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ABSTRACT

High-level nuclear wastes will be processed at the Savannah River Plant (SRP) to separate the high-level fraction from the low-level fraction. The separation will be accomplished in existing waste tanks by a process combining precipitation, adsorption, and filtration. The high-level fraction will be vitrified into borosilicate glass in the Defense Waste Processing Facility (DWPF) for disposal in a Federal repository. The low-level fraction, called decontaminated salt solution, will be mixed with a cement-fly ash blend. The resulting product, called saltstone, will be disposed onsite in an engineered disposal area.

Laboratory testing of saltstone has shown the predominant mechanism for release of contaminants to the environment to be diffusion. The diffusion coefficient for nitrate has been determined to be $1.04 \pm 0.09 \times 10^{-8} \text{ cm}^2/\text{sec}$. Field-testing of three 30-ton blocks of saltstone has been underway since January 1984.

Mathematical models, both analytical and numerical, have been applied to predict the impact of saltstone disposal on groundwater quality. Based on model predictions, the saltstone disposal area is designed to meet or exceed groundwater standards for all potential contaminants.

Results of laboratory and field-testing and model results will be discussed.

INTRODUCTION

High-level nuclear waste will be solidified in a facility now being built at the Savannah River Plant (SRP) near Aiken, SC. The Defense Waste Processing Facility (DWPF) is scheduled to begin operations in 1989. The DWPF will solidify high-level waste, now being stored in waste tanks at SRP, by vitrification into borosilicate glass. The vitrified waste will be shipped to a Federal repository.^{1,2}

Before vitrification waste will be processed in the existing waste tanks. During waste processing about 25 million gallons of soluble salts will be decontaminated. The resulting low-level decontaminated salt solution will be solidified with a cement-fly ash mixture and disposed of in surface vaults at SRP. Disposal area design is based on the results of analytical and numerical models of the release of materials from saltstone. The performance objective is to permanently dispose of waste salt in an environmentally sound manner that will meet State groundwater quality standards at the disposal area boundary.³

WASTE AND WASTEFORM CHARACTERISTICS

Most of the radioactivity will be removed from the waste during in-tank processing by the addition of sodium tetraphenylborate to precipitate cesium, and by removing strontium through adsorption onto sodium titanate. The composition of the decontaminated salt solution is shown in Table 1. The waste salt solution is a low-level radioactive waste (radioactivity of about 230 $\mu\text{Ci/L}$). The salt solution is also a hazardous waste by characteristic. The waste is corrosive ($\text{pH} > 12.5$) and EP-toxic (chromium ≈ 160 ppm).

The waste salt solution will be transferred by pipeline from the high-level waste tanks where it is decontaminated to a low-level waste processing area (Z Area). At the waste processing area the salt solution will be mixed with cement and fly ash and pumped to surface disposal vaults. The formulation to be used is shown in Table 2. Figure 1 illustrates the cement hydration process resulting in encapsulation (physical entrapment) on a microscale of the waste salts.

Although the waste salt solution is hazardous, the resulting saltstone is nonhazardous. Testing by the extraction procedure-toxicity test (Table 3) has shown that chromium and other metals in the leachate are at acceptable levels. EP-toxicity testing has also been done on the unset saltstone grout. Samples of grout were subjected to the EP-toxicity test within 3 hours of mixing. The unset grout also passes the test as shown in Table 4. Thus, saltstone can be disposed as a nonhazardous solid waste.

SALTSTONE LEACHING

Laboratory leaching tests have been done on samples of saltstone to define the rate of removal of materials from saltstone to the environment. Leaching tests were done by a proposed ANSI procedure.⁴ Cylindrical samples of saltstone were leached in deionized water. The water was changed daily for the first week, weekly for 2 months, and then every 2 weeks until the end of the test. Leachate was analyzed by ion chromatography and gamma spectrometry.

Typical leaching results are shown in Figure 2 for nitrate, technetium, cesium, and strontium. The leaching curves show a rapid decrease in leach rate between the first and second day. This is due to dissolution of salts from the sample surface. After the second day the leach rate for

nitrate, technetium, and cesium decreases in proportion to the square root of time. This behavior is indicative of a diffusion-controlled release. The leaching of strontium, however, is indicative of a dissolution-controlled mechanism. Strontium probably substitutes for calcium as the cement matrix forms.

Nitrate leach results for nine saltstone samples, prepared in the laboratory and during a large-scale field test, have been analyzed to quantify the effective diffusion coefficient for saltstone. The effective diffusion coefficient was calculated to be $1.04 \pm 0.09 \times 10^{-8} \text{ cm}^2/\text{sec}$.

Leaching tests have also been carried out in unsaturated soil to simulate burial of saltstone on earthen trenches. These tests have been done in the same manner as the deionized water leaching tests, except that unsaturated soil surrounds the saltstone sample instead of water. Typical results of leaching in unsaturated soil are shown in Figure 3 in comparison with results of leaching in water. In this test the soil was at natural field water capacity, about 20% (volumetric) water. In other tests the water content of the soil was reduced. No effect on leach rate was observed until the soil water content was reduced to 1%. Figure 4 illustrates saltstone leaching in water and unsaturated soil. In either case the diffusion of salts from saltstone into the surrounding medium is the controlling mechanism, and the observed leach rate is expected to be the same.

FIELD TESTING OF SALTSTONE RELEASE

In 1983 three lysimeters were constructed to test the performance of the disposal of saltstone in earthen trenches. Thirty-ton monoliths of saltstone were prepared from actual decontaminated SRP waste salt solution. Each monolith was formed by pouring saltstone grout into an earthen trench contained in a "Hypalon-" lined basin. Figure 5 shows the details of construction of the lysimeters. One of the lysimeters contains only a saltstone monolith. This uncapped monolith was formed on December 1, 1983. Another lysimeter contains a saltstone monolith (formed on December 20, 1983) covered by a clay cap to divert infiltrating water. The third lysimeter contains a monolith (formed on January 20, 1984) covered by a gravel cap to test the effectiveness of a capillary barrier to divert infiltrating water. Samples of percolate water have been collected from the lysimeter sumps and analyzed for nitrate and other materials since the lysimeters were installed. Soil moisture samplers were installed within 6 in. of the monoliths prior to pouring of the saltstone. Samples of soil moisture have been collected periodically from the lysimeters and also analyzed.

Nitrate concentrations from the three lysimeter sumps are shown in Figure 6. Nitrate in the two capped lysimeters is coincident with natural levels of nitrate in rain and groundwater; thus, no nitrate has yet migrated to the sumps of the capped lysimeters. The uncapped lysimeter has released significant levels of nitrate to the sump. The maximum concentration observed to date is 209 ppm. Technetium-99 has also been observed in the uncapped lysimeter (maximum concentration of 12,000 pCi/L) but not in the capped lysimeters.

Results of soil moisture samples show significant concentrations of nitrate (up to 15,000 mg/L) and technetium-99 (up to 450,000 pCi/L) adjacent to the two capped lysimeters. This demonstrates that soluble components are released from the saltstone, but that the cap is effective in reducing the amount of water flowing next to the monolith, which could carry the materials to the sump. This delay that the caps provide is one measure of their effectiveness.

SALTSTONE RELEASE MODELING

A performance goal for the disposal of saltstone is maintaining groundwater quality standards at the disposal area boundary. The State of South Carolina has adopted the EPA drinking water standards as the standard to be applied to groundwater similar to that underlying the saltstone disposal area. Mathematical modeling (both analytic and numeric) was applied to predict releases of nitrate and other materials from various saltstone disposal designs.

Numeric models were used at the Savannah River Laboratory (SRL) and by a subcontractor (Intera Technologies, Austin, TX). Numeric models were validated by applying them to the saltstone lysimeters and comparing model predictions with lysimeter observations. Results of model validation are shown in Figure 7. The SRL model assumed water moved through the soil as if the soil were saturated with water (potential flow). The Intera model used measured rainfall at the lysimeter site and measured unsaturated flow properties of soil and saltstone in a full two-phase, unsaturated model to simulate the movement of water through unsaturated porous media. The comparison of Intera model predictions with observations is quite favorable. The SRL predictions appear to be low.

The SRL model was applied to the disposal of saltstone in unlined earthen trenches containing one day's production of saltstone (about 350 yd³), situated at least 5 ft above the water table. The results are shown in Figure 8. Nitrate concentrations in groundwater are predicted to exceed the groundwater standard by about 6 times; thus, disposal in unlined earthen trenches is not an acceptable design.

DISPOSAL AREA DESIGN

Models were applied to assess disposal area design features. Features considered were monolith size, monolith liners, and disposal area caps.

Because the controlling release mechanism is diffusion, the monolith surface area to monolith volume ratio affects the rate of release. Increasing the size of the monolith from containing one day's production of saltstone to containing one year's production will reduce the surface/volume ratio and, consequently, the release rate by about 3 times.

Lining the saltstone monolith with a diffusive barrier of clay or concrete will delay and reduce the flux of materials from the saltstone to the environment. A 2-ft-thick liner of concrete will reduce peak groundwater

concentrations by about 14 times while a 5-ft-thick clay liner will reduce concentrations by 11 times.

Capping the disposal area with clay will reduce the amount of precipitation that infiltrates the soil. Reduced infiltration will tend to reduce the rate at which materials released from saltstone are transported to the water table.

A saltstone disposal design has been developed that will be effective in maintaining groundwater quality. The design incorporates all of the design elements discussed above. The design, shown in Figure 9, is a surface disposal vault constructed of concrete and containing about one year's production (56,000 yd³) of saltstone. The floor is 2.5 ft thick, the sidewalls are 1.5 ft thick, and the sloped concrete top is 2 ft thick. The surface disposal vault would be closed, in accordance with South Carolina waste disposal regulations, when the concrete top is installed. However, at some future date the disposal site will be decommissioned. A potential decommissioning concept involving mounding with earth and installing a clay cap over the vault is shown in Figure 10.

Predicted maximum concentrations of all contaminants from the surface vault are below groundwater standards, as shown in Table 5. No contaminants are released to the groundwater for about 200 years; maximum groundwater concentrations do not occur until 1,000 years after final closure.

CONCLUSION

Processing waste salt solution into saltstone produces a nonhazardous wasteform suitable for disposal in surface vaults. Disposal will meet all environmental standards.

ACKNOWLEDGMENT

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FIGURE 1. Microencapsulation Schematic

Figure 2. Saltstone Leach Rates, Saturated Conditions

FIGURE 3. Nitrate Leach Rate

Soil	Saltstone (cured)	Water
$D = 5 \times 10^{-6}$ (cm ² /sec)	$D = 5 \times 10^{-9}$ (cm ² /sec)	$D = 2 \times 10^{-5}$ (cm ² /sec)

$$D_{\text{saltstone}} \approx 10^3 < D_{\text{soil}}$$

$$D_{\text{saltstone}} \approx 4 \times 10^3 < D_{\text{water}}$$

FIGURE 4. Diffusion through Cured Saltstone Controls Release

FIGURE 5. Tank 24 Saltstone Lysimeter Tests

FIGURE 6. Saltstone Lysimeters, Nitrate Release

FIGURE 7. Uncapped Saltstone Lysimeters, SRL and Intera Technologies Model Results

FIGURE 8. Saltstone Landfill Day Hole Design, SEL Model Predictions

FIGURE 9. Saltstone Surface Vault

FIGURE 10. Saltstone Surface Vault, Clay Cap Concept

TABLE 1. COMPOSITION OF DWPF SALT SOLUTION

Nonradioactive		Radioactive	
Component	g/L	Component	Ci/L
Na	117.0	⁹⁰ Sr	0.9
NO ₃ ⁻	130.0	⁹⁹ Tc	75.3
NO ₂ ⁻	30.0	¹³⁷ Cs	24.6
OH ⁻	20.0	Total alpha emitters	0.2
NaB(C ₆ H ₅) ₄	69.0	-----	
Cr	0.2 (160 ppm)	Total radioactivity	230.0
Hg	1.5 x 10 ⁻⁶ (0.01 ppm)		
Ag	1.1 x 10 ⁻⁷ (0.0008 ppm)		

pH	14		
Density	1.23 gm/cc		

TABLE 2. BLENDED CEMENT FORMULATION, WT %

Portland cement (Class H)	11.5	57.5 wt % cement
Fly ash (Class C)	46.0	
Salt	12.3	42.5 wt % solution
Water	30.2	

TABLE 3. EP-TOXICITY TESTING OF SALTSTONE

<u>Metal</u>	<u>Extract, mg/L</u>		<u>Characteristic of EP-Toxicity</u>
Ag	<0.002	<0.002	5.0
Ba	0.13	0.11	100.0
Cd	<0.002	<0.002	1.0
Cr	0.021	<0.003	5.0
As	0.003	0.004	5.0
Hg	<0.0002	<0.0002	0.2
Pb	<0.002	<0.002	5.0
Se	0.005	0.007	1.0

TABLE 4. EP-TOXICITY TESTING OF UNSET SALTSTONE GROUT

Metal	Extract, mg/L		Characteristic of EP-Toxicity
	Calculated*	Actual	
Ag	0.012	--	5.0
Ba	0.4	--	100.0
Cr	3.8	2.7	5.0
Hg	0.0006	--	0.2

* Assuming 100% extraction.

TABLE 5. CALCULATED MAXIMUM RELEASE FROM SALTSTONE
(1,000 Years after Decommissioning)

Element	Concentration in Saltstone	Predicted Peak Groundwater Content	Proposed Groundwater Quality Standard
N(NO ₃ ⁻)	9,300 ppm	0.6 ppm	10.0 ppm

Radionuclide	Concentration in Saltstone, pCi/L	Predicted Peak Groundwater Content, pCi/L	EPA Drinking Water Standards, pCi/L*
⁹⁰ Sr	510,000	3.0×10^{-10}	50.0
⁹⁹ Tc	44,200,000	700.0	5,000.0
¹⁰⁶ Ru	20,400,000	$<1.0 \times 10^{-10}$	300.0
¹³⁷ Cs	15,300,000	2.3×10^{-8}	100.0

*ICRP-30 Dose Model

END

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