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Evaluation of Interim and Final Waste Forms for the Newly Generated Liquid Low-Level Waste Flowsheet

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Chemical Technology Division

**EVALUATION OF INTERIM AND FINAL WASTE FORMS FOR THE
NEWLY GENERATED LIQUID LOW-LEVEL WASTE FLOWSHEET**

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ACRONYMS AND ABBREVIATIONS

AASC	alkali-activated slag cement
ANS	American Nuclear Society
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
BWR	boiling water reactor
cf.	compare
D_i	effective diffusivity
DOE	Department of Energy
EMCOM	Environmental Management Career Opportunities for Minorities
EPA	Environmental Protection Agency
HAC	high-aluminate cement
HBCU-MI	Historically Black Colleges and Universities—Minority Institutes
HEPA	high-efficiency particulate air
KCCF	potassium cobalt hexacyanoferrate
kPa	kilopascal
LLW	low-level liquid waste
MPa	megapascal
MVST	Melton Valley Storage Tank
NGLLLW	newly generated low-level liquid waste
NRC	Nuclear Regulatory Commission
OPC	ordinary portland cement
ORNL	Oak Ridge National Laboratory
psig	pounds per square inch (gauge)
PWR	pressurized water reactor
SLLW	solid low-level waste
SPC	sulfur polymer cement
U.S.	United States



ABSTRACT

The purpose of this review is to evaluate the final forms that have been proposed for radioactive-containing solid wastes and to determine their application to the solid wastes that will result from the treatment of newly generated liquid low-level waste (NGLLLW) and Melton Valley Storage Tank (MVST) supernate at the Oak Ridge National Laboratory (ORNL). Since cesium and strontium are the predominant radionuclides in NGLLLW and MVST supernate, this review is focused on the stabilization and solidification of solid wastes containing these radionuclides in cement, glass, and polymeric materials—the principal waste forms that have been tested with these types of wastes.

Several studies have shown that both cesium and strontium are leached by distilled water from solidified cement, although the leachabilities of cesium are generally higher than those of strontium under similar conditions. The situation is exacerbated by the presence of sulfates in the solution, as manifested by cracking of the grout. Additives such as bentonite, blast-furnace slag, fly ash, montmorillonite, pottery clay, silica, and zeolites generally decrease the cesium and strontium release rates. Longer cement curing times (> 28 d) and high ionic strengths of the leachates, such as those that occur in seawater, also decrease the leach rates of these radionuclides.

Lower cesium leach rates are observed from vitrified wastes than from grout waste forms.

However, significant quantities of cesium are volatilized due to the elevated temperatures required to vitrify the waste. Hence, vitrification will generally require the use of cleanup systems for the off-gases to prevent their release into the atmosphere.

Although the addition of transition-metal hexacyanoferrates to grout has been suggested as a mechanism to control cesium leaching from the waste form, very little information is available on the final waste forms for potassium cobalt hexacyanoferrate (KCCF) wastes. Studies of the solidification and stabilization of these wastes are required.

The waste stabilization/solidification results reported in this review cannot be completely extrapolated to the wastes at ORNL because of the complexities of the latter wastes as compared with those that have been discussed in the literature. However, the review should serve as an excellent resource for including or eliminating certain factors in the selection of the final waste forms for ORNL wastes. Further, it would be useful to study those waste components (e.g., KCCF) for which adequate literature information is not available and to determine their effects on cesium or strontium retention in cement, polymeric materials, or glass before deciding on a final waste form.

1. INTRODUCTION

Approximately 400,000 gal of liquid low-level waste is produced annually at Oak Ridge National Laboratory (ORNL) as the result of experimental activities and isotope production. Such waste is currently collected and transferred to the ORNL Liquid Waste Collection and Transfer System, where the total volume is reduced by evaporation to about 20,000 gal. The concentrated product is then transferred to underground storage vaults known as the Melton Valley Storage Tanks (MVSTs). The liquid low-level wastes (LLLWs) have been accumulating in the MVSTs since 1984. The current inventory of the eight tanks is 287,000 gal of supernate and 175,000 gal of sludge (Collins et al. 1995). The volume of liquid associated with the sludge is about 90,000 gal.

The contents of the MVSTs have been characterized in a recent sampling campaign; the compositions of the tank supernates and sludges have been summarized in a report by Sears et al. (1990). The predominant constituents of the MVST supernates are NaNO_3 , NaOH , Na_2CO_3 , KNO_3 , and NaCl . The major chemicals and radionuclides present in the supernate of a particular tank, W-29, are listed in Table 1.

The chemical composition of the evaporated LLLW has been projected for wastes that will be generated at ORNL in the future, referred to as newly generated LLLW (NGLLLW). The projected composition of the LLLW is based on survey data obtained by canvassing current LLLW generators at ORNL; the rationale for estimating the chemical composition of the NGLLLW has been described by Arnold et al. (1994). Table 1 summarizes the

Table 1. Composition of simulated waste solutions

Component	NGLLLW, pH 13	NGLLLW, pH 8 ^a	Concentrated MVST W29 supernate, pH 13	Concentrated MVST W29 supernate, pH 8 ^a
Chemical, mol/L				
NaOH	0.125	NP ^b	0.313	NP
Na ₂ CO ₃	0.1	NP	0.182	NP
NaHCO ₃	NP	0.096	NP	0.167
NaNO ₃	0.061	0.059	5.07	4.64
NaCl	0.034	0.033	0.13	0.119
Na ₂ SO ₄	NP	0.108	NP	0.227
LiCl	0.025	0.024	NP	NP
KNO ₃	NP	NP	0.312	0.286
Al(NO ₃) ₂	NP	NP	0.0065	NP
NaAlO ₂	0.0117	NP	NP	NP
Al(OH) ₃	NP	0.0101	NP	0.0061
CaCO ₃	NP	NP	0.00013	0.00012
Zn(NO ₃) ₂	NP	NP	0.0013	0.0012
Radionuclide, mCi/L				
⁹⁰ Sr	19.4		0.26	
^{134, 137} Cs	99.5		7.9	
^{103, 106} Ru	132		<5E-8	
pH	13.1	8.0	13.1	8.0
Density, g/mL	1.074	1.059	1.308	1.608

^a Concentration estimates assume that 5.4 N H₂SO₄ is used to neutralize the waste.

^b NP = Not present.

concentrations of the major chemical constituents and the activities of the radionuclides anticipated in the NGLLLW.

Because of the limited storage space in the MVSTs, treatment methods are now being developed to process future LLLW as it is generated at ORNL. An option also under consideration is to blend the NGLLLW with MVST contents prior to treatment to help reduce the inventory in the MVSTs. The goal of the new waste-treatment method is to concentrate the radioactive contaminants into the smallest possible volume of highly radioactive Greater-than-Class-LII solid waste. This concentrated solid product would then be disposed of at DOE facilities or held in retrievable storage facilities at ORNL until permanent disposal facilities are available. Criteria for Class LII waste are given in Table 2. The treated liquid waste might be discharged to the environment, or it could be solidified and disposed of on-site as Class LII waste.

The new treatment process will need to remove the majority of the ^{90}Sr , ^{137}Cs , ^{103}Ru , and ^{106}Ru from NGLLLW and blends of up to 50% MVST supernate in NGLLLW. A flow-sheet has been proposed for the treatment of LLLW (see Fig. 1 for the current version). This proposed flowsheet contains four unit operations: strontium coprecipitation, ruthenium sorption on ferric hydroxide, and cesium sorption using two sequential treatments with potassium cobalt hexacyanoferrate (KCCF). In the first unit operation, the radioactive strontium will be separated by adding 50 mg/L stable strontium (as the chloride salt) to the waste solution at pH 13 in order to effect the precipitation of both the radioactive and the nonradioactive strontium as the carbonate salt. Other solids resulting from the strontium coprecipitation unit operation will be ferric hydroxide, which is added as a settling agent for

Table 2. Draft concentration limits for Class LII waste at the Central Solid Waste Disposal Facility

Nuclide	Concentration (Ci/m ³)	Nuclide	Concentration (Ci/m ³)
³ H	1.2E+06	¹⁵⁵ Eu	1.0E+06
¹⁰ Be	2.0E+00	²³² Th	4.5E--07
¹⁴ C	2.0E-04	²³³ U	2.5E-05
²² Na	1.0E+06	²³⁵ U	2.5E-05
⁶⁰ Co	1.0E+06	²³⁸ U	2.7E-05
⁶³ Ni	2.8E-02	²³⁷ Np	1.0E-08
⁹⁰ Sr	8.9E-01	²³⁸ Pu	1.5E-05
⁹³ Zr	2.6E-04	²³⁹ Pu	2.9E-07
⁹⁹ Tc	5.5E-06	²⁴¹ Pu	9.4E-03
^{113m} Cd	9.8E+03	²⁴² Pu	5.0E-04
^{121m} Sn	5.7E-02	²⁴¹ Am	1.3E-04
¹³⁷ Cs	2.5E-01	²⁴³ Am	1.8E-05
¹⁵¹ Sm	2.6E+01	²⁴³ Cm	1.0E+00
¹⁵² Eu	1.3E+03	²⁴⁴ Cm	2.1E-04
¹⁵⁴ Eu	5.1E+06	²⁵² Cf	1.0E+06

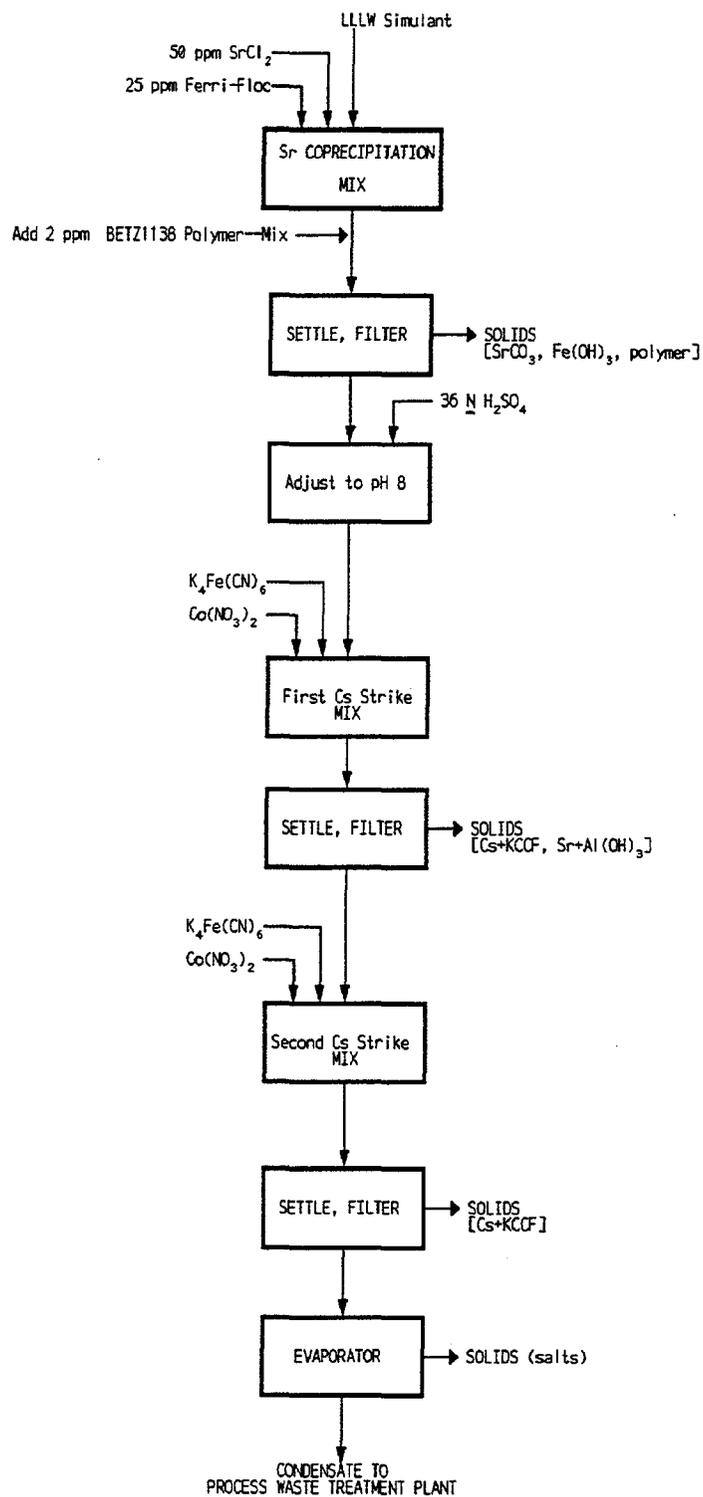


Fig 1. Proposed flow sheet for the treatment of NGLLLW.

SrCO₃, and a polyacrylamide polymer used as a flocculant (e.g., Betz® 1138). The first unit operation is completed with the separation of the precipitated solids from the remaining LLLW. The treatment strategy for the removal of ^{103,106}Ru from NGLLLW is still under development. The most successful approach found thus far involves the addition of 25 mg/L iron, as Fe₂(SO₄)₃•9H₂O, following the adjustment of pH of the NGLLLW from a nominal value of 13 to 11.

Because sorption of ruthenium on ferric hydroxide does not decontaminate the NGLLLW to the extent required for final discharge of the liquid waste, other processes are being explored for ruthenium removal. The treatment process for cesium in the waste has been fairly well defined. The last two unit operations of the proposed flow sheet involve cesium sorption on KCCF solids formed in situ. Because cesium removal is most efficient at pH 8, the pH of the NGLLLW is adjusted to this value with the addition of H₂SO₄ prior to the formation of KCCF in the waste. The KCCF sorbent is formed in situ by the sequential addition of potassium ferrocyanide, K₄Fe(CN)₆, and cobalt nitrate, Co(NO₃)₂, solutions. The solids generated at the completion of the first KCCF strike will include cesium-laden KCCF, a polymeric settling agent, and aluminum hydroxide, which precipitates from the neutralized waste. The only solids generated in the second KCCF strike are KCCF particles and, possibly, a polymeric settling agent. After the solids have been removed, the LLLW resulting from the second KCCF strike will probably be evaporated to yield a final salt cake containing much lower levels of radionuclide contaminants.

Estimates of the compositions of the LLLW and the solid wastes generated at the end of each unit process of the flow sheet are provided in the Appendix. Tables A.1 through A.18

show the variations in the liquid and solid waste compositions resulting from the processing of various blends of MVST supernate mixed with NGLLLW. Note that only the activities of ^{90}Sr and $^{134,137}\text{Cs}$ have been calculated for the tables because the treatment technology for only these radionuclides has been defined. The activities of $^{103,106}\text{Ru}$, as well as those of other radionuclides such as ^{99}Tc , will be added to the spreadsheet as the design of the flow-sheet matures.

As part of the implementation of the flow sheet, efforts are now under way to identify the appropriate waste forms required for the stabilization and final disposal of the solids generated from each unit operation. Because the treatment for ruthenium is still under development, this literature review considers the disposition of solids resulting from only the strontium coprecipitation and KCCF unit operations, with emphasis on the stabilization of cesium and strontium. The purpose of this report is to review those current solidification and stabilization technologies which can be used as interim and final waste forms for the radioactive-containing solids that will be generated by the treatment of the MVST supernates and the NGLLLW. Both the merits and the limitations of stabilization of the cesium- and strontium-bearing solid wastes in cement, glass, bitumen, and encapsulation in polymeric materials are discussed.

2. PERFORMANCE CRITERIA FOR WASTE FORMS

The U.S. Nuclear Regulatory Commission (NRC), which regulates the U.S. commercial nuclear power industry, has established performance guidelines for stabilized/solidified products (see Table 3). Although the DOE facilities are not licensees of the NRC, the

Table 3. Solidified-product guidance

Tests	Methods	Criteria
Compressive strength	ASTM C 39 or D 1074	414 kPa (60 psi)
Radiation stability	See 1983 TP ^a	Compressive strength of 414 kPa after 10E + 8 rads
Biodegradation	ASTM G 21 and G 22	No growth ^b and compressive strength > 414 kPa
Leachability	ANS 16.1	Leach index of ≥ 6
Immersion	See 1983 TP ^a	Compressive strength of 414 kPa after 90 d
Thermal cycling	ASTM B 553	Compressive strength of 414 kPa after 30 cycles
Free liquid	ANS 55.1	0.5%
Full-scale	See 1983 TP ^a	Homogeneous and correlates to laboratory-size test results

^a The 1983 Branch Technical Position (TP) paper class for a minimum compressive strength of 345 kPa (50 psi). This value has been increased to 414 kPa (60 psi) to accommodate an increased maximum burial depth at the Hanford Site of 55 ft (from 45 ft) as defined by the U.S. Nuclear Regulatory Commission publication, *Draft Regulatory Guide on Low-Level Waste Form Stability* (a proposed revision to 10 CFR 61, "RG LLW Form Stability," Rev. 4, October 1986).

^b The 1983 Branch TP calls for the following multistep procedure for biodegradation testing: If observed culture growth rated "greater than 1" is observed following a repeated ASTM G 21 test, or any growth is observed following a repeated ASTM G 22 test, longer-term testing (for at least six months) is recommended, using the Barth-Pramer Method. From this test, a total weight loss extrapolated for full-size waste forms to 300 years should produce less than a 10% loss of total carbon in the sample.

criteria established by the latter are generally accepted as performance benchmarks. Other proposed waste-form performance criteria have recently been reviewed by Franz et al. (1994). Many of the recommended testing protocols (e.g., compressive strength, immersion testing, thermal cycling, etc.) are intended to assess the durability of the waste form for long-term storage under conditions of a hypothetical below-grade disposal scenario. A major concern under any disposal scenario that includes the possibility of water intrusion is the potential to leach radioactive or hazardous constituents from the waste form for uncontrolled release into the environment. Leachability testing may be assessed by testing protocols such as the ANSI/ANS-16.1 procedure, which measures the "effective diffusivity" (D_e) of the contaminants of interest into demineralized water under static leaching conditions (American Nuclear Society, 1986). The negative logarithm of the average effective diffusivity (in cm^2/s) is the defined leachability index; the NRC minimum requirement is a leach index ≥ 6 (Table 3). Higher values of the leachability index are desirable since they represent smaller values for contaminant diffusivity.

3. STABILIZATION OF CESIUM BY SOLIDIFICATION IN GROUT

3.1 OVERVIEW

Cement grout is a mixture of portland cement and other materials such as blast-furnace slag (alkali-activated slag cement), fly ash, and lime. Cesium ion is highly soluble in the pore water of ordinary portland cement (OPC) grout and, thus, is susceptible to leaching out of the waste form into aqueous systems—providing a pathway for release into the environment. Leachability can be minimized (thereby enhancing the retention of the radionuclide in the

waste form) by using grout additives that decrease the effective pore size or increase the effective pore tortuosity in the waste form (e.g., use of high-aluminate cement, blast-furnace slag, or silica fume) or by adding certain aluminosilicate minerals (e.g., illitic clays or zeolites) that have a selective sorptive affinity for the cesium cation. The ANSI/ANS-16.1 leachability index for cesium in simple OPC grouts can be lower than 6 (i.e., not acceptable by the NRC criterion), whereas the leachability index for cesium in modified grouts may be as great as 8 to 10, depending on the grout formulation used.

3.2 LITERATURE SURVEY

3.2.1 Disposal in PC Grout

Until recently, cement-stabilized low-level radioactive wastes have been disposed of by burying or by dumping in the ocean. A major concern about this type of disposal is the potential for the radionuclides to be leached from the cement and, subsequently, to be released into the surrounding environment. To aid in mitigating such problems, the leaching of radioactive materials from cement has been extensively studied (American Nuclear Society, 1984; Bernard et al., 1982; Habayeb, 1985; International Atomic Energy Agency, 1971; Kumar and Roy, 1986; Kumar et al., 1987; Fuhrmann and Colombo, 1989; Walter et al., 1988).

The low retention of ^{134}Cs by OPC has been demonstrated by Krishnamoorthy et al. (1993), who showed that 42.7% of the initial amount of ^{134}Cs in cement cured for 28 d was released during the first day of testing. The amount leached increased to 73.3 and 76.9% after 12 and

100 d, respectively. The measured ^{134}Cs diffusivity of $3 \times 10^{-5} \text{ cm}^2/\text{s}$ (equivalent to a leachability index of ≈ 4.5) is similar to that reported by Matsuzuru et al. (1978).

Other investigators (Zamorani and Serrini, 1990) have shown that, at 25°C , the quantity of cesium leached increased linearly with time and that the cesium was completely leached after 13 d. The cesium leaching rate was reported to be independent of the cement curing conditions of 30°C for 28 d or 60°C for 11 d. A diffusion coefficient of $8.2 \times 10^{-8} \text{ cm}^2/\text{s}$ (equivalent to a leachability index of ≈ 7.1) of cesium in cement was obtained.

In contrast, Crawford et al. (1985) have concluded that the rate of cesium release from solidified OPC is strongly dependent on the curing time. Their results showed that, after 80 d of leaching, only about 5% of the cesium was leached from cement that had been cured for 95 d. About 15 and 25% of the ^{134}Cs was leached within the same time from cements that had been cured for 30 and 57 d, respectively. A common characteristic of the samples was that a rapid leaching of cesium occurred during the first 20 d, followed by slower release rates. For leach periods greater than 28 d, the corresponding diffusivities for the samples cured for 30, 57, and 95 d were 1.2×10^{-9} , 5.9×10^{-10} , and $4.2 \times 10^{-11} \text{ cm}^2/\text{s}$. A 100-fold reduction in cesium leaching was observed when 10% SiO_2 was added to the cement. It was suggested that the additive reduced cesium leaching by filling the large pores in the cement, as well as acting as sorption sites for cesium.

McCulloch et al. (1984) have shown that the incorporation of silica into cement results in significant adsorption of cesium at neutral pH values. However, at high pHs, such as those that occur in cement, cesium adsorption is initially enhanced but the cesium is desorbed as

the silica reacts with calcium hydroxide, forming sites with limited adsorption for cesium. The promotion of cesium adsorption by silica has been attributed to its negative surface charge.

The retention of cesium by OPC, high-aluminate cement (HAC), and alkali-activated slag cement (AASC) during 42 d of leaching has been reported by Xuequan and coworkers (1991). Their leaching tests at 25 or 45°C show that the quantity of cesium released from the solids is greater at 45°C due to increased solubilities of the cements in water and to the increase in the diffusion of ions at the higher temperature. At 25°C, the order of cesium leachability was: OPC > AASC > HAC; at 45°C, it was: OPC > HAC > AASC. The AASC exhibited the highest compressive strength after heat treatment of the samples at 75, 275, or 425°C, probably because of its lower porosity as compared with those of the other two cements tested. Therefore, AASC was suggested as a more effective immobilization medium for radioactive cesium than either OPC or HAC.

3.2.2 Effects of Waste Loading and Waste Composition

The effectiveness of 15 formulations of cement as a medium for the disposal of ¹³⁷Cs has been evaluated by Plecas et al. (1992), using leaching, diffusion efficiencies, and compressive strength tests. Their studies were conducted on samples of products with different waste-to-cement ratios, and leaching tests were performed for times ranging from 7 to 365 d. At the end of the 365-d test, two of the formulations were rated as "excellent" for the retention and disposal of radioactive cesium (see Table 4). The ¹³⁷Cs leach rates for

these samples were about 2×10^{-8} cm²/s (leachability index ≈ 7.7), while their compressive strengths were 14.4 and 15.8 MPa, respectively (cf. Table 2 criteria).

Table 4. Mortar compositions (g/1000 cm³ mortar)

Portland cement	Sand, ~2 mm	Dried sludge	Water	Additive (unspecified)	Cement-to-waste ratio
636	146	701	473	9.75	0.9
580	193	580	492	8.8	1.0

The influence of sludge-drying temperature prior to mixing with a commercial HAC on cesium release rate has been investigated by Scheetz et al. (1985), using sludge/cement ratios of 30/70 or 70/30%. They have shown that for waste forms containing 0.1% cesium, the leach rate was lower when the sludge had been calcined at 600°C than when it had been dried at 250°C for 60 h. The specimens were cured for 28 d at 27°C prior to the leaching tests. The reported leach rates for the 30 or 70% sludge dried at 250°C were 8.0 and 1.5 g/m²·d of cesium, while the rates for the same compositions were 2.5 and 0.3 g/m²·d of cesium for the samples that had been calcined at 600°C. However, the cementitious product sludge dried at 250°C had a slightly higher compressive strength (35,800 kPa) than the one that had been dried at 600°C (29,200 kPa).

In an effort to simulate the retention of cesium in wastes containing high concentrations of sodium sulfate, the migration of cesium from sodium sulfate pellets has been studied by Chino et al. (1990). The cylindrical pellets (10 x 20 cm) used in their tests contained 63 mg of cesium per gram of pellet, with ¹³⁴Cs as a tracer. The pellets were packed into a dry

cement case, which was then placed in a larger cement case (containing deionized water) that had been cured at 25°C for 21 d. Analysis of the water over a 30-d period showed that the amount of cesium extracted into solution increased linearly with time; the ^{134}Cs diffusion coefficient was $3.0 \times 10^{-7} \text{ cm}^2/\text{s}$.

Atkinson and Nickerson (1988) found that cesium sorption onto sulfated portland cement is weak and reversible. The sorption at 25°C increased as the liquid-to-solid ratio of the cement increased. This observation was ascribed to competing ions such as Na^+ and K^+ in the solution.

Fuhrmann and Colombo (1989) have shown, using an initial ^{137}Cs concentration of 70 μCi in specimens measuring 4.8 cm in diameter and 6 cm in height and the ANS 16.1 leaching test (American Nuclear Society, 1984), that 50% of the radionuclide was released from a solidified portland type I cement after 88 d of immersion in distilled water. In contrast, the amount of ^{137}Cs released within the same time period using synthetic seawater leach solution at 5°C was 5.6%. The reduction of the leaching rate was attributed to the ionic strength of the seawater. The addition of sodium sulfate to the cement-cesium blend to simulate power reactor waste resulted in a further 30% release of ^{137}Cs in water after 25 d. Significant cracking of the specimens occurred, with the effect being more accelerated in seawater. It was noted that deterioration of the physical integrity of solidified cement in seawater is a common phenomenon in cement-sulfate systems. Sulfate ions react expansively with certain aluminum-containing phases in the concrete, forming ettringite (a calcium aluminum sulfate hydrate) and causing stress cracks to form in the concrete host (Atkinson and Hearne, 1990).

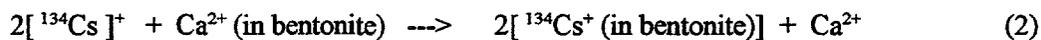
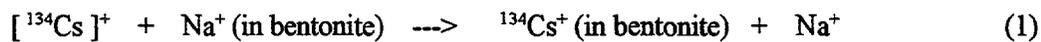
3.2.3 Effect of Leaching Medium

The dependence of cesium leachability from cement on temperature, leaching medium, volume of the leachant (250, 500, or 750 mL), and cement curing time has been investigated by De Angelis and co-workers (1992). The leaching media were deionized water, tap water, and synthetic seawater. The studies were conducted with cylindrical cement blocks, 5.0 cm diam x 5.0 cm high, containing 50, 100, or 1000 mg of cesium introduced as CsCl. The cements were cured for 3 or 28 d. After 5 d of leaching at 25°C, the extent of cesium release was 8, 13.8, and 20% from the synthetic seawater, tap water, and deionized water, respectively. The quantity of cesium leached increased as the temperature was increased to 40 or 70°C; the effect was more pronounced at the latter temperature. Cesium desorption from the cement-based grouts was independent of the initial cesium concentration and the volume of the leachants.

In a study involving the leaching of ^{134}Cs and ^{137}Cs from cement, it has been shown that 51.9 and 79.9%, respectively, were leached from the cement immersed in 600 mL of Hanford Site groundwater at the end of a 35-d ANS 16.1 leach test (Walter et al., 1988). The rate of release of the radionuclides was highest in the first 5 d, followed by a much slower release during the remainder of the test period. The leaching water contained several trace cations (e.g., Al^{3+} , Fe^{2+} , Fe^{3+} , K^+ , Na^+ , Cd^{2+} , Zn^{2+}) and anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , or PO_4^{3-}); however, the effects of these ions on cesium leachability were not discussed.

The leachabilities of ^{134}Cs from portland type 30 cement, portland type 30/bentonite, and portland type 30/silicate matrices in the presence of various aqueous solutions have been

investigated by Habayeb (1985). The solutions contained sodium carbonate, sodium bicarbonate, hydrogen peroxide, potassium permanganate, sodium hydroxide, acetic acid, potassium persulfate, or phosphoric acid. The results show that 3 to 29% of the ^{134}Cs was leached from the cement-bentonite matrix, while 46 to 85% and 58 to 81% were leached from the cement alone and the cement-silicate matrix, respectively, after 80 d of leaching. The lower rate of cesium release from the cement-bentonite solid was attributed to the exchange of cesium ions for sodium or calcium ions in the solidification matrix as shown in Eqs. (1) and (2):



The effects of the various solutions on ^{134}Cs leachability were similar; each solution enhanced ^{134}Cs leaching from the solids. In general, aqueous soluble salts such as persulfates and phosphates resulted in higher rates of ^{134}Cs release from cement than did less soluble salts such as barium carbonate and manganese dioxide (Habayeb, 1985).

3.2.4 Effects of Waste-Form Additives

Additives have been employed for reaction with, and stabilization of, specific components in the waste materials. McDaniel et al. (1989) have shown that the leach rates of ^{137}Cs can be significantly reduced by the addition of various substances to the cement. Compared with cement alone, the incorporation of conasauga shale into the cement reduced the ^{137}Cs release by almost three orders of magnitude after leaching in distilled water for over 120 d, while the

inclusion of pottery clay reduced the leachability by only about two orders of magnitude. Grundite also reduced ^{137}Cs extraction from the cement, although the effect was less dramatic than that for conasauga shale or pottery clay. These naturally occurring minerals have inherent selective cation-exchange capacities to help retain cesium ion.

The effects of different cement/zeolite compositions on the retention of cesium have been studied by Plodinec (1977). Each solidified matrix consisted of 2.0 g of cesium-loaded zeolite (containing 0.5 meq of cesium per gram of sorbent spiked with ^{137}Cs tracer), 66.0 g of HAC, and 32.0 g of simulated sludge. The zeolites tested were clinoptilolite; vermiculite; Linde AW-300, or AW-500; and Norton Zeolon 200, 500, or 900. Vermiculite decreased the compressive strength (1100 psig) as compared with that for concrete without the additive (2300 psig), while AW-500 and Z-900 each increased the compressive strength to 3200 psig. These sorbents (AW-500 and Z-900) also produced the highest cesium-leach resistant concretes; the cesium leachabilities were 4.6 and 3.9%, respectively. The corresponding releases of cesium from the concrete without these additives were 5.7 and 6.0%.

Kumar and coworkers (1986, 1987) have shown that at 27, 38, or 60°C, the diffusion of Cs^+ in solidified OPC is significantly reduced by the addition of 10 to 20% montmorillonite, silica fume, or zeolite to the cement, as compared with that in cement alone. A similar retardation in cesium diffusivity, measured after 7 or 28 d, was observed for a grout formulation containing 35% cement and 65% blast-furnace slag. The reduced cesium migration has been attributed to an electronegative surface charge created by the additives.

This charge promotes electrostatic adsorption of Cs^+ to the negatively charged pore walls of the solidified matrix and reduces Cs^+ transport. The reduced mobility may also be due to a decrease in the porosity and pore size of the blended materials as compared with the pure OPC paste.

Anderson et al. (1981) have reported the diffusivity of cesium in a mixture of cement and blast-furnace slag to be $1 \times 10^{-10} \text{ cm}^2/\text{s}$. They found that the cesium sorbed onto the cement/slag matrix more strongly than on the cement alone. Using an assumed diffusivity of $1 \times 10^{-9} \text{ cm}^2/\text{s}$ for cesium, they estimated that a solution separated from a cesium solution by a 0.4-m-thick concrete wall will attain a residual concentration of 1% cesium in 3900 years.

Results obtained in studies of the addition of montmorillonite clay or the structural materials plastocrete and xypex to OPC have shown improvements in the leach resistance of ^{134}Cs from the composite matrix as compared with the original cement. The effects of the additives, in order of decreasing leachability, were: montmorillonite > plastocrete > xypex. However, the compressive strength of the waste cement blocks decreased after additives were mixed with the cement (Mikhail and Abdel-Gawad, 1993).

Torstenfelt and Hedin (1989) have reported significant differences in the leaching rates of cesium-ion-exchange resin matrix from OPC and cement mixed with montmorillonite zeolite placed in synthetic seawater. The diffusivity of ^{134}Cs in OPC mixed with powdered anion-exchange resin was in the range $0.6 \times 10^{-6} \text{ cm}^2/\text{s}$ to $1.3 \times 10^{-6} \text{ cm}^2/\text{s}$ (i.e., a leachability index of 5.9 to 6.1), while it was $0.8 \times 10^{-8} \text{ cm}^2/\text{s}$ to $1.0 \times 10^{-8} \text{ cm}^2/\text{s}$ for the cement mixed with 5%

of the zeolite. The initial amount of ^{134}Cs ranged from 3.1 to 4.1 MBq in a cylindrical waste form (50 mm in diameter by 50 mm high), and the leach time was 28 or 95 d.

The behavior of ^{137}Cs in the presence of a simulated spent ion-exchange resin (Amberlite IRA-402) solidified in a mixture of portland cement and blast-furnace slag has been reported by Muurinen (1985). The cement was cured at 40°C for 7 d and then at 23°C for 28 d. The leaching tests were performed in deionized water or groundwater at 20 to 23°C. The test solutions were changed periodically during the 3.5 years of the testing. Analytical results for these solutions showed that the leach rates decreased with time and were independent of the leachant. The rate of cesium release increased as the quantity of resin in the cement increased. Although the specimens developed cracks, the compressive strengths increased in most cases. Therefore, it was suggested that compressive strength should not be used as a predictor of cracking. The ^{137}Cs diffusion coefficients varied between 5×10^{-8} and 15×10^{-8} cm²/s.

4. STRONTIUM STABILIZATION IN CEMENTITIOUS MATRIX

4.1 OVERVIEW

Strontium is chemically similar to calcium, a major component in cement gel. In contrast to cesium, it has a relatively low solubility in the pore water of OPC grout. This behavior is presumably due to the formation of sparingly soluble strontium or calcium/strontium carbonate or sulfate phases, as well as probable host mineralization by partial substitution for calcium within the cement matrix gel phases (e.g., calcium aluminum sulfate hydrate, ettringite, etc.). In general, strontium salts are well retained in grout; the ANSI/ANS-16.1

leachability index for strontium in simple OPC grouts may be as great as 11 to 12, easily exceeding the minimal NRC criterion.

4.2 LITERATURE SURVEY

4.2.1 Disposal in OPC Grout

Atkins et al. (1991) have reported that more than 99% of the strontium added (as strontium nitrate) to OPC was immobilized in the solid cement. Calcium aluminate sulfate hydrates were suggested as the major constituents responsible for the immobilization, with minor contributions from calcium silicate hydrates. Fifty days of leaching in deionized water solubilized only 1.5% of the strontium. No diffusion coefficients were reported.

Atkinson and Nickerson (1988) have shown that the sorption of ^{85}Sr onto sulfate-resisting portland cement in water is time dependent and that strontium is reversibly sorbed onto cement. The desorption flux of strontium from the cement was estimated to be less than $7.0 \times 10^{-12} \text{ cm}^2/\text{s}$. In another study on the mechanism of strontium leaching from cement, Atkinson et al. (1983) have suggested that strontium is chemically bonded to cement by the exchange of Sr^{2+} for Ca^{2+} in hydrated silicate or ettringite. It was found that coprecipitation of Sr^{2+} with Ca^{2+} and the formation of gypsum or ettringite occur when the waste contains high concentrations of sulfate. Dissolution of carbon dioxide in the leachant can also result in the incorporation of strontium in insoluble carbonates.

Bernard et al. (1982) have shown that the cumulative fractional release of ^{90}Sr from cement, after 18 months of continuous leaching, ranged from 1.0×10^{-4} to 3.3×10^{-3} for an initial ^{90}Sr concentration of 0.06 to 0.20 Ci contained in 200-L-cylinder monoliths.

It has been reported by Krishnamoorthy et al. (1993) that 6% of the ^{85}Sr was released from cement after 100 d of leaching in distilled water at 25 to 30 °C. A diffusion coefficient of about $2.1 \times 10^{-7} \text{ cm}^2/\text{s}$ was reported. Based on leaching results for cement immersed in deionized water containing 15% sodium sulfate, Matsuzuru and Ito (1978) have estimated the cumulative fraction of ^{90}Sr leached in 200 years to be in the 1.5×10^{-2} to 6.8×10^{-3} range.

Using a combination of leaching tests and MINTEQ geochemical computer calculations (Felmy et al. 1984), Walter et al. (1988) have predicted the long-term behavior of ^{90}Sr in cement. The computer code MINTEQ has the capability for predicting the dissolution/precipitation of solid phases. Walter and coworkers have shown that at pH values above 10, the rate of strontium release is controlled by carbonates (e.g., CaCO_3 , MgCO_3) since under these conditions the strontium can be exchanged for calcium ions in the cement.

4.2.2 Effects of Additives

The retention of strontium in portland type I cement and cement with 5% sodium sulfate after exposure to distilled water or simulated seawater has been studied by Fuhrmann and Colombo (1989). They have reported that after 88 d of leaching, 4% of the ^{85}Sr had been

released into the distilled water, while only 0.2% had been released into the simulated seawater. It was suggested that the lower release rate for strontium in seawater was due to the high concentration of salts that reduced the concentration gradient between the pore water in the waste form and the leaching solution. The calculated diffusion coefficient for ^{85}Sr leached by seawater was $2.5 \times 10^{-12} \text{ cm}^2/\text{s}$. X-ray diffraction analyses of the cements prior to and after leaching for 150 d revealed the presence of magnesium hydroxide, calcium carbonate, and aragonite in the cement leached in the synthetic seawater. These minerals were absent in the unleached cement. The higher retention of strontium in the presence of seawater was attributed to the greater ability of aragonite to incorporate strontium ions into its crystal lattice than calcite, a component of cement. Thus, strontium may be more effectively retained in cement by the addition of aragonite. After 25 d of leaching, the release of ^{85}Sr from the cement—sodium sulfate matrix was 30% greater than that from cement alone. Significant cracking of the cement occurred in the presence of the sulfate ions.

Scheetz et al. (1985) have shown that the rate of strontium release from concrete formulated from an HAC is lower when the sludge was dried at 600°C instead of 250°C before being mixed with cement. The leaching was conducted for 28 d on samples of concrete that contained 0.1% strontium and waste (sludge) at waste/cement ratios of 30/70 or 70/30%.

In a study of the leachability of stable strontium from grout containing an initial strontium content of 2.04 or 3.04 mg per gram of grout, McDaniel et al. (1982) have reported a strontium diffusion coefficient of $5.3 \times 10^{-12} \text{ cm}^2/\text{s}$ and 3.9% cumulative strontium release for the “best” grout (cured for 182 d) after 80 d of leaching. The corresponding values for

the "worst" grout were 1.0×10^{-9} cm²/s and 50.6% cumulative release. Strontium leachability decreased by a factor of 3 to 5 when the curing time was increased from 28 to 91 d. The grouts were formulated from different proportions of type I portland cement, fly ash, pottery clay, bentonite, and dried sludge. The reported diffusivities for both cesium and strontium from cement-based material in various leachants are summarized in Table 5.

5. VITRIFICATION OF CESIUM-BEARING WASTES

5.1 OVERVIEW

Cesium salts are relatively volatile, and significant quantities of cesium may partition to the off-gas during high-temperature thermal processing (Stockdale et al., 1994; Burger, 1995). In the case of radiocesium, this imposes a burden to the off-gas cleaning system; the off-gas must be cooled to allow particulate condensation, and fines must be removed by high-efficiency particulate air (HEPA) filtration. Reportedly, retention of cesium in the melt phase may be improved somewhat by the addition of alumina or titania, or with use of a cold-cap melter design. Residual cesium at the near surface of the glass waste form (hydrated layer) may be subject to somewhat facile leaching or ion exchange for other monovalent cations.

Table 5. Diffusivities of cesium and strontium in ordinary portland cement (OPC) and cementitious materials^a

Radionuclide	Medium	Diffusivity (cm ² /s)	Reference
¹³⁴ Cs	OPC	5.1 x 10 ⁻⁷	Krishnamoorthy et al., 1993
¹³⁴ Cs	OPC	1.2 x 10 ⁻⁹	Crawford et al., 1985
¹³⁴ Cs	OPC	5.9 x 10 ⁻¹⁰	Crawford et al., 1985
¹³⁴ Cs	OPC	4.2 x 10 ⁻¹¹	Crawford et al., 1985
¹³⁴ Cs	OPC + ion-exchange resin (medium: seawater)	0.6 to 1.3 x 10 ⁻⁶	Torstenfelt and Hedin, 1989
¹³⁴ Cs	OPC + 5% zeolite (medium: seawater)	0.8 to 1.0 x 10 ⁻⁸	Torstenfelt and Hedin, 1989
¹³⁷ Cs	OPC	3.2 x 10 ⁻¹⁰	Plecas et al., 1992
¹³⁷ Cs	OPC	3.4 x 10 ⁻¹⁰	Plecas et al., 1992
¹³⁷ Cs	OPC + blast-furnace slag	5.0 to 15 x 10 ⁻⁸	Muurinen, 1985
Cs (stable)	OPC + blast-furnace slag	1 x 10 ⁻¹⁰	Anderson et al., 1981
⁸⁵ Sr	OPC + 5% Na ₂ SO ₄	2.5 x 10 ⁻¹²	Fuhrmann and Colombo, 1989
⁸⁵ Sr	OPC	3.5 x 10 ⁻⁹	Krishnamoorthy et al., 1993
⁸⁵ Sr	Sulfated cement	7.0 x 10 ⁻¹²	Atkinson and Nickerson, 1988
Sr (stable)	OPC	1.0 x 10 ⁻⁹	McDaniel et al., 1982
Sr (stable)	OPC	5.3 x 10 ⁻¹²	McDaniel et al., 1982

^aThe leachant was distilled water, unless noted otherwise.

5.2 LITERATURE SURVEY

5.2.1 Cesium Volatility During the Vitrification Process

In a study of the volatilization of cesium from a synthetic basalt, Sill (1988) has shown that the volatility increases linearly with temperature from 400 to 900°C. The basalt contained 1% cesium (added as cesium chloride) and 1 μCi of ^{137}Cs as a tracer. The volatilities at 100, 400, and 900°C were 0.0020, 0.067, and 22.7% per hour, respectively. It was estimated that, at these rates, complete volatilization would occur in 1 h at 1030°C. However, after the vitrification, the volatility decreased markedly and the corresponding rates of cesium loss were 0.059 and 0.316% per hour at 1300 and 1500°C.

Klein et al. (1985a, 1985b) have reported that about 5% of the ^{134}Cs was released when a simulated liquid waste solution containing the radionuclide was fed to the surface of molten glass at 400°C. Their results showed that the cesium volatilization increased to about 30% when the temperature of the molten glass was increased to 900°C. They have also demonstrated that 30 to 70% of the cesium, introduced as CsNO_3 , was volatilized and entrained in the off-gas during the vitrification of a simulated high-level waste.

Spalding (1994) has reported that the volatilization of ^{137}Cs from soil samples collected from the White Oak Creek at ORNL, as well as from mixtures of this soil and limestone, was greatly enhanced by the addition of small amounts of chloride-containing species, including sodium chloride, calcium chloride, hydrochloric acid, and polyvinyl chloride. The effect was most pronounced with NaCl; > 90% of the cesium was volatilized at 1000°C by

using 5% NaCl as an additive. The average concentration of ^{137}Cs in the soil was 7.33 $\mu\text{Ci/kg}$. In the presence of NaCl, essentially no volatilization of cesium occurred below 800°C. Most of the cesium was released at 800 to 1000°C, a range which is below the melting point (1200°C) of the soil. No further volatilization of cesium was observed after the soil had melted into glass at 1200°C. The effect of adding sodium borate was similar to that observed on addition of NaCl. However, incorporation of up to 10% of other additives such as sodium, potassium, or lithium carbonate; sodium nitrate; sodium phosphate; sodium sulfate; sodium or calcium fluoride, polystyrene; graphite; stainless steels; iron, zinc, or antimony oxide; or limestone produced similar levels of ^{137}Cs volatilization as compared with the soil without additives. Significant cesium releases occurred for soil samples containing >25% limestone, and ^{137}Cs was essentially completely volatilized for limestone additions >50% (Spalding et al., 1989).

5.2.2 Cesium Volatility in the Presence of Additives

Ghattas and Eskander (1983) have shown that the retention of cesium during vitrification is strongly dependent on the composition of the glass-forming material. They have reported that the cesium volatilization for glass compositions containing a simulated high-level radioactive waste (5.18 g/L of cesium added as cesium nitrate) was 30% after heating at 1100°C for 4 h. However, the addition of 4.2% titanium oxide reduced the cesium loss to 10% within the same period. Cesium volatility was highest within the first 2 h and decreased sharply thereafter, possibly due to the formation of less-volatile cesium silicates.

Wilds (1979) has reported only a slight suppression of cesium volatility on addition of TiO_2 , although the vitrification temperature (1150°C) was similar to that used by Ghattas and Eskander (1983). Rastogi et al. (1966) found that reductions in cesium volatilities on addition of TiO_2 were only significant at temperatures below 1000°C and for vitrification times less than 1 h. Boric oxide was also reported to suppress cesium release during vitrification, although the effect was less than that observed for TiO_2 . The simultaneous addition of titanium dioxide and boric oxide reduced the effectiveness of TiO_2 (Rudolph, 1972).

The vitrification of cesium and its removal from the off-gas have been reported by Kepak et al. (1992). The vitrification was conducted at 1050°C , and the cesium nitrate concentration in the glass-forming mixture (i.e., "ballotini") prior to heating was 0.19%. The radioactive ^{134}Cs and ^{137}Cs contents were 2.4×10^{14} and 5.3×10^{15} Bq, respectively. The gas-cleaning system consisted of polyethylene fibers, an unspecified granulated natural material, glass-fiber material, and a high-efficiency filter made of glass microfibers. These filtration components were arranged in series. The decontamination factor for cesium was 3.3×10^6 , and the average level of cesium removal from the gas phase was 95.7%.

5.2.3 Thermal Stability of Vitrified Waste Forms

Kamizono et al. (1986) have studied the volatilization of ^{134}Cs from a borosilicate glass containing ~12.7% of simulated fission products and actinides and 1.89×10^{10} Bq of ^{134}Cs . The glass was melted at 1200°C and cooled to room temperature at the rate of $40^\circ\text{C}/\text{h}$. The glass waste forms were placed in canisters, and each was heated at a selected temperature for

4 d. No leaching tests were reported. Analysis for radioactive cesium in the air inside the canister showed that no ^{134}Cs was present at 200 or 400°C. For temperatures above 500°C, the cesium activity in the air increased as the temperature was increased; about 14% of the radioactive cesium was volatilized at 1000°C.

In another study, Kamizono and Muraoka (1992) have reported that, at 600°C, no ^{137}Cs could be detected in a canister containing glass loaded with the radionuclide, although the volatility was estimated to be 1.8×10^2 Bq/s at 400°C (Kamizono et al., 1986). However, at 1000°C, cesium was transported to the surface of the glass, resulting in the release of ^{137}Cs into the canister.

The volatility of ^{137}Cs from a simulated high-level waste glass contained in a stainless steel double-walled crucible has been investigated by Nakamura et al. (1988). At 400°C, the measured volatility of the radioactive cesium was 1.6×10^{-6} g/cm²-d; at 800°C, it was 2×10^{-2} g/cm²-d. The cesium deposited on the outer surface of the crucible dissolved in water at room temperature, suggesting that aqueous solution could be used to decontaminate cesium condensation deposits on stainless steel.

Gray (1980) has also reported that (1) the release of nonradioactive cesium from glass increased as the temperature increased, and (2) 100% release of cesium occurred at 1200°C. Addition of 10% Al_2O_3 to the glass before vitrification at 1100°C decreased the cesium loss from about 27% to 8% after 4 h, while TiO_2 increased the volatility under the same conditions. Cesium volatilization was negligible at temperatures below 700°C. Thus, both

vitrification and the exposure of cesium-containing glass to high temperatures (e.g., due to accidental fire) during storage could promote cesium volatilization.

5.2.4 Leaching Characteristics of Vitrified Waste Forms

The leaching behavior of cesium from borosilicate glass has been studied by Murakami and Banba (1984). The investigations were conducted on glass waste forms containing 0.72% Cs_2O , and the leaching was performed in deionized water at 100°C for 200 d using the Soxhlet leach test. Examination of the glass using energy-dispersive x-ray spectroscopy, wavelength-dispersive x-ray spectroscopy, and transmission electron microscopy showed that cesium was completely leached from the surface layers (100 to 1000 Å) at the end of the test.

Vance and Armad (1983) have shown that cesium extraction from a cesium-containing crystalline zeolite, $\text{CsAlSi}_5\text{O}_{12}$, fired for 2 d at 1400°C, was proportional to the square root of the dissolution time. The leaching medium was deionized water or an aqueous solution of HCl, KOH, NaOH, NaCl, NaHCO_3 , or CaCl_2 . The Soxhlet leach times ranged from 1 to 50 d, and the pH of the solutions varied between 1.0 and 9.0. The maximum cesium release of 4.0% occurred after 50 d of leaching at 70°C in HCl solution at pH 1.0; the minimum loss was 0.17% in HCl solution at pH 4.0.

Bibler et al. (1993) have reported that the vitrification of sludge, frit, and a resorcinol-based ion-exchange resin used to remove ^{137}Cs from a supernate resulted in the formation of low-

durability glass, as indicated by high rates of boron, lithium, silicon, and sodium leaching from the glass.

6. VITRIFICATION OF STRONTIUM-BASED WASTES

In contrast to the high losses observed for cesium, Sill (1988) has reported that strontium, loaded as $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, could not be detected in the volatilized products of a synthetic basalt that contained 1% strontium plus 1 μCi of ^{85}Sr tracer and was heated at 100°C intervals from 400 to 900°C. The heat-treatment time at each temperature was 1 h.

Nakamura et al. (1988) have reported that the volatility of strontium from a double-walled stainless steel crucible was about $1.6 \times 10^{-6} \text{ g/cm}^2\text{-d}$ at 400°C, a value which is similar to that obtained for ^{137}Cs under similar conditions.

In Soxhlet leach tests in deionized water at 100°C, Murakami and Banba (1984) have shown that strontium was completely removed from a borosilicate glass after 200 d of leaching. The glass contained 0.24% SrO ; strontium was detected using wavelength-dispersive x-ray spectroscopy, which had a sample depth of 100 to 1000 Å from the glass surface.

7. ENCAPSULATION IN BITUMEN

7.1 OVERVIEW

Bitumen (asphalt), a thermoplastic organic suspension, has been used for more than 20 years to immobilize low-level radioactive wastes. It is relatively insensitive to waste composition

(although high concentrations of salts in the waste form can cause swelling from osmotic forces when the waste form is immersed in water). It has a moderate compressive strength (Buckley et al., 1989, report a value of 130 psi) and can achieve volume reduction for some wastes. Unfortunately, it has only a modest solubility in water (~0.5 %), which may cause increased leachability over time (Matsuzuru et al., 1980); thus, its long-term durability may be suspect. Bitumen absorbs some water (especially if the waste contains relatively high concentrations of salts) and swells as it does so; it also deforms or "creeps" under pressure and, therefore, must be containerized to retain dimensional stability. Concern exists for encapsulating high concentrations of oxidizing material, such as nitrate salts, and bitumen may be subject to microbial degradation. Perhaps as a result of these uncertainties, this technology appears to have fallen in disfavor recently within the United States and may not now be commercially available there (Beck et al., 1994).

7.2 LITERATURE SURVEY

Mattus and coworkers (1987) have shown that bitumen containing about 40, 50, or 60 wt % of surrogate waste and a cesium concentration of 48.9 mg/L exceeded the NRC's minimum leach index of 6 after 90 d of leaching in distilled water. A leach index greater than 8 was observed for each of the three samples tested. It was noted, however, that bitumen waste forms containing water-soluble salts swell as a result of osmotic forces when immersed in water. Such swelling can cause waste-form degradation after prolonged exposure to water (Broderson, 1986).

Analogously, Mattus et al. (1987) demonstrated that the product obtained by the encapsulation of 47 mg/L of strontium in bitumen containing about 40, 50, or 60 wt % surrogate waste had an average leach index of 10 after leaching in distilled water for 90 d and, therefore, met NRCs requirements (i.e., a minimum leach index of 6). However, cracking of the waste form occurred after prolonged (150 d) immersion in water.

In an 18-month study, Bernard et al. (1982) have shown that the fractional release of ^{137}Cs from cement matrix is higher (1×10^{-2}) than from bitumen (1×10^{-4}). Besides cesium, the waste contained other radionuclides (^{241}Am , ^{60}Co , ^{239}Pu , and ^{90}Sr), as well as nonradioactive materials such as sodium nitrate, sodium chloride, sodium fluoride, and sodium phosphate. However, the possible effects of these materials on the release of ^{137}Cs were not discussed.

The release rates of ^{137}Cs from bitumen are reported by Cowgill (1991) to be more than two orders of magnitude lower than from cement; the release rates for ^{90}Sr are slightly lower from bitumen than from cement. Although in the short term, both Cowgill (1991) and Buckley (1989) report that the radionuclide retention ability of bitumen is much better than that of cement, long-term swelling and degradation are the more important issues. Leaching is increased if bitumen swelling is not kept under control. Other parameters that affect swelling, in addition to the high water solubility of the medium, are waste compositions characterized by small particle sizes and strong salt solution—both of which may increase swelling (Broderson et al., 1983). Additives such as polypropylene can reduce leaching from bitumen and increase waste-loading capability.

The primary limitations that may preclude the use of bitumen for the disposal of Lockheed Martin Energy Research Corporation (LMER) wastes are the lack of commercial availability for the technology and the fact that bitumen has been identified as a human carcinogen and, thus, is assigned a high health hazard (Beck et al., 1994).

8. ENCAPSULATION IN POLYMERIC MATERIALS

8.1 OVERVIEW

Unlike the usual situation in cement-based grouts, waste encapsulated in polymeric materials is not stabilized by chemical interactions but is physically isolated by encapsulation in a hydrophobic binder; hence, it is rendered less leachable. Encapsulation of low-level waste in polymeric materials since the mid-1980s has included the use of catalyzed and promoted resins (e.g., epoxy resin and vinyl ester styrene) and thermoplastics (such as polyethylene and, more recently, sulfur polymer cement). Polymers generally have an advantage over cement-based grouts in that they have higher waste loading efficiencies, always undergo a solidification reaction, and are relatively insensitive to waste composition (although the thermal-setting resins are intolerant of high moisture content).

8.2 EPOXIDE RESIN

The leaching of ^{137}Cs from epoxide resin (based on a diglycidyl ether of bisphenol A cured with diaminodiphenylmethane) has been reported to be independent of the leachant renewal frequency and the surface area-to-volume ratio (Burnay, 1986). The aqueous leachants

contained 100 to 200 μCi of ^{137}Cs . The ^{137}Cs mean diffusion coefficient was $1.2 \times 10^{-15} \text{ cm}^2/\text{s}$ at 20°C (equivalent to a leach index of 14.9).

8.3 POLYETHYLENE ENCAPSULATION PROCESSES

Over the past few years, the application of polyethylene as an encapsulation medium for mixed wastes has been investigated by Kalb et al. (1991a, 1991b, 1992, 1993) at Brookhaven National Laboratory. Their studies have focused on the encapsulation of surrogate wastes containing sodium nitrate, the predominant waste in the 149 single-shell storage tanks (SST) at the Hanford Site. The stored wastes amount to about 200,000 metric tons of material, with a total radioactivity of approximately 60 MCi, most of which is due to ^{137}Cs and ^{90}Sr . Accelerated leach tests (duration, 24 h) at 70°C in distilled water on polyethylene containing 50 and 70 wt % sodium nitrate gave average diffusion coefficients of 9.7×10^{-9} and $2.3 \times 10^{-7} \text{ cm}^2/\text{s}$, respectively. The corresponding compressive strengths of these samples, after storage for 3 months at 70°C , were 1960 and 1580 psi. It has been estimated that 5 to 17% of the original contaminants (50 or 70 wt % sodium nitrate) encapsulated in polyethylene will be released after 300 years of leaching in water at 70°C . Future polyethylene encapsulation studies will involve the actual wastes and assessment of the retention of the radionuclides by polyethylene.

8.4 VINYL ESTER STYRENE POLYMER

Vinyl ester styrene (VES) polymer waste forms have been demonstrated to meet the structural stability and durability requirements specified by the NRC in 10 CFR Part 61.

Wastes or surrogates tested by the Dow Chemical Company (1984) included: (1) boiling-water reactor (BWR) concentrates (primarily sodium sulfate solution), (2) pressurized-water reactor (PWR) concentrates (primarily boric acid solutions), (3) ion-exchange bead resin slurry, (4) filter aid sludge (Celite), (5) powdered ion-exchange slurry, (6) decontamination waste, and (7) volume-reduced dry salts (sodium sulfate plus ash fines).

On the basis of data presented in a topical report submitted by Diversified Technologies (1991), VES waste forms were accepted by NRC. The data demonstrated the stabilization of decontamination waste concentrate containing up to 54% total dissolved solids, at a waste loading of 60%. Surrogate decontamination waste contained metal chelates (sulfates or citrates of Fe, Ni, Cu, Cr, etc.). The stabilized waste form met the structural stability requirements specified in 10 CFR Part 61 for the disposal of Class B and Class C wastes (i.e., reasonable assurance that the waste form will maintain structural stability for an interval of greater than 300 years). Compressive strengths ranged from ~4000 to 4700 psi, vs the NRC minimum requirement of 60 psi (see Table 4 in 10 CFR Part 61), and compressive strength was maintained after 90-d water immersion testing, with no indication of physical change. The waste form passed NRC criteria for thermal degradation, radiation stability (at exposures up to 20 times the criterion of 1×10^8 rads), and resistance to biodegradation. The reported leachability index for ^{60}Co was 10.8 vs the minimum requirement of greater than 6. It was assumed that other radionuclides would have similar leachability indexes.

8.5 SULFUR POLYMER CEMENT

Sulfur polymer cement (SPC) is similar to other thermoplastic encapsulation processes, except that dried waste solids are added to molten sulfur plus phase-modifying additives. The temperature of the melt must be maintained within a relatively narrow range ($110\text{ }^{\circ}\text{C} < T < 150\text{ }^{\circ}\text{C}$) for processibility. Minimal viscosity is observed at about $135\text{ }^{\circ}\text{C}$, but phase changes occurring near the upper limit of the operating temperature range cause a severe increase in viscosity (Heiser and Milian, 1994). Toxic hydrogen sulfide may be liberated if the melt is heated above $160\text{ }^{\circ}\text{C}$. The addition of dried waste may cause a process upset due to significant changes in the temperature (and, thus, the rheology) of the melt, thereby complicating processibility. The dense, hardened polymer is resistant to acid attack but cannot be used under highly alkaline conditions. Compressive strengths may be near 2000 psi at 40% waste loading, and the nonporous waste form is essentially impervious to water. This emerging technology is under development by researchers at Brookhaven National Laboratory (Kalb et al., 1991a, 1991b) and in Europe (van Dalen and Rijpkema, 1989).

9. STABILIZATION OF SOLID FERROCYANIDES AND RADIOACTIVE WASTES

Solid ferrocyanides have been studied extensively for use in removing cesium from nuclear waste solutions. These nonstoichiometric materials have the general formula $A_n M_{(2-n/2)} \text{Fe}(\text{CN})_6$, where A is sodium or potassium; M is a metal such as nickel, cobalt, copper, or zinc; and $n < 2$. Potassium cobalt hexacyanoferrate (KCCF) is currently being

evaluated for application to cesium removal from MVST supernates and NGLLLW streams at ORNL.

A review of the literature shows that very little research has been conducted on the final waste form of radionuclide-containing ferrocyanides. Some researchers have suggested that the spent ferrocyanides could be incorporated into cement. However, wastes with high concentrations of nitrates and/or nitrites would represent a potential hazard by creating high temperatures in the waste form (Campbell and Lee, 1991). Also, cyanide formed from the decomposition of dried or decomposed ferrocyanides in highly alkaline or highly acidic media could oxidize to cyanogen and be released to the air. A rapid exothermic reaction might occur if high concentrations of these compounds were heated with nitrates (e.g., sodium nitrate), resulting in high pressures and possible explosions.

Based on available literature discussions of safety issues concerning the use and storage of KCCF solids, uncontrolled exothermic reactions or explosions are considered unlikely under the conditions in which the NGLLLW or MVST supernate would be treated. The nitrate/hexacyanoferrate ratios in dried solids from the KCCF treatment, assuming that the solids contain the dried salts from the 90% entrained NGLLLW or a 50:50 mixture of NGLLLW and MVST supernate solution, would not be in a range that reacted explosively in studies performed by Scheele et al. (1993).

In a patented work, Schultz and Dressen (1977) have shown that Ni, Co, Cu, Fe, Cd, Mn, or UO₂ containing ferrocyanides can be converted into glass if the glass-forming material contains about 10 to 30% ferrocyanides, 15 to 25% sodium carbonate, 40 to 60% basalt,

40 to 60% silica, and 5 to 10% calcium oxide. In a review of studies performed to evaluate the application of ferrocyanides to cesium removal from waste solutions, Haas (1993) has recommended further research on final waste forms for ferrocyanides containing radioactive constituents.

10. SUMMARY AND RECOMMENDATIONS

The limited facilities for the storage of LLLW at ORNL have made it necessary to develop a flow sheet to treat the waste as it is generated. The primary objective of the flow sheet currently under development is to remove the majority of the radioactive species from the waste, so that the treated LLLW can be evaporated to a final salt cake that will meet Class LII limits and, thus, will be suitable for storage on-site. Processes for the removal of ^{90}Sr and ^{137}Cs , two of the primary radionuclides present in the NGLLLW, are an integral part of the proposed treatment sequence. As the flow sheet matures, unit processes will be included to treat additional components of the waste.

As part of the implementation of the flow sheet, a literature survey was initiated to identify possible stabilization techniques and waste forms that might be amenable to the immobilization of the solids produced at the completion of the strontium and cesium treatment operations. The ^{90}Sr will be present as strontium carbonate solids; ^{137}Cs will be sorbed on KCCF solids. The literature review focuses on the stabilization and solidification of these radionuclides in cement, polymeric materials, or their incorporation into glass, the principal media that have been applied to such radioactive wastes. The concomitant

chemical compounds that will be contained in the LLLW entrained with the solids have been identified and listed in the Appendix.

According to Cowgill (1991), the general order of radionuclide leach resistance in solidified waste forms is: cement < polymers < bitumen < glass. Several studies have shown that both cesium and strontium are leached by distilled water from solidified cement-based waste forms, although the leachabilities of cesium are generally much higher than those of strontium under similar conditions. The situation is exacerbated by the presence of sulfates in the solution, as manifested by cracking of the grout. Additives such as bentonite, blast-furnace slag, fly ash, montmorillonite, pottery clay, silica, and zeolites generally reduce cesium and strontium release rates. These materials possibly exert their influence by reducing the pore sizes in the cement and by increasing the negative charge densities in the cement, thus promoting electrostatic attraction between the radioactive cations and the negative sites in the cement. Longer cement curing times (>28 d) also reduce the leaching rates of the radionuclides, as do high ionic strengths such as those that occur in seawater.

The properties of cement-stabilized wastes are controlled by several factors, including the waste characteristics, the composition of the cement blend, the chemical interactions between the waste and the cement blend (reviewed by Mattus and Gilliam, 1994), and the processing and storage conditions. Because of these complexities, studies of waste stabilization have been conducted primarily on relatively simple systems to promote understanding of the chemistry between the waste and the cement. As discussed earlier and as detailed in the Appendix, the solid wastes that will result from treatment of the MVST supernates and the NGLLLW will contain other components, such as nitrates, carbonates, sulfates, and

organics—all of which can influence the properties of the final waste form. The undesirable cracking of grout by sulfates has been discussed earlier in this report, and the detrimental effects of organic wastes on cement hydration and durability are well known.

Since cement-based grout solidification has been the predominant method used to stabilize many types of low-level wastes for several decades, the system has been studied thoroughly; thus, many of its limitations have already been identified. Some of the occasional performance or regulatory compliance difficulties associated with the use of cement-based waste forms have been summarized by the NRC (1989), and problems identified with use of the technology within the DOE complex have been summarized (Lomenick, 1992). In general, most of these problems involve inadequate process quality control or unexpected interactions between the waste components and the grout formulation.

Vitrification or glass encapsulation is recognized by the U.S. Environmental Protection Agency (1992) as "Best Available Demonstrated Technology" for the treatment of many types of hazardous and/or radioactive wastes. The perceived benefits of this technology for such applications have been reviewed recently by Bickford and Schumacher (1995); at present, the additional processing costs associated with vitrification, relative to cement-based stabilization, are considered justifiable for simple hazardous or radioactive waste in cases where the volume reduction of the vitrification process can reduce life-cycle disposal costs, or where site-specific conditions require the high durability of glass waste forms. Although vitrified waste is much more resistant to leaching than is cement grout, the vitrification process results in significant volatilization of cesium, organics, and inorganic wastes with low decomposition/melting temperatures. Hence, vitrification will generally

require the use of gas cleanup systems to prevent release of the volatilized wastes into the atmosphere. Thorough literature search and review show that although vitrification and waste encapsulation in polymeric materials have been extensively studied, relatively little work has been done on specific applications to cesium or strontium stabilization.

Polymer encapsulation of radioactive waste is a promising solidification technology. Polymers generally have certain advantages over cement-based grouts in that they have higher waste loading efficiencies, an assured solidification reaction, and a relative insensitivity to waste composition (although the thermal-setting resins are intolerant of high moisture content). Waste disposal in bitumen (asphalt) matrix has been extensively used in Europe, but the current commercial availability of this technology in the United States is in doubt. This situation is, perhaps, due to uncertainties regarding its performance with respect to dimensional stability and long-term durability. Waste solidification based on the use of SPC is an emerging technology with excellent waste-form characteristics, but process implementation has been somewhat problematic, primarily because of a very limited range of process operating temperatures. Catalyzed, promoted polymers, such as polyethylene and VES, appear to be viable waste solidification options. The VES technology has been approved by the NRC for use in conditioning commercial nuclear waste for disposal.

Studies with KCCF and other cyanoferrates have demonstrated effective removal of cesium from waste solutions; however, very little information is available on the final waste forms of KCCF-bearing wastes. Studies of the solidification and stabilization of these wastes are required.

It is clear that the types of wastes reviewed in this report cannot be easily extrapolated to the wastes at ORNL since the latter are more complex than those that have been investigated and reported in the literature. However, the information presented here should provide a good foundation for including or eliminating certain variables in selecting the final forms for the ORNL wastes. It would be useful to conduct studies of those waste components (e.g., KCCF) for which adequate data are not available in the literature. Such studies would allow us to determine the effects of these constituents on cesium or strontium retention in cement, polymeric materials, or glass before final waste forms are selected for the MVST or the NGLLLW solids. Alternatively, the various liquid wastes could be treated separately using processes such as adsorption and precipitation followed by final stabilization/solidification and disposal of the various end products.

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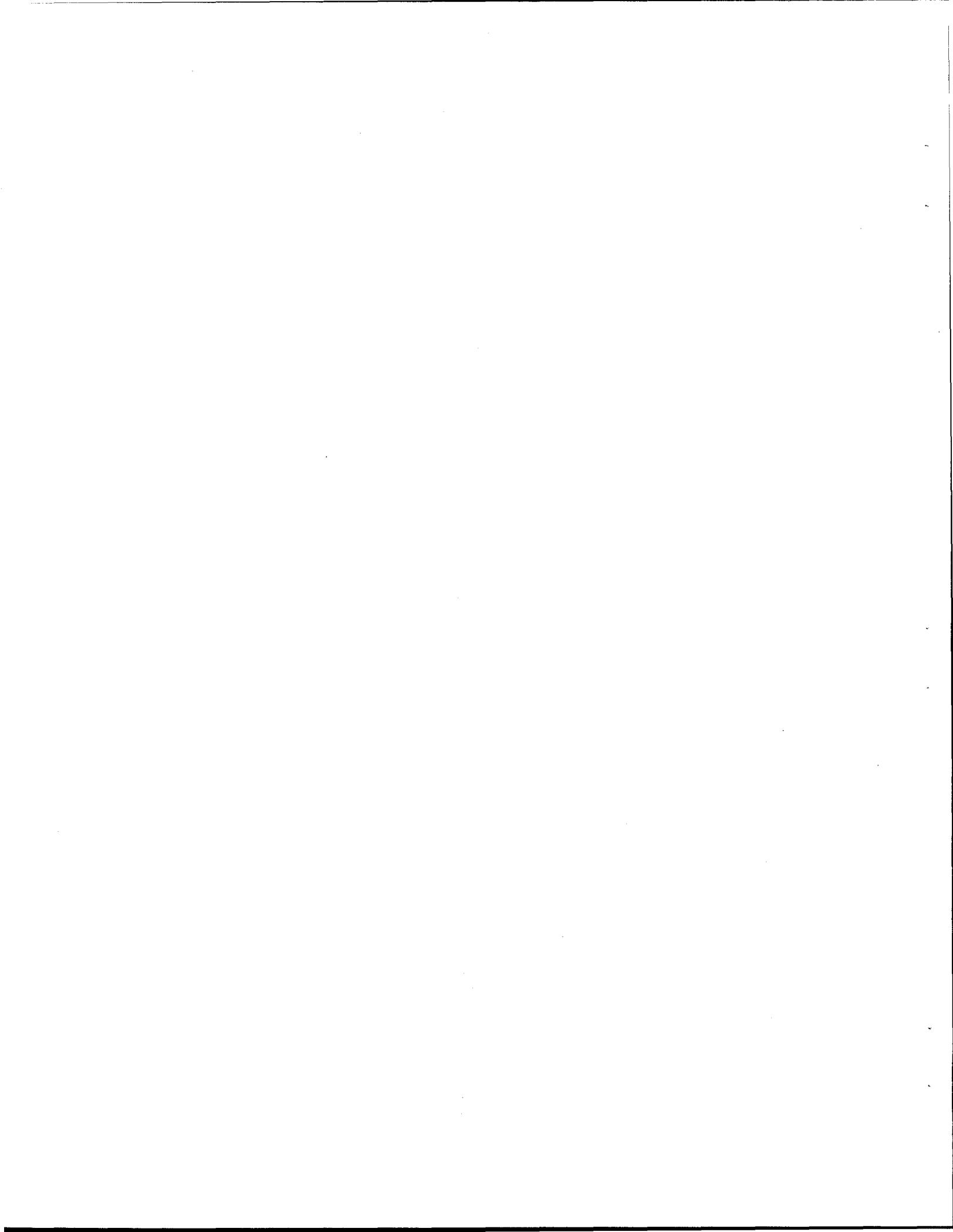
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Appendix

CALCULATION OF THE COMPOSITION AND QUANTITIES OF LLLW AND SLLW GENERATED USING THE PROPOSED NGLLLW FLOW SHEET

A.1. Background. A flow sheet has been proposed for the partial treatment of newly generated low-level waste (NGLLLW) and NGLLLW blended with LLLW supernate stored in the Melton Valley Storage Tanks (MVSTs). The primary radionuclides of concern in the LLLW are ^{90}Sr , $^{134,137}\text{Cs}$, $^{103,106}\text{Ru}$, and ^{99}Tc . As discussed in the main text of this report, the proposed flow sheet addresses the removal of ^{90}Sr and $^{134,137}\text{Cs}$ from undiluted and blended NGLLLW. Further development of the flow sheet is currently under way to define the unit processes required for the removal of $^{103,106}\text{Ru}$ and ^{99}Tc . The first four process units of the current flow sheet include (1) strontium coprecipitation, (2) acid neutralization of the treated waste, (3) cesium sorption on 100 ppm of potassium cobalt hexacyanoferrate (KCCF), and (4) cesium sorption on 50 ppm of KCCF. (A schematic diagram of the proposed flow sheet can be found in Fig. 1 of this report.)

To complement the development of the NGLLLW flow sheet, a literature study has been initiated to determine the most promising interim and final waste forms for the disposition of the solids that will be generated as a result of LLLW treatment using the flow sheet. The tables presented here were prepared to help characterize the chemical and radiochemical compositions of solids that will be generated on the completion of each of the four specified unit operations. They also summarize the variations in the liquid and solid compositions that will be encountered as the amount of MVST supernate blended into NGLLLW is altered from 0 to 100%. The Appendix is ordered such that the table describing the LLLW at the start of each unit operation is paired with a table listing the solids that are generated at the completion of that particular unit operation.

A.2. General Assumptions. The accurate interpretation of these tables is dependent on an awareness of the assumptions made in formulating the table entries. Assumptions that affect all

calculations in the spreadsheet include the fact that the composition of the NGLLLW is based on the estimation of future wastes that will be generated at ORNL. (An estimation of the composition of the NGLLLW is presented in Table 1 of the text.) As such, there are no analytical data to characterize this waste; nor is there any assurance that programmatic changes at ORNL will not alter the estimation of the composition of NGLLLW as presented in Tables A.1-A.19. Additionally, the composition of the MVST supernate is based on analytical data that describe the composition of the unfiltered supernate sampled from tank W-29 in 1989. The chemical constituents of supernate vary in each of the ten storage tanks; however, the data in the tables refer to chemical components for the tank W-29 supernate only. Additionally, only the presence of ^{90}Sr and ^{137}Cs in the treated LLLW and resulting SLLW are quoted in the tables. It should not be assumed that $^{103,106}\text{Ru}$ and ^{99}Tc (as well as other minor radionuclides) are not present in these wastes. Rather, the disposition of these additional radionuclides at each point in the flow sheet has not been determined and, therefore, could not be accurately represented in the spreadsheet at this time. As the proposed flow sheet matures, the disposition of the additional radionuclides will be included in the spreadsheet.

The concentrations of ^{90}Sr and ^{137}Cs in the LLLW were based on the following assumptions: The initial total strontium concentration in NGLLLW is equivalent to 0.141 ppm, or $1.6 \times 10^{-6} \text{ M}$; the ^{90}Sr activity is 19.4 mCi/L. According to data summarized by Sears et al. (1990), the total strontium concentration in the MVST tank W-29 supernate is 2.1 ppm and the ^{90}Sr activity is 0.2 mCi/L. However, most of the strontium in the supernate is present as suspended solids that can be removed by filtration prior to treatment. A value of 0.4 ppm was selected as an upper limit for the initial soluble strontium concentration. This value reflects data reported recently by Collins et al. (1995), in which the total strontium concentration of tank W-25 supernate was reduced from 23 to 0.4 ppm after filtration through a $0.45\text{-}\mu\text{m}$ -pore membrane. The total cesium concentrations quoted in the tables were derived by assuming that stable cesium, produced as the result of fission, is present

at two to three times that of the ^{137}Cs concentration (Croff 1986). The ^{137}Cs concentration was multiplied by 3 to arrive at the total cesium concentration as presented in the tables. As the LLLW is processed through the flow sheet, the values for strontium and cesium concentrations remaining in the liquid phase after each unit operation were calculated by using decontamination factors typically encountered in laboratory batch tests when a high-speed centrifuge was used for liquid/solid phase separations.

Several assumptions were also made in deriving the table entries for the composition of the solids generated at the completion of each unit operation. These include the following: (1) The quantities of solids in the table are those that will be generated during the treatment of 1 L of NGLLLW at that point in the flow sheet. (2) A 100% efficiency is assumed in collecting the solids generated at the end of each unit operation. This should give a worst case for the total radioactivity that might be found in the solids. (3) The wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% of the treated, entrained LLLW. The activity of the dry solids assumes that the slurry has been dried completely to remove the water. As such, the calculated activity of the dried solids is a factor of 10 times larger than the corresponding nuclide content stipulated for the wet solids.

A.3. Strontium Coprecipitation Unit Operation. In addition to the global assumption made for the development of the overall waste spreadsheet, certain assumptions were required to calculate entries for the specific unit operations of the proposed spreadsheet. Tables A.1 and A.2 represent the feedstream composition to the proposed NGLLLW flow sheet as it exists just prior to the strontium coprecipitation unit operation. These two tables list the major and minor components, respectively, that are present in various blends of MVST supernate with NGLLLW. The first line in each of the tables summarizes the composition of undiluted NGLLLW. These values match those presented in Table 1 of the text. The final line in each table summarizes the composition of 100%

MVST supernate as it probably exists in tank W-29. The supernate of the tank has been air-sparged over the past 3 years to reduce the tank volume by 30%. Thus, the values for the concentrations of the various components of 100% MVST (see column entitled "Percent concentrations MVST supernate") presented in the Appendix tables were calculated by multiplying the analytical data compiled by Sears et al. by a factor of 1.3. The intermediate lines of data in each table display the concentrations of various components as the result of blending 5, 10, 20, 35, and 50% concentrated MVST supernate with NGLLLW.

The ^{90}Sr is removed from the LLLW by coprecipitating the radionuclide with the addition of 50 ppm of strontium chloride (SrCl_2) to form strontium carbonate in the highly alkaline waste. Settling of the carbonate solids is aided by the addition of 25 ppm of iron and 2 ppm of a polyacrylamide flocculating agent. The composition of the dry solids, regardless of the quantity of MVST supernate blended into the NGLLLW, is presented in Tables A.3 and A.4. Most of the solids derived from the treatment of 1 L of LLLW is present as carbonate salts weighing approximately 0.2 g. The activity of this SLLW decreases significantly as the amount of MVST supernate increases in the treated LLLW, primarily due to the smaller quantities of ^{90}Sr present in the supernate. The quantity of $^{134,137}\text{Cs}$ in the SLLW is a result of the presence of treated LLLW that is entrained in the solid waste slurry before it is dried.

A.4. Acid Neutralization Unit Operation. After the carbonate solids have been removed, the pH of the LLLW is decreased from 13 to 8 by addition of sulfuric acid (H_2SO_4). The concentrations of the major and minor components of the LLLW after pH adjustment are summarized in Tables A.5 and A.6. The calculation of the concentration of the components was based on using 5.4 NH_2SO_4 to acidify the waste. The resulting dilution of the LLLW incurred with the addition of the acid is tabulated under the column heading " H_2SO_4 dilution factor." In the actual processing of LLLW, 36 NH_2SO_4 will probably be used so that the dilution factor will be no greater

than 1.02 for any blended feed composition. The significant component that is altered in the acidification of the waste is the production of sodium bicarbonate (NaHCO_3) resulting from the reaction of H_2SO_4 with the NaCO_3 in the waste feedstream.

The total strontium concentration in this unit operation, as well as any following operation, is governed by the addition of the 50 ppm of SrCl_2 . The addition of this quantity of stable strontium is so much greater than the total strontium in either the NGLLLW or the MVST supernate that the strontium concentration in the treated waste is independent of the LLLW source. The stated concentration in the table is the result of dividing the stable strontium addition (50 ppm) by the decontamination factor (DF) of 150 typically encountered for the removal of ^{90}Sr by the strontium coprecipitation unit operation.

A.5. First KCCF Unit Operation. The aluminum hydroxide [$\text{Al}(\text{OH})_3$] solids that precipitate upon neutralization of the LLLW are not immediately removed. Instead, they are used to help settle the KCCF solids generated in the first KCCF unit operation. Equimolar solutions of potassium ferrocyanide and cobalt nitrate are added to the neutralized LLLW to form 100 ppm KCCF in situ. Cesium is sorbed by the KCCF solids as the LLLW is stirred for 1 h. After the equilibration time, 2 ppm of polyacrylamide flocculent may be added to the slurry to help settle the fine KCCF solids prior to a liquid/solid separation. Tables A.7 and A.8 summarize the composition of the LLLW after the first KCCF unit operation. As indicated by the values for the concentration of total strontium, additional amounts of strontium are removed in this unit operation by sorption onto the precipitated $\text{Al}(\text{OH})_3$. The cumulative strontium DF for both the strontium coprecipitation and first KCCF unit operations is approximately 4900. The cesium DF for the first KCCF unit operation is 5000; thus, the ^{137}Cs concentration is about $1 \times 10^{-9} M$, or $12 \mu\text{Ci/L}$.

The characteristics of the solids collected at the conclusion of this unit of operation are summarized in Tables A.9 and A.10. Approximately 1 g of dry solids is accumulated from this unit

operation per liter of LLLW processed. The primary constituent of the solids is $\text{Al}(\text{OH})_3$. The 1-g quantity of dry solids is contaminated with approximately 1 mCi of ^{90}Sr and 100 mCi of ^{137}Cs . Because the wet weights are calculated on the basis of containing 90% entrained, treated LLLW, the same curie content is present in ten times greater solid mass.

A.6. Second KCCF Unit Operation. Additional radioactive cesium is removed from the processed LLLW by adding sufficient potassium ferrocyanide and cobalt nitrate to form 50 ppm of KCCF in the clarified waste from the first KCCF unit operation. Values presented in Tables A.11 and A.12 are similar to those appearing in Tables A.7 and A.8, except for the further reduction in total cesium concentration. With efficient solids removal, the cumulative cesium DF for the two KCCF strikes is 2×10^7 so that the ^{137}Cs concentration is approximately $4 \times 10^{-13} \text{ M}$, or 5 nCi/L.

A total of approximately 0.05 g of KCCF solids is generated per liter of LLLW treated in this unit operation (Table A.13). The dry-weight activities of the solids are 3.5×10^{-5} mCi per gram of ^{90}Sr and 0.35 mCi per gram of ^{137}Cs , as presented in Table A.14.

A.7. Composition of the Final Salt Cake. Two scenarios were considered in calculating the composition of the final salt cake that might result from the evaporation of the final LLLW stream exiting the second KCCF unit operation. Tables A.15 and A.16 summarize the characteristics of the salt cake, assuming that the nitrates have been removed from the LLLW. The denitrification unit operation has not been identified yet; therefore, the calculations of the mass of dry solids presented in this table do not include the mass of any alkaline or alkaline earth salts that will probably be formed during the denitrification process. Depending on the percentage composition of MVST supernate in the treated LLLW, the unidentified sodium salt could make up a significant portion of the final dried salt cake. Of the identified sodium salts, a partial dry weight of 115 g of solids is generated per liter of treated LLLW. Approximately 55% of this weight is comprised of

sodium sulfate and 40% is sodium bicarbonate. The dry-weight activities are 3.5×10^{-5} mCi and 4.5×10^{-8} mCi for ^{90}Sr and ^{137}Cs , respectively, per gram of dry solids.

Tables A.17 and A.18 summarize the chemical and radiochemical compositions of the final salt cake if the nitrates are not removed from the LLLW prior to evaporation. As illustrated in Table A.17, the contribution of sodium nitrate solids to the total mass of the salt cake is inconsequential if only NGLLLW is processed; however, the nitrate salts become the major constituent of the salt cake if MVST supernate is blended into the LLLW in significant portions. The total mass of the salt cake increases from 122 g to 377 g per liter of LLLW processed, depending on whether NGLLLW or MVST supernate is being treated. Most of the activity in the salt cake will be attributed to the ^{90}Sr content, averaging approximately 3×10^{-5} mCi/g. The ^{137}Cs activity is about three orders of magnitude lower.

A.7. Summary. Table A.19 presents an overview of the solids generated at the conclusion of each unit operation. Although the quantities quoted in the table are those calculated for the processing of 1 L of 100% NGLLLW, the values give an estimate of the relative size and composition of the solids generated from any blend of MVST supernate with NGLLLW. The solids generated by each unit operation represent a very small portion of the solids generated by the formation of the final salt cake. The solids generated from strontium coprecipitation and the first and second KCCF unit operations are 0.2, 1, and 0.05 g per liter of LLLW processed, respectively. The primary chemical components of each of these solids are calcium and strontium carbonate— $\text{Al}(\text{OH})_3$ and KCCF, respectively. Because the radioactivity is concentrated in a small mass of solids at the end of each unit operation, the activity per gram of solids appears quite high. The ^{90}Sr activity in the carbonate solids accumulated at the end of the strontium coprecipitation operation is 82 mCi/g. The $^{134,137}\text{Cs}$ activities in KCCF solids are 98 and 0.38 mCi/g for the first and second strikes, respectively.

The mass of the final salt cake is much greater than that of the solids generated during the flow sheet; however, the activity of the cake is significantly lower. The ^{90}Sr and $^{134,137}\text{Cs}$ activities are 3×10^{-5} and 4.4×10^{-8} mCi/g, respectively. The mass of the final salt cake can be reduced significantly if nitrates are removed before evaporation of the LLLW when treating 100% MVST supernate. The actual volume reduction will be dependent on the type of denitrification processing that is selected.

Appendix Reference:

A. G. Croff, *ORIGEN2--A Revised and Updated Version of the Oak Ridge Isotope Generation and Depletion Code*, ORNL-5621, Oak Ridge National Laboratory, March 1986.

Table A.1 Concentrations of major components in the LLLW feed to the proposed NGLLW flow-sheet components

Percent NGLLW	Percent conc. MVST supernate	[NaOH]	[Na ₂ CO ₃]	[NaNO ₃]	[NaCl]	[LiCl]	[KNO ₃]	[NaAlO ₂]
100	0	0.125	0.1	0.061	0.034	0.025	0	0.0117
95	5	0.134	0.104	0.311	0.039	0.024	0.016	0.0111
90	10	0.144	0.108	0.562	0.044	0.023	0.031	0.0105
80	20	0.163	0.116	1.063	0.053	0.020	0.062	0.0094
65	35	0.191	0.129	1.814	0.068	0.016	0.109	0.0076
50	50	0.219	0.141	2.566	0.082	0.013	0.156	0.0059
0	100	0.313	0.182	5.070	0.130	0	0.312	0.0000

Table A.2. Concentrations of minor components in the LLLW feed to the proposed NGLLLW flow sheet

Percent NGLLLW	Percent conc. MVST supernate	Concentration (mol/L)							Total [Cs] ^a	⁹⁰ Sr (Ci/L)	^{134,137} Cs (Ci/L)
		[Al(NO ₃) ₃]	[CaCO ₃]	[Zn(NO ₃) ₂]	Total [Sr]	[^{134,137} Cs]	Total [Cs] ^a	⁹⁰ Sr (Ci/L)			
100	0	0	0	0	1.60E-06	8.40E-06	2.52E-05	1.94E+01	9.95E-02		
95	5	3.25E-04	6.50E-06	6.50E-05	1.75E-06	8.01E-06	2.40E-05	1.84E-02	9.50E-02		
90	10	6.50E-04	1.30E-05	1.30E-04	1.90E-06	7.63E-06	2.29E-05	1.75E-02	9.04E-02		
80	20	1.30E-03	2.60E-05	2.60E-04	2.20E-06	6.85E-06	2.06E-05	1.56E-02	8.12E-02		
65	35	2.28E-03	4.55E-05	4.55E-04	2.65E-06	5.69E-06	1.71E-05	1.27E-02	6.75E-02		
50	50	3.25E-03	6.50E-05	6.50E-04	3.10E-06	4.53E-06	1.36E-05	9.83E-02	5.37E-02		
0	100	6.50E-03	1.30E-04	1.30E-03	4.60E-06	6.64E-07	2.00E-06	2.60E-04	7.87E-03		

^aThe ORIGEN code calculates the production of stable cesium concentration of two to three times greater than that of the ^{134,137}Cs concentration. The value of total cesium is calculated as a factor of 3 greater than the ^{134,137}Cs concentration present in the NGLLLW and the MVST supernate.

**Table A.3. Chemical composition of solids generated by
treating 1 L of LLLW with the strontium coprecipitation unit operation**

Solid	Dry weight (g)	% Dry weight	% Wet weight
CaCO ₃	0.100	42.70	4.27
SrCO ₃	0.084	36.01	3.60
Fe(OH) ₃	0.048	20.44	2.04
Polyacrylamide	0.002	0.85	0.09

**Table A.4. Radiochemical composition of the solids generated by
treating 1 L of LLLW with the strontium coprecipitation unit operation**

Percent NGLLLW	Percent conc. MVST supernate	⁹⁰ Sr activity (mCi/g, dry wt)	^{134,137} Cs activity (mCi/g, dry wt)	⁹⁰ Sr (mCi/g, wet wt) ^a	^{134,137} Cs (mCi/g, wet wt) ^a
100	0	82.36	0.834	8.24	0.083
95	5	78.30	0.795	7.83	0.080
90	10	74.23	0.757	7.42	0.076
80	20	66.11	0.680	6.61	0.068
65	35	53.92	0.565	5.39	0.056
50	50	41.73	0.450	4.17	0.045
0	100	1.10	0.065	0.11	0.007

^aThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A5. Concentrations of major components in 1 L of LLLW after pH adjustment unit operation

Percent NGLLLW	Percent conc. MVST supernate	H ₂ SO ₄ dilution factor	Concentration (mol/L)					
			[NaHCO ₃]	[NaNO ₃]	[NaCl]	[LiCl]	[KNO ₃]	[Na ₂ SO ₄]
100	0	1.04	0.096	0.059	0.033	0.024	0	0.108
95	5	1.04	0.100	0.298	0.037	0.023	0.015	0.114
90	10	1.05	0.103	0.537	0.042	0.022	0.030	0.120
80	20	1.05	0.111	1.011	0.051	0.019	0.059	0.133
65	35	1.06	0.122	1.713	0.064	0.015	0.103	0.151
50	50	1.07	0.132	2.405	0.077	0.012	0.146	0.169
0	100	1.09	0.167	4.644	0.119	0.000	0.286	0.227

Table A.6. Concentrations of minor components in LLLW after pH adjustment unit operation

Percent NGLLW	Percent conc. MVST supernate	[CaCO ₃]	[Zn(NO ₃) ₂]	[⁹⁰ Sr] (DF = 150)	Total [Sr] (DF = 150)	[^{134,137} Cs] (DF = 1)	Total [Cs] ^a (DF = 1)
100	0	0	0	1.07E-08	3.80E-06	8.40E-06	2.52E-05
95	5	6.23E-06	5.75E-05	1.01E-08	3.80E-06	8.31E-06	1.99E-05
90	10	1.24E-05	1.15E-04	9.61E-09	3.80E-06	8.22E-06	2.29E-05
80	20	2.47E-05	2.28E-04	8.56E-09	3.80E-06	8.05E-06	2.06E-05
65	35	4.30E-05	3.97E-04	6.98E-09	3.80E-06	7.78E-06	1.71E-05
50	50	6.09E-05	5.63E-04	5.40E-09	3.80E-06	7.52E-06	1.36E-05
0	100	1.19E-04	1.10E-03	1.39E-10	3.80E-06	6.63E-06	1.99E-06

^aThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A.7. Concentrations of major components in the LLLW after the first KCCF strike unit operation

Percent NGLLLW	Percent conc. MVST supernate	Concentration (mol/L)					
		[NaHCO ₃]	[NaNO ₃]	[NaCl]	[LiCl]	[KNO ₃]	[Na ₂ SO ₄]
100	0	0.096	0.059	0.033	0.024	0	0.108
95	5	0.100	0.298	0.037	0.023	0.015	0.114
90	10	0.167	4.644	0.119	0.000	0.286	0.227
80	20	0.111	1.011	0.051	0.019	0.059	0.133
65	35	0.122	1.713	0.064	0.015	0.103	0.151
50	50	0.132	2.405	0.077	0.012	0.146	0.169
0	100	0.167	4.644	0.119	0	0.286	0.227

Table A.8. Concentrations of minor components after the first KCCF unit operation

Percent NGLLW	Percent conc. MVST supernate	[CaCO ₃]	[Zn(NO ₃) ₂]	[⁹⁰ Sr] (Cum. DF = 4900)	[Sr] (Cum. DF = 4900)	[^{134,137} Cs] (DF = 5000)	Total [Cs] ^a (DF = 5000)
100	0	0	0	3.27E-10	1.16E-07	1.68E-09	5.04E-09
95	5	6.225E-06	6.23E-05	3.10E-10	1.16E-07	1.60E-09	4.81E-09
90	10	1.191E-04	1.19E-03	2.94E-10	1.16E-07	1.53E-09	4.58E-09
80	20	2.472E-05	2.47E-04	2.62E-10	1.16E-07	1.37E-09	4.11E-09
65	35	4.296E-05	4.30E-04	2.14E-10	1.16E-07	1.14E-09	3.42E-09
50	50	6.094E-05	6.09E-04	1.65E-10	1.16E-07	9.06E-10	2.72E-09
0	100	1.191E-04	1.19E-03	4.24E-12	1.16E-07	1.33E-10	3.98E-10

^aThe ORIGEN code calculates the production of stable cesium concentration as two to three times greater than that of ^{134,137}Cs concentration. The value of total cesium is calculated as a factor of 3 greater than the ^{134,137}Cs concentration present in the NGLLW and the MVST supernate.

Table A.9. Chemical composition of solids generated by the neutralization and the first KCCF unit operation

Percent NGLLLW	Percent conc. MVST supernate	Al(OH) ₃ (g)	KCCF (g)	Polymer (g)	Total dry solids (g)
100	0	0.913	0.100	2E-03	1.010
95	5	0.892	0.100	2E-03	0.994
90	10	0.872	0.100	2E-03	0.974
80	20	0.831	0.100	2E-03	0.933
65	35	0.771	0.100	2E-03	0.873
50	50	0.710	0.100	2E-03	0.812
0	100	0.507	0.100	2E-03	0.609

Table A.10. Radiochemical composition of solids generated by the neutralization and the first KCCF unit operation

Percent NGLLW	Percent concentration MVST supernate	Dry ⁹⁰ Sr activity (mCi/g solids)	Wet ⁹⁰ Sr activity ^a (mCi/g solids)	Dry ^{134,137} Cs (mCi/g solids)	Wet ^{134,137} Cs activity ^a (mCi/g solids)
100	0	1.23E-01	1.23E-02	9.80E+01	9.80
95	5	1.20E-01	1.20E-02	9.54E+01	9.54
90	10	1.16E-01	1.16E-02	9.27E+01	9.27
80	20	1.08E-01	1.08E-02	8.69E+01	8.69
65	35	9.38E-02	9.38E-03	7.72E+01	7.72
50	50	7.80E-02	7.80E-03	6.61E+01	6.61
0	100	2.75E-03	2.75E-04	1.28E+01	1.28

^aThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A.11. Concentrations of major components after the second KCCF unit operation

Percent NGLLLW	Percent conc. MVST supernate	Concentration (mol/L)					
		[NaHCO ₃]	[NaNO ₃]	[NaCl]	[LiCl]	[KNO ₃]	[Na ₂ SO ₄]
100	0	0.096	0.059	0.033	0.024	0	0.108
95	5	0.100	0.298	0.037	0.023	0.015	0.114
90	10	0.167	4.644	0.119	0.000	0.286	0.227
80	20	0.111	1.011	0.051	0.019	0.059	0.133
65	35	0.122	1.713	0.064	0.015	0.103	0.151
50	50	0.132	2.405	0.077	0.012	0.146	0.169
0	100	0.167	4.644	0.119	0	0.286	0.227

Table A.12. Concentrations of minor components after the second KCCF unit operation

Percent NGLLLW	Percent conc. MVST supernate	Concentration (mol/L)					
		[CaCO ₃]	[Zn(NO ₃) ₂]	[⁹⁰ Sr] (Cum. DF = 4900)	Total [Sr] (Cum. DF = 4900)	[^{134,137} Cs] (Cum. DF = 20,000,000)	Total [Cs] ^a (Cum. DF = 20,000,000)
100	0	0	0	3.27E-10	1.16E-07	4.20E-13	1.26E-12
95	5	6.2E-06	6.2E-05	3.10E-10	1.16E-07	4.01E-13	1.20E-12
90	10	1.2E-04	1.2E-03	2.94E-10	1.16E-07	3.81E-13	1.14E-12
80	20	2.5E-05	2.5E-04	2.62E-10	1.16E-07	3.43E-13	1.03E-12
65	35	4.3E-05	4.3E-04	2.14E-10	1.16E-07	2.85E-13	8.54E-13
50	50	6.1E-05	6.1E-04	1.65E-10	1.16E-07	2.27E-13	6.80E-13
0	100	1.2E-04	1.2E-03	4.24E-10	1.16E-07	3.32E-14	9.95E-14

^aThe ORIGEN code calculates the production of stable cesium concentration as two to three times greater than that of ^{134,137}Cs concentration. The value of total cesium is calculated as a factor of 3 greater than the ^{134,137}Cs concentration present in the NGLLLW and the MVST supernate.

**Table A.13. Chemical composition of solids generated from
the 1 L of LLLW remaining for the second KCCF strike unit operation**

Percent NGLLLW	Percent conc. MVST supernate	KCCF (g)	Polymer (g)	Total dry solids (g)
100	0	0.050	2.000E-03	5.200E-02
95	5	0.050	2.000E-03	5.200E-02
90	10	0.050	2.000E-03	5.200E-02
80	20	0.050	2.000E-03	5.200E-02
65	35	0.050	2.000E-03	5.200E-02
50	50	0.050	2.000E-03	5.200E-02
0	100	0.050	2.000E-03	5.200E-02

Table A.14. Radiochemical composition of solids generated from the 1 L of LLLW remaining for the second KCCF strike unit operation

Percent NGLLLW	Percent MVST supernate	Dry ⁹⁰ Sr activity (mCi/g solids)	Wet ⁹⁰ Sr activity ^a (mCi/g solids)	Dry ¹³⁷ Cs activity (mCi/g solids)	Wet ¹³⁷ Cs activity ^a (mCi/g solids)
100	0	3.61E-05	3.61E-06	3.83E-01	3.826E-02
95	5	3.43E-05	3.43E-06	3.65E-01	3.650E-02
90	10	3.26E-05	3.26E-06	3.47E-01	3.473E-02
80	20	2.90E-05	2.90E-06	3.12E-01	3.121E-02
65	35	2.37E-05	2.37E-06	2.59E-01	2.592E-02
50	50	1.83E-05	1.83E-06	2.06E-01	2.063E-02
0	100	4.84E-07	4.84E-08	3.00E-02	2.999E-03

^aThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A.15. Chemical composition of the salt cake generated by the evaporation of the 1 L of denitrified LLLW remaining at the end of the proposed NGLLLW flow sheet

Percent NGLLLW	Percent conc. MVST supernate	Na ₂ SO ₄ (g)	NaHCO ₃ (g)	NaCl (g)	LiCl (g)
100	0	65.7	49.3	1.70	0.89
95	5	64.2	47.6	1.96	0.85
90	10	62.6	45.9	2.23	0.80
80	20	59.6	42.5	2.77	0.71
65	35	55.0	37.4	3.58	0.58
50	50	50.4	32.3	4.38	0.45
0	100	35.2	15.3	7.07	0

Table A.16. Radiochemical composition of the salt cake generated by the evaporation of the 1 L of denitrified LLLW remaining at the end of the proposed NGLLLW flow sheet

Partial dry ^a solids (g)	Dry ⁹⁰ Sr activity (mCi/g solids)	Wet ⁹⁰ Sr activity ^b (mCi/g solids)	Dry ^{134,137} Cs activity (mCi/g solids)	Wet ^{134,137} Cs activity ^b (mCi/g solids)
1.18E+02	3.67E-05	3.67E-06	4.57E-08	4.57E-09
15E+02	3.58E-05	3.58E-06	4.48E-08	4.48E-09
1.12E+02	3.48E-05	3.48E-06	4.38E-08	4.38E-09
1.06E+02	3.28E-05	3.28E-06	4.16E-08	4.16E-09
9.66E+01	2.92E-05	2.92E-06	3.77E-08	3.77E-09
8.76E+01	2.49E-05	2.49E-06	3.31E-08	3.31E-09
5.76E+01	1.00E-06	1.00E-07	7.33E-09	7.33E-10

^aThe denitrification unit operation has not been defined as yet. The calculation of the mass of dry solids of the denitrified LLLW, therefore, does not include the mass of any alkaline or alkaline-earth salts that probably will be generated by a denitrification process.

^bThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A.17. Chemical composition of the salt cake generated from the evaporation of LLLW remaining at the end of the proposed NGLLLW flow sheet (nitrate salts present)

Percent NGLLLW	Percent conc. MVST supernate	Percent								Total dry solids (g)
		Na ₂ SO ₄ (g)	NaHCO ₃ (g)	NaCl (g)	LiCl (g)	KNO ₃ (g)	NaNO ₃ (g)	Zn(NO ₃) ₂ (g)		
100	0	65.7	49.3	1.7	0.89	0	4.42	0	122	
95	5	63.8	47.4	1.9	0.85	1.13	19.7	0.006	135	
90	10	61.8	45.6	2.1	0.8	2.26	35.0	0.012	147	
80	20	58.0	41.8	2.4	0.71	4.53	65.5	0.024	173	
65	35	52.2	36.2	3.0	0.58	7.93	111.3	0.042	211	
50	50	46.4	30.5	3.6	0.45	11.3	157.1	0.060	249	
0	100	27.1	11.8	5.4	0	22.6	309.7	0.119	377	

Table A.18. Radiochemical composition of the salt cake generated by the evaporation of 1 L of LLLW remaining at the end of the proposed NGLLLW flow sheet (nitrate salts present)

Percent NGLLLW	Percent conc. MVST supernate	Dry ⁹⁰ Sr activity (mCi/g, solids)	Wet ⁹⁰ Sr activity (mCi/g, solids)	Dry ^{134,137} Cs activity (mCi/g, solids) ^a	Wet ^{134,137} Cs activity (mCi/g, solids) ^a
100	0	3.53E-05	3.53E-06	4.41E-08	4.41E-09
95	5	3.04E-05	3.04E-06	3.80E-08	3.80E-09
90	10	2.63E-05	2.63E-06	3.30E-08	3.30E-09
80	20	2.00E-05	2.00E-06	2.53E-08	2.53E-09
65	35	1.34E-05	1.34E-06	1.71E-08	1.71E-09
50	50	8.76E-06	8.76E-07	1.14E-08	1.14E-09
0	100	1.53E-07	1.53E-08	8.61E-10	8.61E-11

^aThe wet-nuclide activities are based on the assumption that the solids are present as a slurry containing 90% entrained LLLW.

Table A.19. Summary of solid wastes generated in the proposed NGLLLW flow sheet

Unit operation	Mass of dry solids generated (g/L NGLLLW)	Major chemical component of dry solid	⁹⁰ Sr activity (mCi/g dry wt)	^{134,137} Cs activity (mCi/g dry wt)
Strontium coprecipitation	0.2	CaCO ₃ , SrCO ₃	82	0.083
Neutralization and first KCCF strike	1.0	Al(OH) ₃	0.12	98
Second KCCF strike	0.05	KCCF	3.6E-05	0.38
Final salt cake containing nitrates	122	Na ₂ SO ₄ , NaHCO ₃	3.5E-05	4.4E-08
Denitrified final salt cake	188 ^a	Na ₂ SO ₄ , NaHCO ₃	3.6E-05	4.6E-08

^aBecause the denitrification process has not been defined, this value does not include the mass of secondary waste that might be generated from the addition of chemicals required to denitrify the NGLLLW.

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