DEFENSE WASTE SALT DISPOSAL AT THE SAVANNAH RIVER PLANT

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ABSTRACT

A cement-based waste form, "saltstone," has been designed for disposal of Savannah River Plant low-level radioactive salt waste. The disposal process includes emplacing the saltstone in engineered trenches above the water table but below grade at SRP. Design of the waste form and disposal system limits the concentration of salts and radionuclides in the groundwater so that EPA drinking water standards will not be exceeded at the perimeter of the disposal site.

INTRODUCTION

Background

The Defense Waste Processing Facility (DWPF) at the Savannah River Plant (SRP) is scheduled to begin operation in 1989. Two types of waste will be processed: high-level defense waste (primarily Fe, Mn and Al hydroxides) and low-level waste (primarily sodium salts generated as spent industrial processing chemicals). A schematic of both operations is shown in Fig. 1. The high-level sludge waste will be vitrified at SRP prior to shipment to a federal geologic repository. The processed salt waste will be buried in engineered trenches at SRP.

The disposal process for low-level waste, primarily $NaNO_3$, $NaNO_2$, $NaAl(OH)_4$, Na_2SO_4, and NaOH, involves reconstitution of the salts into a concentrated solution (about 32 wt % solids), decontamination, solidification in a cement-based waste form, and burial at SRP. The average bulk composition of decontaminated aged salt solution is shown in Table I. The decontamination process consists of cesium removal by precipitation of cesium tetraphenylborate and strontium removal by adsorption onto sodium titanate particles. Radionuclide concentrations in the average decontaminated solution are listed in Table II. The total projected amount of reconstituted liquid waste which will be disposed of in this manner is about 400 million liters.

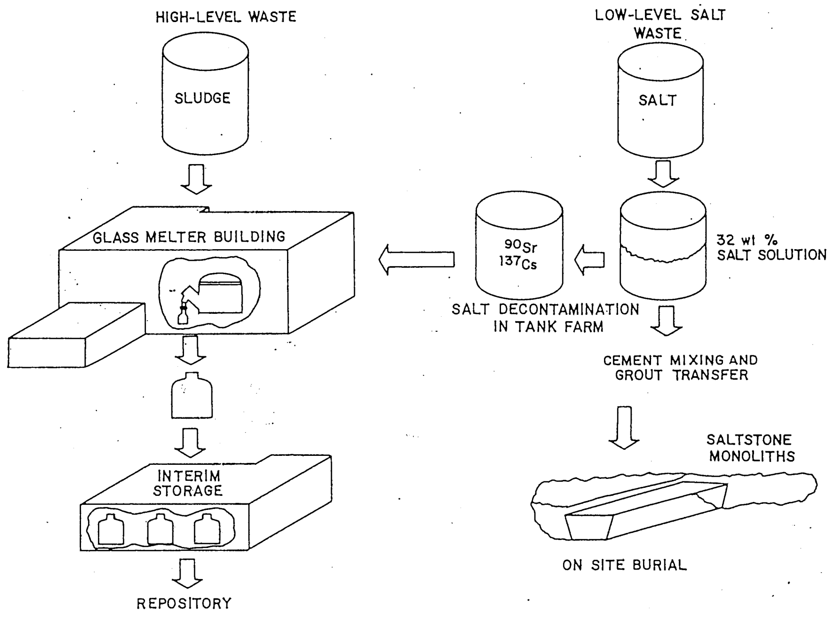

Fig. 1. Schematic Diagram Illustrating SRP Defense Waste Processing Facilities.

TABLE I

Average Chemical Composition of Decontaminated, Aged Salt Solution[a]

Component	Decontaminated Salt Solution wt %
H_2O	68
$NaNO_3$	15.6
$NaNO_2$	3.9
NaOH	4.2
$NaCO_3$	1.7
$NaAl(OH)_4$	3.6
Na_2SO_4	1.9
NaF	0.06
NaCl	0.12
Na_2SiO_3	0.04
Na_2CrO_4	0.05
$Na_2C_2O_4$	0.31
Na_3PO_4	0.13
$NaB(C_6H_5)_4$	0.06
Other Salts	0.20

[a] Adjusted to account for precipitation and filtration.

TABLE II

Average Radionuclide Composition of Decontaminated, Aged Salt Solution

Radionuclide (half-life, yrs)	Supernate (aged 15 yrs) (nCi/g)
^{14}C (5730)	0.009
^{60}Co (5.27)	0.2
^{59}Ni (80,000)	0.0002
^{63}Ni(100)	0.02
^{79}Se(approx. 6.5 x 10^4)	0.3
^{90}Sr (29)	0.7
^{90}Y (3.1 hr)[a]	0.7
^{99}Tc (2.1 x 10^5)	4 x 10^1
^{106}Ru (1.0)	4 x 10^1
^{106}Rh (2.18 hr)[a]	4 x 10^1
^{125}Sb (2.73)	9
^{126}Sn (approx. 10^5	0.2
^{125m}Te (58 da)[a]	0.2
^{126}Sb (12.5 da)[a]	0.02
^{125m}Sb (19 min)	0.2
^{129}I (1.7 x 107)	0.2
^{137}Cs (30.2)	2 x 10^1
^{137m}Ba (2.5 min)[a]	2 x 10^1
^{147}Pm (2.62)	4
^{151}Sm (93)	2
^{154}Eu (8.2)	1
^{155}Eu (4.76)	0.3
^{238}Pu (87.7)	0.05
^{239}Pu (24,000)	0.0005
All TRU elements	0.2

[a] Daughter of preceding isotope.

Pertinent Regulations

SRP is operated under the jurisdiction of the U. S. Department of Energy. Therefore, all applicable DOE regulations must be met. These include DOE Order 5820[1] which establishes policies and guidelines for disposal of low-level radioactive waste and DOE Order 5480[2] which pertains to hazardous and radioactive mixed waste. The latter order stipulates that DOE facilities will follow, to the extent practiceable, regulations issued by the EPA. Therefore, although the processed saltstone does not fall into the hazardous waste category,[3] it is required that SRP preserve the quality of the groundwater so that it will meet drinking water limits at the landfill boundary (EPA 40CFR141).[4] Likewise, although NRC 10CFR61[5] does not apply to the defense waste generated at SRP, the goal is to equal or exceed these requirements for disposal of commercially-generated radioactive waste.

Waste Description

An estimate of the volume and of the amount of contaminants in the SRP salt waste is summarized in Table III. The reconstituted, decontaminated salt solution is a low-level radioactive waste containing about 190 nCi/g. The most environmentally significant radionuclides account for about 61 nCi/g and are listed in Table III. Hazardous chemicals in this solution include: Cr (VI), present as chromate; a small amount of Hg, present as Hg (0 and II); and benzene which is formed by the breakdown of $NaB(C_6H_5)_4$ (used to remove Cs from the solution). Non-hazardous chemicals which must be controlled to meet drinking water standards include: N present as $NaNO_3$ and $NaNO_2$, and OH^- present as NaOH. (The solution pH is 14).

TABLE III

Salt Waste Description

DWPF Salt Solution	Total Quantity	Concentration
Volume	4 x 10^8 liters	32 wt % salts
Radioactive Isotopes ^{137}Cs, ^{99}Tc, ^{90}Sr	3 x 10^4 Ci	61 nCi/g
EPA Hazardous Chemicals		
Cr	36 metric tons	130 ppm
Hg	3.2 kilograms	0.011 ppm
Benzene	127 metric tons	526 ppm
Non-Hazardous Chemicals		
$NaNO_3$ - $NaNO_2$	9 x 10^4 metric ton	157,000 ppm
NaOH	1.8 x 10^4 metric ton	pH 14

Waste Disposal Systems

Selection of a disposal system for the decontaminated salt solution was based on an assessment of the waste inventory and a review of several disposal options which could potentially meet all state and federal requirements. A review of these disposal alternatives has been presented elsewhere.[6]

Methods considered for containment of the salt waste involve stabilization via a treatment process to reduce contaminant mobility. This can be accomplished by one or a combination of techniques including; solidification to eliminate spills and airborne contamination, microencapsulation to reduce leaching, and chemical fixation. The two disposal options considered for the resulting waste form were emplacement in secured landfills (clay-lined - clay-capped trenches with leachate collection systems) and burial in engineered trenches without leachate collection.

The secured landfill option was rejected as a final means of salt disposal. Since sodium salts do not chemically degrade or decay, continual monitoring for leachate would be necessary to assure groundwater quality. Leachate generated by this landfill scenario would also require disposal and would ultimately lead to repetitive treatment and burial of the salt waste.

Final disposal of stabilized waste in engineered trenches without leachate collection systems was adopted after initial laboratory testing indicated that the various potential contaminants could be adequately contained in cement-based waste forms. This total system provides a mechanism for slow, controlled release of the salts which constitute most of the waste. In addition, migration of the radionuclides and hazardous chemicals, Cr and Hg, into the groundwater is negligible due to retention in the waste form and immediately adjacent soils.

Saltstone: SRP Cement-Based Waste Form

Several materials including polymers, bitumen, and cementitious grouts were initially considered for salt waste encapsulation. A cement-based waste form, saltstone, was chosen because both slurry properties and final bulk properties of this material can be tailored to meet mixing, emplacement, contaminant stabilization, and durability requirements. In addition, existing technology and commercially available equipment are suitable for high-volume grout processing.

The current reference formulation is shown in Table IV. The preblended cement and fly ash is mixed with decontaminated salt solution to form a grout. A discussion of the development of this formulation and physical properties of the slurry and cured product has been presented by Langton, et. al, 1983.[7]

TABLE IV

Saltstone Reference Formulation

Ingredient	Wt %	
Portland Cement (Class H)	12	60 wt % Cement
Fly Ash (Class C)	48	
Salt	13	40 wt % Solution
Water	27	

Saltstone Microencapsulation Mechanism

Microencapsulation of the waste in saltstone is achieved as the result of hydration reactions between the cement and water component of the solution. As a result of these reactions, the waste is trapped in pore spaces and/or chemically fixed as metal hydroxides. Cations such as Sr^{2+} substitute for Ca^{2+} in the hydration products.

Upon mixing the blended cement and solution, hydrated calcium silicate gel, CSH, begins to form. Reaction products also include $Ca(OH)_2$ and small amounts of other cyrstalline and non-crystalline phases. As water is consumed by the hydration process, the pore solution becomes super-saturated with respect to the various constituent salts. At this point, remaining pore space is filled with CSH gel and salt crystals. In the final cured product, crystals of the sodium salts are disseminated throughout the cement gel matrix. In saltstone, as in construction concrete, pore solution in excess of that required for complete hydration is retained in the microstructure as interstitial capillary pore fluid. A schematic illustration of this microencapsulation process is shown in Fig. 2. An SEM image of saltstone illustrating the resulting micro structure is shown in Fig. 3.

Disposal Site Selection

Compatibility between the waste form and the disposal environment is an integral part of the containment system. The following criteria were used to select the saltstone disposal site: good drainage, downward hydraulic gradient, adequate area to accommodate 8 x 10^5 cubic meters of grout emplaced in trenches at least 5 meters below grade[a] and 1.5 meters above the historic high water table,[b] and proximity to H Area where the waste will be decontaminated. A suitable site has been identified at SRP and is referred to as Z Area.

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[a] At SRP, root penetration and burrowing animal habitats are limited to the upper 5 m of soil.

[b] The groundwater underlying the disposal site is 15.5-19.5 m below grade.

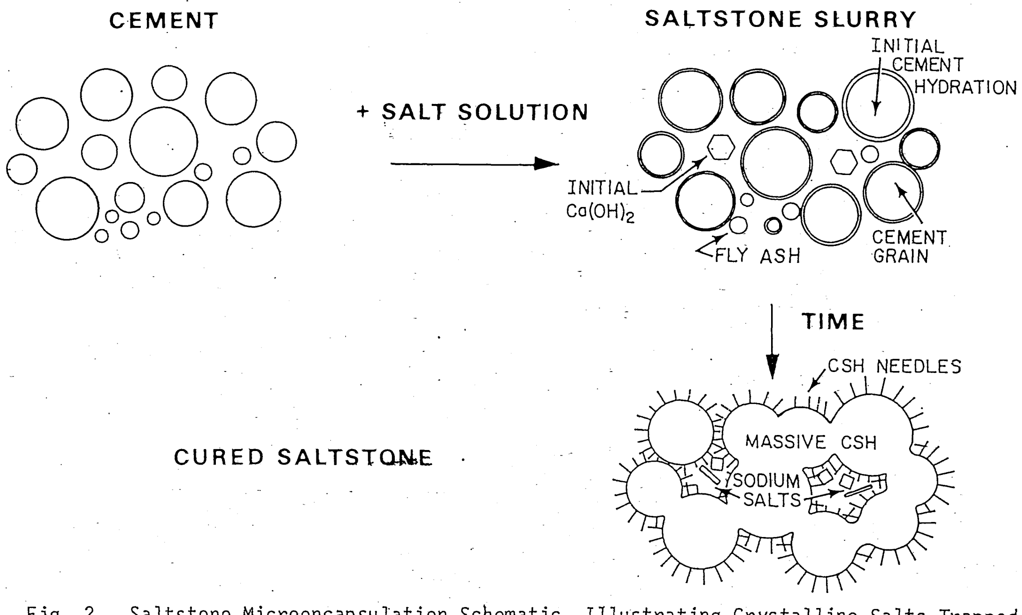

Fig. 2. Saltstone Microencapsulation Schematic, Illustrating Crystalline Salts Trapped in Pore Spaces of Hydrated Cement. Modified from References 8 and 9.

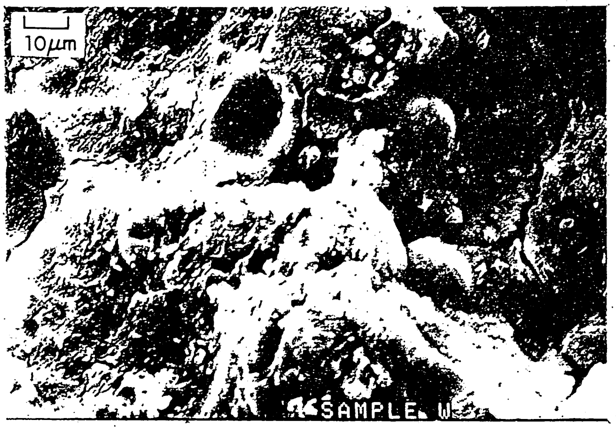

Fig. 3. SEM Secondary Electron Image of the Reference Saltstone Formulation after Curing for 28 Days. Round Spheres are Unreacted or Partially Reacted Fly Ash. CSH Gel after 28 days Appears Massive. Salt Crystals are Small Bright Crystals Disseminated Throughout the Gel.

Relatively constant moisture content and hydraulic conductivities of the soils making up the host sediments in Z-Area result in an unsaturated steady state environment. These conditions are desirable for long-term curing of the saltstone monoliths. Also this environment minimizes the potential for cyclical wetting and drying which could be detrimental to saltstone durability. Likewise, location of the monoliths in the unsaturated zone above the water table also minimizes the potential for accelerated leaching under saturated conditions.

Trench Design

Emplacing saltstone in engineered trenches and backfilling to grade assures waste form integrity and precludes contaminant release directly into surface runoff. A variety of trench geometries, dimensions, and layouts have been generated by computer modeling of the disposal system. Variables considered in these studies include soil and saltstone properties and projected rainfall. Many of these designs meet the criteria for maintaining drinking water standards in the groundwater at the site boundary. The current reference trench and landfill layout are shown in Fig. 4. In this design, the monoliths are covered with clay caps made from a mixture of Z-Area soil and 6-12 wt % bentonite. These caps assure that water does not accumulate on top of the monoliths and further reduce the possibility of root and burrowing animal penetration of the saltstone.

CONCLUSION

The disposal system for the DWPF salt waste includes reconstitution of the crystallized salt as a solution containing 32 wt % solids. This solution will be decontaminated to remove ^{137}Cs and ^{90}Sr and then stabilized in a cement-based waste form, saltstone. Laboratory and field tests indicate that this stabilization process greatly reduces the mobility of all of the waste constitutents in the surface and near surface environment.[7,10] Engineered trenches for subsurface burial of the saltstone have been designed to assure compatibility between the waste form and environment. The total disposal system, saltstone-trench-surrounding soil, has been designed to contain radionuclides, Cr, and Hg, while allowing for very slow, controlled release of soluble N and OH^- as the salts themselves. In this way, final disposal of the SRP low-level waste can be achieved and the quality of the groundwater at the perimeter of the disposal site will not exceed EPA drinking water standards.

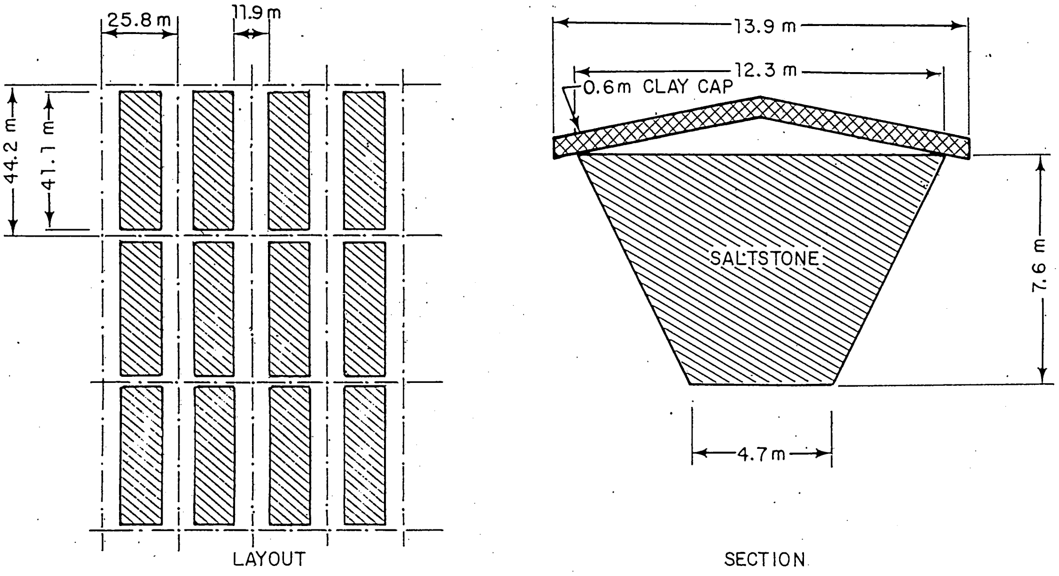

Fig. 4. Reference Trench Lay-Out and Cross Section.

ACKNOWLEDGMENT

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U. S. Department of Energy.

REFERENCES

1. "Radioactive Waste Management (DRAFT)," U. S. Department of Energy, DOE Order 5820 (March 25, 1983).

2. "Hazardous Waste Management," U. S. Department of Energy, DOE Order 5480 (December 1982).

3. "Hazardous Waste Management Regulations," South Carolina Department of Health and Environmental Control (March 31, 1980, amended January 29, 1981).

4. "National Interim Primary Drinking Water Regulations," U. S. Environmental Protection Agency, EPA 570/9-76-003 (1975).

5. "Licensing Requirements for Land Disposal of Radioactive Waste," U. S. Nuclear Regulation Commission, NRC 10CFR61 (December 30, 1982).

6. R. W. BENJAMIN, W. R. McDONELL, and J. E. HOISINGTON. "Alternatives for Defense Waste Salt Disposal," Proceedings of the Symposium on Waste Management, Tuscon, AR, February 27 - March 3, 1983, Vol. I.

7. C. A. LANGTON, M. D. DUKES, and R. V. SIMMONS, "Cement-Based Waste forms for Disposal of Savannah River Plant Low-Level Radioactive Salt Waste," Proceedings of the Materials Research Society 1983 Annual Meeting, Boston, MA, November 14-17, 1983.

8. F. M. LEE, The Chemistry of Cement on Concrete, Chemical Publishing Co., New York, NY (1971).

9. D. C. CHRISTENSEN and W. WAKAMIYA, "A Solid Future for Solidification/Fixation Processes," Toxic and Hazardous Waste Disposal V. 4 Neward Promising Ultimate Disposal Options, Ed. R. B. Pojasek, Ann Arbor Science, Ann Arbor, MI, p. 75-89 (1982).

10. M. D. DUKES, H. C. WOLF, and C. A. LANGTON, "Disposal of Decontaminated Salts at the Savannah River Plant by Solidification and Burial," Am. Nuclear Society 1983 Winter Meeting, San Francisco, CA, (October 1983).