Direct Grout Stabilization of High Cesium Salt Waste: Salt Alternative Phase III Feasibility Study

by

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**DIRECT GROUT STABILIZATION OF HIGH CESIUM SALT WASTE:
SALT WASTE ALTERNATIVE PHASE III FEASIBILITY STUDY (U)**

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SUMMARY

The direct grout alternative is a viable option for treatment/stabilization and disposal of salt waste containing Cs-137 concentrations of 1-3 Ci/gal.

The composition of the direct grout salt solution is higher in sodium salts and contains up to a few hundred ppm Cs-137 more than the current reference salt solution. However it is still similar to the composition of the current reference salt solution. Consequently, the processing, setting, and leaching properties (including TCLP for Cr and Hg) of the direct grout and current saltstone waste forms are very similar.

The significant difference between these waste solutions is that the high cesium salt solution will contain between 1 and 3 Curies of Cs-137 per gallon compared to a negligible amount in the current salt solution. This difference will require special engineering and shielding for a direct grout processing facility and disposal units to achieve acceptable radiation exposure conditions. The Cs-137 concentration in the direct grout salt solution will also affect the long-term curing temperature of the waste form since 4.84 Watts of energy are generated per 1000 Ci of Cs-137. The temperature rise of the direct grout during long-term curing has been calculated by A. Shaddy, SRTC.¹

The effect of curing temperature on the strength, leaching and physical durability of the direct grout saltstone is described in this report. At the present time, long term curing at 90°C appears to be unacceptable because of cracking which will affect the structural integrity as evaluated in the immersion test. (The experiments conducted in this feasibility study do not address the effect of cracking on leaching of contaminants other than Cr, Hg, and Cs.) No cracking of the direct grout or reference saltstone waste forms was observed for samples cured at 70°C.

At the present time the implications of waste form cracking at elevated curing temperatures has not been fully addressed. The direct grout falls within the definition of NRC Class C waste. NRC requires that Class C waste forms or their containers demonstrate structural integrity to qualify for disposal. Direct grout cured at 90° C will not meet the integrity requirement. However, the disposal vault may meet this requirement.

BACKGROUND

Direct disposal of the cesium in grout is one of the alternatives identified in WSRC-RP-98-00166.² In this proposed process, Cs-137 is not separated from the salt waste or concentrated supernate. It is instead sent to the new shielded Saltstone Facility. The resulting waste form would be classified as Class C low-level waste if disposal was regulated by the NRC. A new grout production facility is needed for this option. The new facility requires remote maintenance capabilities and a shielded cell for the grout production equipment. The test plan for this effort is presented elsewhere.³

Comparison of Reference Z-Area Salt Solution and High-Cesium salt Solution

The average composition of the direct grout salt solution is listed in Table 1 and compared to the current reference salt solution composition. The average cesium concentration in the direct grout waste stream is estimated to be $1.65\text{E-}4\text{M}$ (1.5 Ci/gal).⁴ This waste and the resulting direct grout waste form which has about 40 % less curies per volume (about 250 Ci/cubic meter of saltstone) due to dilution with the cementing reagents fall within the NRC Class C waste category. The Cs-137 concentration limit for Class C waste is 4600 curies per cubic meter.⁵

Table 1. Compositions of the Reference Salt Solution and the Direct Grout, High Cesium Salt Solution.^{4,6}

Component	Reference Salt Solution (Molar)	Direct Grout High Cesium Salt Solution (Molar)
NO_3^-	2.04	2.49
NO_2^-	0.62	0.581
OH^-	1.17	2.181
CO_3^{2-}	0.15	0.181
AlO^{2-}	0.41	0.355
SO_4^{2-}	0.15	0.169
F^-	0.0015	0.0361
Cl^-	0.023	0.0282
$\text{C}_2\text{O}_4^{2-}$	0.025	0.0136
PO_4^{2-}	0.01	0.009
Na^+	4.94	6.44
K^+	-	0.0168
Cs^+	20 n Ci/g	0.000165
Hg	0.012 mg/L	33 mg/L
Cr	161 mg/L	161 mg/L

Class C Requirements for Low-Level Waste Disposal⁷

In addition to the minimum requirements for Class A, B, and C wastes, NRC has structural stability requirements for Class B and C waste.⁷ Stability requires that the waste form maintains its structural integrity under the expected disposal conditions. Structural stability is necessary to inhibit a) slumping, collapse, or other structural failure of the disposal unit if an engineered structure is not used and b) radionuclide release from the waste form that might ensue due to increases in leaching that could be caused by premature disintegration of the waste form. Stability is also considered in the intruder pathways where it is assumed that wastes are recognizable after the active control period. To the extent practical, Class B and C waste forms should maintain gross physical properties and identity over a 300 year period. To ensure that Class B and C wastes maintain stability the following conditions should be met:

- The waste should be a solid form or in a container or structure that provides stability after disposal.
- The waste should not contain free standing and/or corrosive liquids.
- The waste or container should be resistant to degradation caused by radiation effects.
- The waste or container should be resistant to biodegradation.
- The waste or container should remain stable under the compressive loads inherent in the disposal environment.
- The waste or container should remain stable if exposed to moisture or water after disposal.
- The as-generated waste should be compatible with the solidification medium or container.

NRC identifies the following tests, which can be used to demonstrate waste form stability:

- Compressive strength; ASTM C-39 (60 psi minimum).
- Resistance to thermal cycling degradation; ASTM B-553.
- Radiation stability at 10E+8 Rads in gamma irradiator or equivalent.
- Resistance to biodegradation; ASTM G-21 and G-22.
- Leach testing; ANS 16.1 (Cs leach index minimum of 6).
- Immersion testing, i. e., compressive strength after 90 day immersion period should be 500 psi minimum and not less than 75 % of the pre-immersion compressive strength.
- Free standing liquids (less than 0.5 volume per cent per Method described in Appendix 2 of ANSI/ANS 55.1).
- Full-scale testing.

EXPERIMENTAL METHOD

Preparation of the Reference Salt Solution and Direct Grout, High Cesium Salt Solution⁸

Simulated salt solution was made according to the following recipes. Cesium, mercury and chromium were spiked in amounts greater than the concentrations listed in Table 1 in order to determine differences between leaching performance in the various leaching tests. This was necessary given the detection level for non radioactive cesium used in these experiments.

Table 2. Ingredients in the Reference Salt Solution and the Direct Grout, High Cesium Salt Solution.

Ingredient	Reference Salt Solution (g/L)	Direct Grout High Cesium Salt Solution (g/L)
NaNO ₃	173.4	211.6
NaNO ₂	43.1	40.09
NaOH	46.7	87.24
Na ₂ CO ₃ H ₂ O	18.5	22.44
NaAlO ₂ H ₂ O	40.6	34.48
Na ₂ SO ₄	20.9	24.00
NaF	0.62	1.52
NaCl	1.35	1.65
Na ₂ C ₂ O ₄	3.44	1.82
Na ₃ PO ₄	2.9	-
Na ₂ PO ₄ 12H ₂ O	-	3.42
KNO ₃	-	1.69
CsNO ₃	-	0.643*
HgCl ₂	0.338**	0.338**
Na ₂ CrO ₄	0.623 ***	0.623***

* Cs spiked at 0.0033 M Cs using CsNO₃. This is 20 times more than the concentration projected for the direct grout case.

** Hg spiked at 250 ppm as HgCl₂ in direct grout solution prepared for this feasibility study.

*** Cr spiked at 1830 mg/L as Na₂CrO₄.

Preparation of Reference Saltstone and High Cesium, Direct Grout

The ingredients and proportions in the reference saltstone are shown below:

Cement Type I/II	4 wt %
Fly ash Class F	25 wt %
Slag Grade 120	25 wt %
Salt solution	46 wt %
(containing 71 wt % water)	

The water to total cementitious solids of this mixture is 0.6048.

The ingredients and proportions used in the direct grout saltstone containing the high cesium loading are shown below. The water to the total cementitious solids ratio is 0.6092 and is similar to that of the reference saltstone.

Cement Type I	4	wt %
Fly ash Class F	24	wt %
Slag Grade 120	24	wt %
Salt solution	48	wt %
(containing 66 wt. % water)		

The dry cementitious reagents were premixed to simulate the Z-Area process and then added to the salt solution. Mixing was carried out in a Waring blender for one minute at low speed. Samples were immediately cast into the appropriate containers for the various tests.

Testing

The approach was to compare the high-cesium, direct grout to reference saltstone with respect to the following properties:

- Set time

- Bleed water

- Processing (flowability of grout –subjective evaluation)

- Compressive strength (28 days)

- Leaching

 - TCLP for Cr, Hg, Cs

- Radiolytic gas generation

- Durability Evaluation (limited testing modified ANS 16.1 soak test).

Curing

The curing was conducted at ambient temperature, 45°, 70° and 90° C +/-5° C and 100 % relative humidity. This curing range is representative of the range of initial and long-term curing temperatures which could be encountered under actual field conditions.

Irradiation Experiments

Two samples of direct grout were cast in cylindrical containers approximately 1 x 4 inches in size. These containers were sealed during the 28-day cure period. One sample was cured at 24.5° C and the other at 90° C. The moisture contents of these samples were measured to be 24 and 27 wt. %, respectively. The porosity of each sample was estimated to be 30 to 40 volume percent. These two samples were irradiated simultaneously at a dose rate of 4.2 E+5 rad/hour for 185 hours in a Co-60 source. The dose accumulated in the 185 hr irradiation experiment is equivalent to an approximate 34 year dose at a nominal Cs-137 curie loading of 250 Ci/m³. Given the nominal density of the direct grout, 1617 kg/m³, this corresponds to 7.242 E-4 Watts/kg, or a dose rate of 261 rad/hr. Experimental details pertaining to the Co-60 irradiation, gas analyses, and dose calculations are given elsewhere.⁹

RESULTS AND DISCUSSION

Processability, Set Time and Bleed Water

Processability was evaluated by visual observation. The direct grout slurry was compared to the reference saltstone slurry. The direct grout slurry was easily mixed in the Waring blender. The resulting slurry was fluid and was easily poured into the sample containers. The direct grout gelled (thickened to the extent that it was no longer pourable) in 25 to 30 minutes. The reference saltstone slurry was also very fluid and pourable. However, it gelled in 20 to 25 minutes. Bleed water was not observed on either slurry formulation. Processing results are summarized in Table 3.

Table 3. Processing results for Reference Saltstone and Direct Grout.

Mix Design	Qualitative Flow Properties	Gel Time (minutes)	Bleed Water (volume %)	Set Time (hours)
Reference Saltstone	Very Fluid, Pourable	20-25	0	18-24
Direct Grout	Very Fluid, Pourable	25-30	0	18-24

Compressive Strength

Compressive strength was determined for samples cured for 28 days at 24.5, 45, 70, and 90⁰ C. The relative humidity of all of the samples except those cured at 90⁰ C was maintained at 100 %. The samples cured at 90⁰ C were cured in the presence of excess water/water vapor. However, cracks were observed on these samples when they were removed from the curing chamber. See Figure 1. These samples also appeared dry on the outer surface. This was confirmed when the samples were examined after the compressive strength tests. The outer centimeter of the samples was obviously drier than the inner core.

Consequently the 90⁰ C samples experienced some drying. Drying shrinkage is probably not the only explanation for the observed cracks since other samples cured at 90⁰ C in sealed containers showed no drying and were also found to be cracked after curing.

Even though the direct grout and reference saltstone 90⁰ C samples were cracked prior to the strength determinations the strengths were very high. Given the limited number of samples tested, the strengths of the direct grout and reference saltstone are similar for each curing temperature. Compressive strength results are summarized in Table 4.

Figure 1. Photographs Illustrating the Crack Patterns Characteristic of Reference and Direct-Grout Sample Cured at 90 °C (No cracking was observed for samples cured Between Room Temp. and 70 °C).

Table 4. Compressive Strength Results for Direct Grout and Reference Saltstone

Mix Design	Curing Temperature (°C)	Compressive Strength (psi)	Average Compressive Strength (psi)
Direct Grout	24.5	2,050	2,212
		2,375	
	45	4,000	4,075
		4,150	
	70	3,250	3,412
		3,575	
	90	4,675	4,562
		4,450	
Reference Saltstone	24.5	2,225	2,325
		2,425	
	45	3,575	3,525
		3,475	
	70	3,875	3,675
		3,475	
	90	4,250	3,925
		3,600	

Leaching**TCLP**

Samples were prepared for TCLP testing for Cr and Hg, which are the two potentially hazardous constituents in both the high cesium (direct grout) and reference salt solutions. All samples of reference saltstone and direct grout cured between 24 and 90° C passed the TCLP for Cr and Hg. Consequently, these waste forms qualify to exit RCRA.

The TCLP extract was also analyzed for Cs to give a relative comparison of the Cs leachability for the two formulations. The direct grout samples were spiked with about 20 times more cesium than is actually expected (1.5 Ci/gal Cs-137) to assure detection above the reportable limit in the TCLP extracts since the objective was to evaluate the effect of curing temperature on cesium leachability. Based on the total cesium concentration in the direct grout samples (150 ug/g) between 11 and 16 % of the cesium was leached during the 18 hour TCLP test on crushed samples. This is consistent with the limited retention of cesium in the reference saltstone as modeled in the Z-Area performance assessment ($K_d = 2$ for Cs).¹⁰

Table 5. TCLP Results for Direct Grout and Reference Saltstone Cured between 24 and 90°C.

Sample Description	Sample ID	Curing Temperature (°C)	TCLP Results		
			Cr (ug/L)	Hg (mg/L)	Cs (ug/L)
Reference Saltstone	980072A	24.5	< 60	< 0.020	< 40
	98L45B	45	< 60	< 0.020	< 40
	980067A	70	< 60	< 0.020	< 40
	980066A	90	< 60	< 0.020	< 40
Direct Grout	980071A	24.5	< 60	< 0.020	1150
	98SL45A	45	< 60	< 0.020	932
	980068A	70	< 60	< 0.020	807
	980069A	90	< 60	< 0.020	882
TCLP Regulatory Limit*			5000 (5 mg/L)	0.2	NA

* Limit for disposal of treated characteristic waste.

Radiolytic Gas Generation

Two samples (approximately 65g each) of direct grout were irradiated in an air sealed systems containing approximately 55 cc of air. Details of the experimental configuration are given elsewhere.⁸ Preliminary analysis of the gas collected above the irradiated direct grout samples indicates that hydrogen was produced with a G value of 0.02 to 0.03 molecules per 100 eV. These G values are based on the total mass of grout irradiated

(grout plus moisture). Given a nominal moisture content of about 25 wt. %, a $G(H_2)$ based on water alone was calculated to be in the range of 0.08 to 0.12. These G values are significantly lower than the maximum value obtained from pure water, 0.45. Similar results were obtained for dry CST powder irradiation experiments.⁸

Hydrogen concentrations in air of 4 % or more constitute a flammable mixture. Assuming that the direct grout disposed of in the new saltstone vaults will not constitute a closed system (the grout and the concrete vault have open, interconnected porosity), the radiolytic gas production is not expected to result in accumulation of hydrogen in the pores of the saltstone or the air void spaces in the vault.

In addition, visual observation of the samples after irradiation to a 34 year dose indicated no degradation or cracking. However, a difference in the gas pressure versus irradiation time profiles was observed for the direct grout samples cured at 24° and 90° C. Direct grout cured at 24° C showed a linear increase in pressure as a function of irradiation time. A G value for the total gas produced was similar to the G value for hydrogen (0.01 and 0.02, respectively). Direct grout cured at 90°C showed an initial depressurization followed by a linear increase in pressure. This is similar to the profile observed with CST irradiation.⁹ Although the $G(H_2)$ was similar for the two samples, the sample cured at 90° C resulted in more total gas generation. A G value for the total gas produced was higher than the G value for hydrogen (0.07 and 0.03, respectively). This indicates that there was radiolytic production of gas other than hydrogen in the direct grout sample cured at 90° C.

Phase Determination

X-ray diffraction analyses of specimens cured over the entire temperature range indicate the presence of poorly crystalline hydrotalcite, a hydrated magnesium silicate phase characteristic of hydrated slag systems. Gypsum, a hydrated calcium sulfate phase was also detected in all of the samples. The current analysis did not indicate any phase differences over the temperature range studied.

Immersion Test (Durability/Integrity Evaluation)

An immersion test to evaluate structural integrity is in progress. Samples cured at 24.5, 45, 70 and 90°C are currently immersed in deionized water. These samples will be soaked for 90 days and then the compressive strength will be measured. To date, the only type of data available are the result of visual observations. Cracking was observed in the samples cured at 90°C at the time the samples were removed from the molds. Samples cured at 70°C and lower did not show any signs of cracking. See Figure 2. All of these samples were cured in sealed containers and did not experience significant drying. Consequently, the cracking observed in the direct grout and reference saltstone samples cured at 90°C is probably caused by a mechanism other than external drying. Crystallization of soluble or insoluble phases within the matrices of these samples is one possible explanation. However, additional studies are required to understand the cause of the cracking.

Figure 2. Effect of Curing Temperature on the Reference Saltstone and Direct-Grout Samples Prepared for Immersion Testing (All Samples Were Cured in Sealed Containers). Cracks Were Observed in the 90 C Samples at the Time of De-Molding. No Cracks Were Observed in the Other Samples.

CONCLUSIONS

Salt solution containing up to 6.4 M sodium salts and an average Cs-137 concentration of 1.5 Ci/gal can be stabilized in a saltstone waste form. Based on the results of this feasibility study and the current understanding of the effect of curing temperatures on long term properties, no formulation change is required. This statement assumes that pouring strategies,¹ raw materials temperatures and specifications, and Cs-137 and other radionuclide concentrations will be managed to maintain curing temperatures below 90°C. Based on the data available to date, the temperature threshold for cracking is between 70 and 90° C.

Direct grout made from 6.4 M sodium salt solution containing 1830 and 250 mg/L of Cr and Hg, respectively, were determined to be non hazardous based on the TCLP test. The direct grout saltstone has processing properties similar to those of the current saltstone waste form (except for the additional shielding and remote handling required for the higher activity in the high cesium waste).

Based on results obtained in this feasibility study, hydrogen gas generation due to radiolysis of the free water in the saltstone will not result in the accumulation of hydrogen above the explosive limit since the waste form is monolithic and there is no void space inside the closed vaults. In addition, migration of hydrogen gas through the waste form pore spaces is not expected to damage the microstructure of the saltstone since the pore space is interconnected.

Most of the cracking observed in samples cured at 90°C is attributed to drying shrinkage due to water evaporation. However, at least one other mechanism may be present since samples cured in sealed containers also cracked (to a lesser degree). The compressive strengths of the direct grout and reference saltstone cured at 90°C were high in spite of the cracking observed in the samples. This indicates that although the cracks were formed, they did not open. However, the cracks in the 90°C samples are opening in the immersion test, which requires a 90-day soak in deionized water. Depending on the results of this test, the direct grout and reference saltstone cured at 90°C for long term (28 days) may not pass the immersion test which is intended to indicate structural integrity/durability. In the present analysis, there are two options for addressing the results of the immersion test, 1) cure direct grout and saltstone below 90°C (samples cured at 70°C showed no cracking) or 2) take credit for the structural integrity of the vault (waste form container).

RECOMMENDATIONS

Long-term curing experiments of reference saltstone and direct grout as a function of curing temperature are recommended if direct disposal of grout is selected as the preferred or backup technology to replace the current ITP process. This recommendation is consistent with the direct grout feasibility evaluation and the SRTC technical program evaluation conducted by BNFL. (See Attachment for the BNFL comments.)

Leaching experiments on direct grout cured over the temperature range 24 to 90° C is also recommended.

Additional irradiation and gas collection/analysis experiments should be conducted to further investigate the affect of curing temperature on the direct grout performance.

Regulatory and performance requirements for direct grout should be determined.

Production and pouring strategies should be developed to meet the regulatory and performance requirements.

Tests should be conducted to determine the effect of changes in the salt composition on the properties of the direct grout in order to establish acceptable operating ranges.

Based on the results of this feasibility study, the current saltstone formulation range is adequate for the direct grout. However, if the short term curing temperature cannot be managed by applying a multi-cell pour strategy, then substituting granulated slag for Grade 120 slag should be evaluated. The simplest way to control the long term curing temperature is to adjust the curie content of the waste/waste form if long-term curing is an issue.

QUALITY ASSURANCE

Results are recorded in WSRC-NB-98-00204. Testing was conducted in accordance with SRTC procedures.

REFERENCES

1. A. Shadday, "Thermal Modeling of the Saltstone Pouring and Curing Process," (U), M-CLC-A-00144, 9-22-98.
2. P. L. Rutland, et al., "Bases, Assumptions, and Results of the Flowsheet Calculations for the Initial Eighteen Salt Disposition Alternatives," WSRC-RP-98-00166, June 15, 1998.
3. C. A. Langton, "Phase IV Test Plan for Direct Grout" (U), SRT-WED-98-0114, 8-31-98.
4. D. D. Walker, E-Mail correspondence, 7-27-98.
5. CFR Part 61.55.
6. D. D. Walker, E-Mail correspondence, 7-29-98.
7. CFR Part 61.56.
8. D. D. Walker, E-Mail correspondence, 9-24-98.
9. N. E. Bibler and C. L. Crawford, and C. R. Biddle, "Results of Scoping Studies for Determining Radiolytic Hydrogen Production from Moist CST and CST Slurries," WSRC-RP-98-01143, 10-2-98.
10. Martin Marietta Energy Systems, Inc., "Radiological Performance Assessment for the Z-Area Saltstone Disposal Facility" (U), WSRC-RP-92-1360, 12-18-92.

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D. D. Walker, SRTC, and J. R. Fowler provided the high-caesium salt waste composition used to prepare the direct grout formulation.

C. Crawford and N. Bibler, and C. Biddle, SRTC/ITS, conducted irradiation experiments and provided the analysis to the gas generation rate.

L. Tovo, SRTC/ADS, and B. T. Butcher, SRTC/WPT expedited analytical analyses.

ATTACHMENT I

BNFL Response to Questions and SRTC Program Review

Memorandum

To: SRTC

Date: 22 September 1998

From: Graham Jonsson
Ext: +44 19467 72477
Fax: +44 19467 72490

Your ref:
Our ref: CEM/98/51065

Subject: Saltstone Immobilisation Programme

To all at SRTC

SALTSTONE IMMOBILISATION PROGRAMME

This note details comments made by BNFL regarding initial questions raised by SRTC. With respect to the Saltstone immobilisation programme (Section 1), and then in Section 2 a review of the proposed SRTC development programme is given.

SECTION 1

Q1: Does the Saltstone formulation require changing based on the inclusion of the Cs in order to meet TCLP requirements ?

A1: The inclusion of Cs into the wasteform on its own should not affect the leachability of the metals in the TCLP test. Given that the TCLP test would be performed after 28 days, it is very unlikely that the higher overall temperature of the Saltstone monolith will have any effect on metal solubilities. However the longer term effects of the elevated temperatures on metal retention within the system should be part of the forward programme as it is outside of the current scope of experience.

Although this is different to the TCLP test (i.e. a test that is undertaken after 28 days) it is none the less important that the chemistry of the system is understood to predict longer term behaviour. It is also important to realise that in the TCLP test, the sample is actually ground and therefore monolithicity is not a factor. It is the actual effects of heat upon the overall cement system that is the major point to establish.

Q2: If the formulation does need changing to meet TCLP would this be adequate, or would an alternative additive be required ?

22 September 1998

A2 : As stated in Answer 1 it is not certain how the microstructure will be affected by being exposed to high temperatures (greater than 80°C) over extended periods of time. It is not considered that the ability to comply with the TCLP requirements will be affected. If overall radiogenic heat is seen as problematic the simplest alternative may be to just limit the amount of Cs present in the waste. Alternatively different cement systems can be evaluated for suitability.

Q3:What would the bulk temperature rise to based on the heat of hydration, and would the pouring volume need to be limited because of this ?

A3:Information provided by SRTC is now being used by modellers to predict the bulk temperature rise.

Q4:What effect will the higher Cs loading have on the bulk temperatures in the long term ?

A4 : The Cs loading will govern the bulk temperature within the matrix, with overall temperature increasing as the Cs loading increases. Initial results from modelling experiments at SRTC indicate that the bulk temperatures will be around 90°C. This can be substantiated by additional modelling studies in the U.K.

Q5:If curing heat or radiolytic heat is a concern how would we address ?

A5:This can be done by limiting the amount of Cs within the product, changing the cement formulation or considering an alternative matrix.

Q6:Will gas generation be a concern and if so how will it be addressed ?

A6: The porosity and permeability of the cement microstructure will be sufficient to deal with gas generated from any associated reactions. However this will need to be checked during the development programme to establish the effects at the elevated temperatures.

Q7:What tests would be required to demonstrate short and longer term gas generation will not be a problem ?

A7: The sample will need to be exposed to the expected radiation dose that it would need to withstand in order to retain product integrity. Whereas in the U.K. wasteforms are exposed to the cumulative dose that they would experience during up to 100 years' storage and disposal, the actual dose that the Saltstone wasteform will need to withstand will be specific to the waste acceptance criteria (WAC) governing disposal.

Section 2 : Proposed SRTC development programme

Set :

This is normally undertaken to establish throughput requirements for batch plants. As the proposed process is continuous mixing followed by pumping and placement, setting is only important if severe retardation is observed, or if set is achieved too quickly. The latter point may be particularly important if the mix were to be delayed on line to the disposal facility. This could result in blocked pipework and the inherent problems of dealing with remediation where the radiation levels will be significantly higher for manual intervention. Time of set will also need to be established during the pouring stage to establish the effects of pouring additional cemented products on material that may have only undergone partial setting. This can lead to cracking and loss of product integrity.

Bleed water :

Again bleed water is normally associated with plant throughput requirements, although the avoidance of the generation of secondary wastes is also of major importance. Ideally the formulation should provide a bleed free product, however at what time bleed water must not be present will be very specific to this particular project.

Processing :

The proposal is to have a subjective test. Experience in the U.K. indicates that this kind of evaluation is not suitable, and it is suggested that actual methods to evaluate grout processability / fluidity are established.

Compressive strength :

While the test indicates that the test will be undertaken after 28 days, it is recommended that a strength development profile is undertaken. This will allow a prediction to be made of any potential interactions taking place within the matrix. It may also be beneficial to undertake these measurements over longer periods so that the longer term strength development profile can be monitored.

There are also non-destructive tests that can be performed to monitor strength development as opposed to compressive strength.

Leaching :

The standard test is to undertake the TCLP test after 28 days. It is recommended that additional testing is undertaken to establish any likely effects of the higher heat loading on the overall cement microstructure.

Radiolytic gas generation:

The wasteform needs to be exposed to the cumulative radiation dose that the wasteform will experience during the evaluation period. This will not only establish the effects of radiation on the wasteform stability, but can also be used to establish the effects (if any) of dealing with any gas generated upon the cement microstructure.

The curing temperatures will need to reflect the actual core temperatures which the matrix will experience and therefore any tests will need to be able to reflect these temperatures as opposed to simply curing at the temperature under assessment.

General comments:

The overall programme is focussed mainly on passing the necessary WAC. However as this wastestream composition is now fundamentally different to the original Saltstone, it is considered that additional testing would be beneficial in understanding the ongoing cement/waste interactions taking place.

The programme does not indicate any timescales for the test period.

The surrogate needs to be prepared in as near as possible the same way as the waste will be produced during future operations.

The programme appears to be focussed upon dealing with a worst case scenario. It may be beneficial to consider a range of formulations to understand any changes occurring as formulations change.

In terms of the actual process, I have assumed that the relevant operating envelopes and equipment deployed and established for the original plant will still be used in the new facility and are therefore outside the scope of these comments.

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**WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER**

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