.e., oxides.

THE STOPPER PROCESS

The conventional method of forming synthetic pollucite in an aqueous medium has involved the hydrothermal process at elevated temperatures and pressures. [18,19,20] In experiments at Hanford, synthetic pollucite has been made at atmospheric pressure and 90 °C. [12,21,22] One procedure involves holding a mixture for two weeks at 90 °C containing a 4 weight percent solution of cesium hydroxide (CsOH), sodium metasilicate ($\text{Na}_2\text{SiO}_2 \cdot 9\text{H}_2\text{O}$) and aluminum hydroxide [$\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$] in a molar ratio of 1:2:1, to produce a microcrystalline pollucite. If freshly precipitated ferric hydroxide is substituted for the aluminum hydroxide in the same molar ratio, a microcrystalline iron analog of pollucite is obtained. X-ray diffraction analyses confirmed the presence of pollucite in these products. [21]

Evidence of the stability of the pollucite cage is found in the absence of sodium aluminosilicates in the microcrystalline product even though sodium was present in solution at twice the molar concentration of cesium. Formulations similar to that given for pollucite but without cesium hydroxide yielded faujasite, a sodium zeolite. But as no trace of faujasite was found with cesium hydroxide in the system, cesium is believed to control the structure of the product. The formation of cesium ferrosilicate at atmospheric pressure from a highly alkaline solution in which ferric hydroxide has low solubility also indicates the strong influence of cesium in producing the ferrosilicate lattice. Figure 3 shows the formation of pollucite from cesium hydroxide and bentonite after G. S. Barney. [22] Kaolinite plus sodium silicate also has been successfully substituted as the materials for the formation of the aluminosilicate

FIGURE 2. OXYGEN CAGE FOR CESIUM ION IN POLLUCITE WITH DIMENSIONS TO APPROXIMATE SCALE - after R.E. Newnham^[7] and L.E. Brownell et al.^[3]

cage of pollucite. [23,24] These experiments showed that cesium aluminosilicate forms in preference to sodium aluminosilicate when both Group I cations are present.

The STOPPER process has many potential alternative procedures. In one version, containers could be used for collecting commercially processed waste in the form of mixed oxides of Purex type waste. The radionuclide oxides, bentonite and silica gel flour would be mixed, cooled to a temperature below 100 °C and, with cooling continued, the dry mixture added to water. In an alternative version of the process, sodium silicate and sodium aluminate solutions would be substituted for the silica gel, clay and water. The waste container would be charged with the slurry of oxides, aluminosilicates, silicates and water into a special container. Cooling would be continued by submersion of the container in a water canal. The temperature inside the containers could rise to 100 °C without exceeding atmospheric pressure. Within six days, or less, the cesium oxide in the waste would be immobilized as pollucite. [13] Strontium oxide would be converted to crystalline aluminosilicates of two varieties, hexagonal prisms and laths. The lath-like crystals are the orthorhombic polymorph of Sr-feldspar. Any residual plutonium oxide in the system would be converted to plutonium silicate complexes. It is known that both the silicate and complex silicate products of Group II through Group VIII cations are stable and highly immobile. [25]

The growth of complex silicate crystals would be completed in a week or less, at which time the residual water would be allowed to escape by permitting a slight rise in temperature. The container would then be cooled and filled again with a fresh charge of slurry and the process repeated. This would be continued until the container was filled with solid complex silicate.

In the final stage, the cooling water would be slowly removed, causing the temperature to rise and all residual water of hydration to be driven from the container. The container would be permanently sealed by welding. The ceramic radioactive waste in the stainless steel container might be allowed to reach an equilibrium temperature without the use of cooling water but should be stored in a dry environment and kept at an elevated temperature.

FIGURE 3. REACTION PROFILE FOR THE CsOH (3.0M) - BENTONITE REACTION AT 100°C
- after G.S. Barney ^[22]

THE THERMALT PROCESS

The Thermalt process is a pyrochemical reaction which involves aluminum or silicon metal or mixtures of both as a fuel, simulated nitrate salt cake as the oxidizer and crushed basalt or Hanford sand as the silicate matrix and diluent. The Thermalt process differs from the Thermite process in that the desired end product is a complex silicate rather than a metal. The resulting melt when solidified is a silicious rock-like material that is similar in gross chemical composition to basalt.^[4] The final product is highly stable and essentially insoluble with leach rates as low or lower than other melt products described in the literature^[26] (see Table 1). The products have been shown to include sodium aluminosilicate as indicated by crystals of nepheline or carnegieite and amorphous glass. Elemental metal in the product usually is limited to small pellets resulting from unreacted excess aluminum used to maintain a reducing condition.

Initial studies indicate the process is effective for both low-level and high-level radionuclide wastes in the form of nitrate salt cake. The process can utilize low cost ingredients: basalt rock, which occurs naturally in the Hanford region, inexpensive aluminum metal such as aluminum scrap which need not be pure, and the oxidizer which is predominately sodium nitrate salt. Radionuclide wastes in the form of oxides from a calcination process can also be used. The nitrate salt cake or the oxides provide the principal source of oxygen for the reaction. The reaction provides enough heat to melt the ingredients thus eliminating the need for an external heat sources.

A typical batch "burn" of a Thermalt reaction begins with ignition of a starter powder using a spark from a spark plug, a hot glow wire, or a fuse. In conventional burns, ignition is at the top surface of a cylindrical batch of Thermalt premix. However, a number of burns with bottom ignition rather than with top ignition have been reacted successfully. A few seconds after ignition the combustion spreads from the point of ignition over the surface of the batch and the reaction front moves downward. A layer of molten silicate is produced by the heat of the exothermic reaction and forms a fluid blanket over the reaction front. The molten silicate should have a sufficiently high temperature to keep the blanket in a fluid state and thereby permit the escape of gases from the reaction. This temperature may vary considerably, but should be kept

above 1200 °C. If the temperature of the fluid blanket is low, it may restrict the escape of gas. If the reaction rate is excessive, the gas evolution may be sufficient to eject soupy masses of molten silicate. In such burns, a white-hot flame develops above the reaction. Flame temperature measurements with an optical pyrometer showed an average temperature of 2300 °C with lower values of 1900 °C and an upper value of 2600 °C. A white "smoke" or sublimate similar to that produced by burning magnesium is emitted with energetic reactions. The sublimate is believed to consist primarily of SiO with lower oxides of other metals depending upon the formulation and temperature. Preliminary analyses have identified Al_2O_3 , SiO_2 , Cs_2O , K_2O , Na_2O , MgO , and CaO as present in the condensate from high-temperature Thermalt burns. [27] The broad spectrum of oxides, some with very high melting points, was not anticipated. Present theory is that these oxides were sublimed in a lower oxide form, for example, as silicon monoxide (SiO) in the case of silicon. The monoxide is stable under reducing conditions at elevated temperatures. [28] In these reactions the premix charges which were as large as 110 to 330 kilograms, may undergo complete reaction in a period of five minutes or less. Addition of a larger percentage of inert Hanford sand or crushed basalt is one procedure for decreasing the rate of reaction. Another procedure is the substitution of silicon metal for aluminum metal as the fuel.

Figure 4 shows a photograph taken during reaction of a 35 kilogram batch of Thermalt premix (Number 71) in an open container. The high-temperature reaction shown in the photograph was controlled by formulation of this premix with silicon as the fuel to give a fluid melt of silicates and a colorless gas, free from sublimates.

Some of the typical early formulations used in experimental tests were 10-15 percent aluminum and 20 to 30 percent nitrate salt with the balance Hanford sand or basalt. The composition and crystallinity of the products can be varied by the temperature during reaction and during cooling, and the premix formulation. Some products were studied by photomicrograph, X-ray diffraction, and electron microprobe techniques. One typical early formulation studied in this manner was an aluminum-fueled, Hanford sand-moderated reaction with sodium nitrate (simulated waste) as the major source of oxygen. Premix Number 21 was of this type and consisted of 50 weight percent Hanford sand, 30 percent sodium nitrate, 15 percent aluminum powder and 5 percent aluminum scrap. This reaction was

FIGURE 4. PHOTOGRAPH OF REACTION OF A 35 KILOGRAM BATCH OF THERMALT PREMIX NUMBER 71

conducted in an open excavation in Hanford sand without the use of a separate container. The reaction was rapid with a flame temperature of about 2000 °C and gave a good melt down of the product but produced considerable sublimation. The product was a gray-colored, rock-like silicious solid with a density of about 2.9 g/cm³ and considerable crystallinity.

Figure 5 is a photomicrograph of a small sample of Thermalt product Number [29] taken with transmitted light at 160X magnification. [29] Other tests based on X-ray diffraction and microprobe analyses have helped to give identification to the crystals. The needle-shaped crystals were identified to be primarily corundum, α Al₂O₃, with some mullite, Al₄SiO₈. The rectangular grains of high relief also are corundum. The hexagonal-shaped [29] grains are cordierite, and the matrix is nepheline. [29] The corundum crystals are characteristic of premixes containing a high ratio of aluminum to salt cake as used in Thermalt premix Number 21.

In the case of moist salt cake or salt cake with a high caustic content, silicon metal has been substituted for the aluminum as the fuel and iron oxide may be used in place of a portion of the silicious material. [23] With proper formulation, the iron oxide and silicon combine in the Thermalt reaction as an iron silicate, fayalite, or as an iron glass rather than being reduced to the metal. Figure 6, a photomicrograph of a Thermalt product of this type of formulation (premix A7), shows crystals of fayalite in a glassy matrix (magnification is 32X). [29] If such premixes contain 40 percent or more salt cake the product is usually glassy without fayalite.

SOLUBILITY OF ALUMINOSILICATE SYSTEMS

Quantitative data on the solubility of the inorganic silicates and aluminosilicates are very limited. This dearth is due in part to the length of time required to make reliable measurements for a given silicate in a given system. Silicates such as those proposed to encapsulate radionuclides are so insoluble that experiments require many months to make accurate determinations because of the very long time required to reach an equilibrium state. Experiments are presently being conducted using apparatus and procedures similar to those described by Paige [30] to determine leach rates as listed in Table 1 for STOPPER silicates. [31] Leach rates represent rates of dissolution rather than true equilibrium solubility. Leaching tests

FIGURE 5. PHOTOMICROGRAPH OF THERMALT PRODUCT NUMBER 21 SHOWING CORUNDUM AND MULLITE (NEEDLE SHAPED) AND CORDIERITE (HEXAGONAL SHAPED) CRYSTALS IN MATRIX OF NEPHELINE (160x). after J.W. Shade and L.L.Ames. (29)

FIGURE 6. PHOTOMICROGRAPH OF THERMALT PRODUCT NUMBER A7 FROM A PREMIX AND REACTION SIMILAR TO THAT SHOWN IN FIGURE 4. NOTE CRYSTALS OF FAYALITE IN A GLASSY MATRIX (32x).
after J.W. Shade and L.L. Ames. (29)

can be completed in shorter periods than solubility measurements, but specific values depend upon the technique used. Leach rate values for the products of other laboratories listed in Table 1 have been approximately normalized for purpose of comparison using the values of Gera and Jacobs. [26]

Initial estimates of true solubility have been made by studying known solubilities and thermodynamic relationships of some natural silicates and aluminosilicates which are structurally analogous to the synthetic radioactive silicates. However, the solubilities of the radioactive species must be evaluated. The synthetic pollucite has been shown to be structurally identical to the naturally occurring cesium mineral pollucite by X-ray diffraction measurements. One strontium feldspar is analogous in structure to anorthite (calcium aluminosilicate). The plutonium silicate structure is similar to that of the natural mineral zircon (ZrSiO_4). As mentioned previously, the solubilities of the aluminosilicates containing radioactive cesium and strontium are primarily a function of the solubility of the aluminosilicate lattice.

Since little data are available for pollucite, the solubility of the sodium analog, analcite, is shown in Figure 7 after Diebold [32] which illustrates the range of sodium ion concentration as a function of silicic acid concentration and pH in solutions saturated simultaneously with analcite and Na-montmorillonite. These curves were plotted on the basis of thermodynamic data reported by Helgeson. [33] Figure 8 illustrates the equilibrium established between analcite and Na-montmorillonite after R. M. Garrels and C. L. Christ. [34] Pollucite containing cesium is predicted to be much less soluble than its sodium analog, analcite. Cesium cannot be extracted from ideal crystalline pollucite but can be removed by breaking up the lattice itself, whereas in analcite the Na^+ ion is small enough to move into or out of the lattice. [8]

Solubility predictions can be made with more accuracy when considering the analogs of Sr and Ca feldspar. In neither silicate is the cation exchangeable with other ions, so the dissolution of Ca and Sr can only be effected by a corresponding dissolution of their surrounding aluminosilicate lattices. Figure 9 shows a plot of the calcium ion concentration as a function of pH and silicic acid concentration in aqueous solutions simultaneously saturated with calcium feldspar (anorthite)

TABLE 1

CHARACTERISTICS OF SOME HIGH-LEVEL RADIOACTIVE WASTES

No.	Process	Product Form	Water* Leachability $\text{g} \cdot \text{cm}^{-2} \cdot \text{day}^{-1}$	Solubility Cold Water $\text{gm}/100 \text{ ml}$
1.	Cesium Chloride	Salt	>10	186
2.	ITS(Hanford)	Salt Cake	>1	~30 to 50
3.	Pot Calcination	Calcine	5×10^{-1}	10 to 20
4.	Fluid Bed	Granules	5×10^{-1}	10 to 20
5.	Spray Melt	Ceramic or Glass	1×10^{-4}	<1
6.	Phosphate Glass	Phosphate Glass	1×10^{-4} (Stored 600°C) to 5×10^{-6}	<1
7.	Fingal & Others	Borosilicate Glass	5×10^{-6}	Insol.
8.	Marcoule	Silico-boro-phospho molybdic Glass	5×10^{-6}	Insol.
9.	Chalk River	Nepheline Syenite Glass	5×10^{-7}	Insol.
10.	Czech or Hanford	Basalt Melt	1×10^{-6} to 1×10^{-7}	Insol.
11.	Thermalt	Aluminosilicate Melt	2 to 8×10^{-7}	Insol.
12.	Thermite	Ferrosilicate Melt	5×10^{-7}	Insol.
13.	Hanford STOPPER (See Below)	Crystalline Aluminosilicate	$\sim 5 \times 10^{-8}$	Insol.
14.	Pollucite	Crystalline Aluminosilicate	$2.9 \times 10^{-8}^{**}$	Insol.
15.	Anorthite	Crystalline Aluminosilicate	$\sim 5 \times 10^{-8}$	Insol.
16.	Zircon	Crystalline Silicate	< 1×10^{-8} (est.)	Insol.

* Normalized values, after F. Gera and D. J. Jacobs^[26]

** Leach rate after 5 to 32 days of leaching after M. J. Kupfer^[27]

FIGURE 7 CONCENTRATION OF Na^+ IN AQUEOUS SOLUTIONS SIMULTANEOUSLY SATURATED WITH ANALCITE AND Na-MONTMORILLONITE
- after F. Diebold [32]

FIGURE 8 PHASE DIAGRAM IN THE SYSTEM $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$
after R. M. Garrels and C. L. Christ [34]

and calcium-montmorillonite, after Diebold. [32] The curves are based on thermodynamic data from Helgeson. [33] However, it should be noted that the plot presented in Figure 9 is only an estimate from free energy data in the literature and does not take into account effects of other ions, temperature variations, or surface area variations. Again, however, these data are useful in determining approximate ranges of solubilities for future experiments.

Plutonium silicate is analogous to zircon (ZrSiO_4) in structure, but thermodynamic data have not been found for either compound. However, it is doubtful that plutonium silicates would exist in a crystalline state in radioactive wastes. This is due primarily to the fact that plutonium is dilute and would be dispersed within the crystalline silicate lattices of the other elements present. If plutonium silicate were to be of sufficient concentration as to exist as a separate crystalline phase, the solubility is expected to be extremely low. For a qualitative understanding of the degree of solubility of plutonium silicate one might refer to the presence of zircon and thorite in beach and river sands. [35]

POTENTIAL APPLICATIONS

A mineral placed in an environment such that it is at complete chemical equilibrium with that environment is said to be stable. Under these conditions, no net changes, dissolution, or precipitation, of the mineral will take place, although in a dynamic system, some ions in solution exchange with ions in the mineral. The importance of this concept cannot be over-emphasized when considering the disposition of STOPPER or Thermalt silicates. The solubilities of these silicates are very low even in pure water as pointed out previously. If these silicates are stored in an environment which is chemically neutral, the radionuclides contained in those silicates would be virtually immobilized. The conditions necessary for the stability of the STOPPER and Thermalt silicates are important. Silicate minerals will be precipitated by hydrothermal processes in the presence of excess silica and alumina in an alkaline system.

CHAMBERS OF BASALT

A chamber mined out of a thick dense basalt layer may provide a suitable environment for storage of the STOPPER or Thermalt aluminosilicate waste product forms. Such basalt layers exist on the Columbia Plateau in the State of Washington, United States of America.

FIGURE 9 CONCENTRATION OF Ca^{+2} IN AQUEOUS SOLUTIONS SIMULTANEOUSLY SATURATED WITH ANORTHITE AND Ca-MONTMORILLONITE
- after F. Diebold [32]

The Columbia Plateau, upon which the Hanford site is located, is unique in the United States because of the thick sequence of basalt. The stratigraphy (and geologic structure) of the basalt strata underlying Hanford and the Pasco Basin is shown in Figure 10 after D. J. Brown.^[36] In the center of the basin the basalt is more than 3200 meters thick and consists of more than 50 basalt flows many of which are separated by weathered zones. Most flows cover areas of thousands of square kilometers and in general are continuous. Below a depth of 700 meters the strata are not tapped for water, oil, or gas. Certain zones at depths below 900 meters are very dense and essentially impermeable. Based on the chemical analysis of many water samples, the United States Geological Survey stated "The chemical and isotopic characteristics of the groundwater show a strong horizontal zonation of the deeper water in the well, the water from 980 to 1,280 feet, and the shallower water. This zonation indicates that little, if any, vertical movement of water has occurred at the site of the well."^[37]

A typical chemical analysis of basalts at Hanford contains about 13 percent Al_2O_3 , 15 percent FeO , 8-1/2 percent CaO , 4-1/2 MgO , 3 percent Na_2O , 2-1/2 percent TiO_2 , 1-1/2 percent K_2O and 52 percent SiO_2 . The oxides are in combination with silica as complex silicates and the alkali oxides form bases upon reaction with water which are stronger than the silicic acid formed upon reaction of SiO_2 with water. The pH of water from deep basalt formations at Hanford ranges from about 8 to 10.^[37] The chemical composition of groundwater from a deep borehole at Hanford are shown in Table 2. The alkalinity and the abundance of alumina and silica in the basalts are considered beneficial in the stabilization of the STOPPER and/or Thermalt silicates and the continued immobilization of the radionuclides.

STORAGE IN TERRIGENOUS, ARGILLACEOUS SEDIMENTS

Early concepts for the disposal of radioactive waste in the oceans have in general assumed dissolution of the waste in sea water. A possibly safe system could be designed to rely on authigenic processes whereby the radioactive waste would be immobilized as STOPPER or Thermalt products and buried in terrigenous, argillaceous sediments in a sea bed where sediments continue to collect.

In the last dozen years, several investigators including Sillen^[38,39], Helgeson^[40], MacKenzie, Garrels, Bricker and Bickley^[41], and MacKenzie and Garrels^[42], have discussed the role of silicate reactions in ocean chemistry. The clay minerals regulate the silica content of seawater as shown in Figure 11 according to the experiments of MacKenzie, et al.^[41]

FIGURE 10. GEOLOGIC CROSS SECTION THROUGH HANFORD RESERVATION SHOWING BASALT STRATIGRAPHY - after D. J. Brown [36]

TABLE 2

WATER ANALYSIS FROM DEEP WELL SAMPLES^[37]

<u>Depth (Ft)</u>	<u>pH</u>	<u>SiO₂ mg/l</u>	<u>Na mg/l</u>	<u>Ca mg/l</u>	<u>Al mg/l</u>	<u>Fe mg/l</u>	<u>HCO₃⁻ mg/l</u>	<u>CO₃ mg/l</u>	<u>Cl⁻ mg/l</u>
364-2242	9.5	81	141	2.5	0.8	0.0	72	67	83
1330-1520	9.7	81	168	5.0	1.1	0.2	32	86	110
1090-1280	10.2	90	177	5.8	1.1	0.0	--	92	120
2600-2280	8.9	48	87	1.2	0.1	1.0	181	18	13
3166-3196	9.9	120	181	0.7	1.1	0.2	--	125	94
3144-3236	9.6	116	180	0.8	1.1	0.1	49	101	98
3206-3246	9.9	105	176	0.6	1.1	0.7	2	120	98
3320-3451	9.7	63	166	0.2	0.9	1.8	68	75	90
4080-4283	8.9	67	134	0.2	1.3	2.1	164	16	68

FIGURE 11. INFLUENCE OF 1.0g MINERAL SAMPLES IN CONTROLLING SILICA CONCENTRATIONS IN 200 ml OF SEA WATER (1) DEPLETED TO 0.03 ppm $\text{SiO}_{2\text{aq}}$ AND (2) INITIALLY ENRICHED TO 25 ppm $\text{SiO}_{2\text{aq}}$ - after MacKenzie et al.[41]

Duursma and Gross have discussed "Marine Sediments and Radioactivity" in Chapter 6 of the review in 1971 by the National Academy Science entitled "Radioactivity in the Marine Environment." [43] Note is made that "Sedimentary particles have a substantial capacity to remove radionuclides from the ocean, either depositing them on the bottom out of contact with man or concentrating them on particles that may be picked up by filter-feeding organisms..."

Jenne and Wahlberg studied processes by which radionuclides are bound to fresh-water sediments of the Clinch River on the Oak Ridge site and found that in the presence of carbonates ^{90}Sr precipitates in-situ, ^{137}Cs interacts with clay minerals, [44] and ^{60}Co combines with oxides of iron and manganese. [44] Ginnel, Martin and Hatch [45] in early studies at Brookhaven National Laboratory found that montmorillonite clay selectively absorbs fission-product cations and that the radioactive ions can then be sealed within the crystal lattice by heating to 1000 °C. Duursma and Gross suggest that similar mineral-related reactions, each one possibly highly specific, probably control radionuclide uptake in the marine sediments and conclude that these sediments or sedimentary particles can remove radionuclides from seawater and deposit them on the sea bottom.

To explore the immobilization of radionuclides by sediments via authigenic synthesis, tests were conducted at the Hanford site with seawater, bentonite and oxides of some of cations in the fission products. [46] In one series of tests 2.5 gram quantities of cesium hydroxide were dissolved in 10 ml samples of seawater and mixed with 5.9 grams of bentonite. The slurry of bentonite and seawater was used to simulate sea bed sediments. Samples were placed in autoclaves and heated to 300 °C for periods of one hour, seven hours, and 100 hours. X-ray diffraction measurements of the solids after reaction showed strong pollucite peaks for all three products but with the greater intensity in the samples given seven hours and 100 hours reaction times. In another experiment a sample of sea mud from a depth of 1660 meters off the mouth of the Columbia River was obtained through the courtesy of Professor Dean A. McManus of the Department of Oceanography of the University of Washington. X-ray diffraction tests showed that the solids in the sample consisted chiefly of fine quartz and feldspar with lesser amounts of chlorite, illite and montmorillonite. In synthesis tests 10 ml of the sample of sea sediment as received was reacted with 2.5 gm of CsOH at 90 °C for two weeks. The solid

product showed strong X-ray diffraction patterns for pollucite with elimination of patterns for all three clay minerals (chlorite, illite and montmorillonite).^[46] These tests provided experimental verification of the authigenic synthesis of pollucite in seawater from cesium hydroxide such as might be leached from a calcined waste deposited in a sea bed.

Strontium oxide in calcined waste is less soluble in seawater than cesium oxide and reacts with seawater to precipitate as the carbonate and/or the sulfate before there is an opportunity to react with aluminosilicates in the sediments. A laboratory test with seawater and strontium hydroxide produced a double precipitate of strontium carbonate and magnesium hydroxychloride.^[46]

As a consequence of precipitation, strontium ions leached from calcined waste will not follow the same path as cesium ions but still will be immobilized as a result of reaction with seawater. If the concentration of the strontium ion is sufficiently high in the local area of leaching, it may also react with amorphous aluminosilicates in the sediments. Laboratory tests using fresh water demonstrated the formation of a strontium aluminosilicate zeolite at a temperature of 90 °C and a strontium orthorhombic feldspar at 300 °C.

These preliminary tests indicated that radionuclide cations of both cesium and strontium will be immobilized by argillaceous sediments. Further tests are needed to explore the limits of immobilization and to evaluate the effect of convection currents that may be caused by the heat from the wastes. Other radionuclide cations in Groups II through VII are shown to form insoluble silicates and complex silicates. Plutonium and other heavy metal cations also form hydroxides, carbonates, and sulfates of low solubility. This leads to the possibility that radionuclide waste can be immobilized by burial beneath the sea within an advancing front of terrigenous sediments. The degree of isolation and immobilization will be increased by converting calcined wastes to silicified wastes before storage of the waste in a sea bed.

SUMMARY AND CONCLUSIONS

Radioactive wastes in the form of nitrate solutions, salt cake, oxides and hydroxides are handled and stored in the biosphere for short periods by the use of containers of high integrity. The permissible time for such storage

is some fraction of the anticipated life of the container. For very long-term or ultimate storage, the radioactive waste must either be removed positively from the biosphere or rendered immobile. In the absence of, or eventual failure of a container, immobilization becomes important. Silicification of the waste as an aluminosilicate provides a unique method of immobilizing radionuclides.

The STOPPER^[1] (Stone Process for Permanent Encapsulation of Radionuclides) is being developed to hydrothermally convert radionuclide cations to silicate mineral analogs. The Thermalt process^[2] is being developed to convert wastes to silicate or aluminosilicate products in a non-aqueous pyrochemical process. These stable, virtually insoluble products could possibly be stored safely in deep underground chambers in dense, basic or ultra-basic crystalline rock such as basalt, wherein the water has a high pH and is saturated with alumina and silica. Further work may show that other rock or sedimentary formations may be essentially neutral and non-reactive with these product forms. Ultimate storage of silicified radioactive waste in a deep underground cavern in a strata of dense basalt is under consideration. Pore water associated with such basalt is usually of a high pH, and is 50 or more times richer in silica and alumina than seawater. Thus, pore water in confined aquifers associated with deep basalt strata is a rich source of aluminosilicates for possible authigenic synthesis of pollucite, and silicates or aluminosilicates of all the radiocations.

Recent experiments have shown that authigenic synthesis of pollucite ($\text{Cs}_{20}\cdot\text{Al}_{12}\text{O}_3\cdot 4\text{SiO}_2$) is possible at atmospheric pressure at temperatures as low as 90 °C by reaction of cesium with a variety of clay materials, such as kaolinite, montmorillonite, illite, bentonite and sea mud. This opens the possibility of storing STOPPER or Thermalt product forms in bottomset argillaceous sediments. This might be at the front of the silt deposits from a large river where its sediments reach to the bathyal zone. The immobilization of the waste by silicification before deposition in a sea bed would further limit the potential for dissolution. Use of ceramic containers for the waste rather than stainless steel would be advantageous in a salt water environment. The fact that ceramics in the form of art objects and storage containers from early civilizations, such as the Minoan--3000 or more years old, have been recovered from the sea bottom in good condition is indicative of the safety that could be afforded by ceramic containers.

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LIST OF FIGURES

- Figure 1 ^{241}Am Hazard Index - after M. J. Szulinski [1]
- Figure 2 Oxygen Cage for Cesium Ion in Pollucite with Dimensions to Approximate Scale - after R. E. Newnham [7] and L. E. Brownell et al. [3]
- Figure 3 Reaction Profile for the CsOH (3.0M) - Bentonite Reaction at 100 °C - after G. S. Barney [22]
- Figure 4 Photograph of Thermal Reaction of a 35 Kilo-gram Batch of Premix Number 71.
- Figure 5 Photomicrograph of Thermal Product Number 21 Showing Corundum and Mullite (Needle Shaped) and Cordierite (Hexagonal Shaped) Crystals in a Matrix of Nepheline (160X). After J. W. Shade and L. L. Ames. [29]
- Figure 6. Photomicrograph of Thermal Product Number A7 from a Premix and Reaction Similar to that Shown in Figure 4. Note Crystals of Fayalite in a Glassy Matrix (32X). After J. W. Shade and L. L. Ames. [29]
- Figure 7 Concentration of Na^+ in Aqueous Solutions Simultaneously Saturated with Analcite and Na-Montmorillonite - after F. Diebold. [32]
- Figure 8 Phase Diagram in the System $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ - after R. M. Garrels and C. L. Christ. [34]
- Figure 9 Concentration of Ca^{+2} in Aqueous Solutions Simultaneously Saturated with Anorthite and Ca-Montmorillonite - after F. Diebold. [32]
- Figure 10 Geologic Cross Section through Hanford Reservation showing Basalt Stratigraphy - after D. J. Brown. [36]
- Figure 11 Influence of 1.0 g Mineral Samples in Controlling Silica Concentrations in 200 ml of Sea Water (1) Depleted to 0.03 ppm $\text{SiO}_{2\text{aq}}$ and (2) Initially Enriched to 25 ppm $\text{SiO}_{2\text{aq}}$ - after MacKenzie et al. [41]