SALTCRETE FORMULATION

September 28, 1994

Prepared by:
J. M. Connell
S. C. Jorgensen

Edited by:
G. B. Semones

E. C. Garcia, Project Manager

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

870

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Executive Summary

This is an addendum to the report entitled "Saltcrete Evaluation", dated August 16, 1993.

The information gathered since the first report shows that the currently generated waste and most of the waste in inventory has low concentrations of hazardous chemicals and is certifiable for disposable. This is based on preliminary analyses. Sampling and analysis for the purpose of gathering the legally defensible data required for certification and permanent disposal is in progress.

The main technical issue is the expansion of the waste form. Some of the cemented waste expands and damages the containers. According to a petrology study, the expansion is caused by the formation of darapskite, a nitrate-sulfate salt. Darapskite occurs when there is high porosity causing microfractures and waste form expansion. The study showed that the concentration of darapskite was as high as 22 percent by weight (wt%) and that the concentration varied significantly within a single waste form. The variation may be the reason that most container damage occurred on one end only (damage occurred to all sides of some containers). It is also an indication that the saltcrete is not always well-mixed. It was found that after the initial expansion of one to two inches expansion, expansion is insignificant.

Expansion and its problems can be minimized but not eliminated completely. Reducing the waste loading to 30 wt% from 35 wt%, placing 2-inch spacers in each end of the crates, mixing the paste well, accurately weighing the components (brine, salt, and cement) will reduce the expansion or in the case of the spacers, reduce the damage to the container.

Since the earlier report, the load cells that are used to weigh the components have been calibrated to improve and control the accuracy of the additions. The appropriate amount of each component is calculated by measuring the specific gravity of the brine and then calculating the solids content of the brine.

A formulation of 30 wt% (maximum) water, 30 wt% (maximum) salt, and 48 wt% (maximum) cement/flyash blend is recommended. A blend of either three parts type I/II Portland cement one part Class F flyash or pure type I/II Portland cement is suitable. Section 6 describes the formulation and how to mix it in more detail. A key concept in the mixing recommendation is to add the maximum allowable amount of salt and water to the mixture, then to add cement powder until the limits of the mixing equipment are reached. If this method were adopted, the waste loading would never exceed 30 wt% and the amount of unreacted water would be minimized.

Since the constituents in the waste will change over time, methods to test other possible formulations are provided in a separate report issued concurrently. A maintenance work package was initiated to use two brine feed tanks, each of which can be isolated. In this way, a few tests can be performed to determine whether the formulation recommended in this report is compatible with a given tank of brine.

There are also recommendations to improve documentation of the process and the measurement of the process parameters.

TABLE OF CONTENTS

	Executive summary.	i
1.0	Introduction.	1-1
2.0	Process Characterization.	2-1
2.1	Chemical Analysis.	2-1
2.2	Petrology.	2-16
2.3	Time-of-Set.	2-17
2.4	Freeze/thaw cycling.	2-22
2.5	Instrumentation.	2-23
2.6	Measurement of Expansion.	2-24
3.0	Formulation.	3-1
3.1	Operating Envelope, Lab-Scale.	3-1
3.2	Operating Envelope, Full-Scale.	3-3
4.0	Conclusions and Recommendations.	4-1
5.0	References.	5-1

LIST OF TABLES AND FIGURES

Table	2.1-1	Cation Concentrations in Spray Dried Salt.	2-2
Table	2.1-2	Anion Concentrations in Spray Dried Salt.	2-8
Figure	2.1-1	Major Cation Concentrations in Spray Dried Salt.	2-12
Figure	2.1-2	Chloride and Carbonate Concentrations in Spray Dried Salt.	2-13
Figure	2.1-3	Nitrate and Sulfate Concentrations in Spray Dried Salt.	2-14
Figure	2.1-4	LDR Metals Spray Dried Salt.	2-15
Table	2.3-1	Time-of-Set.	2-18
Figure	2.3.1-1	Temperature vs Elapsed Time, Type I/II Cement.	2-19
Figure	2.3.1-2	Temperature vs Elapsed Time, Type I/II Cement Compared to Type V Cement. ...	2-20
Figure	2.3.1-3	Temperature vs Elapsed Time, Type V Cement.	2-21
Table	2.4.1-1	Freeze/Thaw Tests.	2-22
Table	3.1.1-1	Lab-scale Operating Envelope.	3-1
Figure	3.1.1-1	Lab-scale Operating Envelope.	3-2
Table	3.2-1	Full-scale Operating Envelope.	3-6
Figure	3.2-1	Full-scale Test.	3-7
Figure	3.2-2	Full-scale Operating Envelope.	3-8
Figure	3.2-3	Full-scale Operating Envelope and Contingency.	3-9
Figure	3.2-4	Comparison of Full-scale to Lab-scale.	3-9
Table	3.2-2	Full-scale Operating Envelope and Contingency.	3-11

1.0 INTRODUCTION

1.1 Addendum to an Earlier Report

This report is an addendum to "Saltcrete Evaluation, August 16, 1993". The first report contains information about process evaluation, waste characterization, process simulation with actual waste and surrogate waste and preliminary formulation studies. This current report contains additional waste characterization and finalizes the formulation studies.

1.2 Saltcrete Description

Saltcrete is a low level mixed waste produced in Building 374 from concentrated liquid waste brine, spray dried salt from that brine, and cement. The waste is stored temporarily at Rocky Flats Environmental Technology Site until a waste repository is able to accept it for final disposal. In order for a disposal site to accept the waste, proof that the waste meets regulatory standards is necessary.

1.3 Purpose

The purpose of this report is to provide the technical information necessary to produce certifiable waste. The information will be incorporated into other documents, identify important process parameters, provide an operating envelope, and provide methods for testing waste treatment in the future. This report, in conjunction with the August 1993 report, will provide a technical basis for operating the saltcrete process using the current production equipment. It is important to note that major changes to the equipment are beyond the scope of this project.

1.4 Main Technical Issue

The main technical issue is expansion of the waste forms which periodically causes damage to a portion of the waste containers which can make the container unsuitable for offsite shipment. The waste acceptance criteria (WAC) for the Nevada Test Site (NTS) and Envirocare of Utah such as free water and the land disposal restricted (LDR) waste treatment standards are not difficult for the saltcrete process to satisfy. The waste form expansion issue was raised by the inspection of the saltcrete in inventory at which time it was discovered that some of the containers were damaged. The August 1993 report addressed the secondary technical issues.

1.5 Other Issues

The lesser issues concern the physical properties of the waste form, ease of operation, and the chemical properties of the waste form. The chemical properties of the waste form were determined in two ways: by characterizing the untreated waste and by analyzing the treated waste form. The previous analysis of the untreated waste (spray-dried salt) indicated that it met the EPA treatment standards with the exception of nickel. Chemical analysis of the treated waste (HNUS, 1992) indicated that two of three subpopulations (Triwalls®, collapsed Triwalls®, and half-crates) of the waste forms in inventory met treatment standards. These analyses were performed according to EPA methods but are not legally defensible because the required documentation was not generated and because the maximum sample holding times were exceeded. The inventory of waste forms will be resampled with the objective of obtaining legally defensible data to demonstrate regulatory compliance for off-site shipment.

Physical properties of the waste forms that pertain to WAC are free water and particulates. Visual observation of the waste forms in inventory indicate that there were no measurable amounts of particulate matter in the containers. Should particulates be above the limits in the WAC, the method to make the waste form compliant is to use double containment. Since the containers in use employ double containment, particulate matter is a problem assured of being solved with production practices in place at this time (and have been in place since April 1989). No free water was detected during the previous sampling efforts. The detection method was visual observation.

1.6 Sampling the Treated Waste

The saltcrete in inventory was sampled and analyzed twice and the expansion of the waste forms was measured twice. First, the inventory was sampled and analyzed by HNUS for chemical constituents (some of that data is summarized in the August saltcrete evaluation report). Since then, Statistical Applications has performed a statistical analysis of that data and found that two of the three subpopulations do indeed meet LDR. Saltcrete was sampled again in January 1994 for microstructure analysis by Halliburton Energy Services. The extent of bulging was measured in April 1993 and in January 1994.

1.7 Petrology

The microstructure of the saltcrete was analyzed to identify the mechanism that causes the waste form to expand. Containers of waste were cored, inspected, and photomicrographs were made. The photomicrographs of the waste that had expanded were compared to photomicrographs of waste that did not. Laboratory samples that were subjected to freeze/thaw cycling were also analyzed; photomicrographs of samples that had expanded were compared to ones that did not. The laboratory samples were made with various types of cement and flyash. The photomicrographs helped determine how minerals in the cement react with the chemicals in the waste.

1.8 Chemical Analysis

The waste exhibits the approximately the same physical and chemical properties as in the August 1993 report. Chemical analysis was performed on 15 additional samples of untreated waste since the August 1993 report. No additional chemical analysis of the of the saltcrete (the final waste form) was performed since the HNUS report. A Department of Transportation (DOT) test to determine if a material is an oxidizer indicated that the spray-dried salt is not an oxidizer. The untreated waste nearly meets the EPA treatment standards, which means that the treated waste is virtually certain to pass the TCLP. (Two samples of pure waste were slightly over the LDR standard for nickel when they were subjected to TCLP.) Therefore, emphasis was placed on the physical properties of the waste form for the development of the operating envelope.

1.9 Operating Envelope

The operating envelope of the saltcrete process was developed in the laboratory then checked with the full-scale production equipment. The purpose of developing an operating envelope is to establish the limiting conditions for producing certifiable waste. The limits of the envelope were determined by the viscosity that the saltcrete mixer will tolerate and by determining when free water will appear in the final waste form. The envelope is based on the weights of the saltcrete components: water, salt, and cement. In other words, it is based on the amount of each component, not the type of cement or flyash. It was reported in the August 1993 that the type of cement or flyash did not affect the viscosity, but the tendency to expand during freeze/thaw cycling was affected.

1.10 Freeze/thaw Cycling

The type of cement and flyash that expanded least in laboratory testing were identified in the August 1993 report. The amount of cement and flyash are identified in the current report. The conclusions are based on two freeze/thaw cycles of one inch diameter by two inch long samples of saltcrete mixed in the laboratory with actual (not surrogate) waste. Since the full scale waste containers are mixed and stored under different conditions for years rather than days, the freeze/thaw testing and conclusions are potentially misleading. The petrology study indicated that the freeze/thaw test is misleading because the expansion mechanisms for the lab-scale samples was different from the full-scale blocks.

1.11 Time-of-Set

The length of time it takes the saltcrete to harden affects the production rate. The time-of-set for saltcrete crates varies from one week to one month. There is enough room in Building 374 to stage 15 crates (one production run), which is sufficient to process all the liquid waste that goes to Building 374. The time-of-set of various cement and flyash combinations was studied on a laboratory-scale and full-scale. There were two purposes: one was to use the information to predict the time-of-set for full-scale crates, the other was to compare the set times of two cement types.

1.12 Instrumentation

Instrumentation and data acquisition equipment requirements were investigated. This equipment would provide information to the waste processing operators as well as provide documentation for certification. Two data loggers are recommended to record process parameters such as the weights of the components, the density of the brine, and the temperature of the saltcrete as it cures. A nuclear densitometer for continuous measurement of brine density is recommended.

1.13 Crate Measurements

Bulged crates were remeasured to determine whether expansion continued over the past year. The crates were measured in April 1993 and again in January 1994. The amount of expansion over that period was insignificant.

1.14 Recommendations

Detailed recommendations to produce certifiable waste forms are given in Section 4. A brief summary follows:

1. The optimum formulation will change from time to time due to inevitable changes in the untreated waste. The best formula now consists of approximately 30 wt% water, 30 wt% salt, 30 wt% type I/II cement, and 10 wt% Class F flyash.
2. Tests to check for free water, viscosity, and time-of-set should be performed for a tank of brine (approximately eight production runs) If necessary, adjust the formula to treat the waste.
3. Occasionally during a production run, a batch will become very viscous with no warning. The fluid properties indicate that this is due to an increase in the surface area of the particles in suspension. Since there is no way to control this with existing equipment, the situation will have to be dealt with by adding brine. The SOP will include this step and the additional weight will be documented. This will not render the waste uncertifiable.
4. Periodic representative sampling and analysis will be needed to characterize the waste and demonstrate that the final waste form meets WAC.
5. Instruments and data acquisition equipment should be used to document the composition of the final waste form.
6. Tank 826-C in Building 374 should be isolated so that the tests mentioned above and the sampling and analysis can be performed once for eight production runs rather than once per production run.

2.0 PROCESS CHARACTERIZATION

2.1 Chemical Analysis

Chemical analysis on the spray-dried salt and the brine were performed to provide characterization data. These analyses were not intended to be legally defensible. They were performed to gain engineering information about the waste and to learn which test methods give the most reliable results. The data is presented in Tables 2.1-1, 2.1-2, and in Figures 2.1-1, 2.1-2, and 2.1-3. The data indicates that the salt nearly meets the LDR treatment standards even before it is mixed with cement at 30 wt% waste loading. Previous analysis of the backlog saltcrete with waste loading varying from 30 wt% to 55 wt% indicates that the treated waste meets LDR treatment standards. A sampling campaign to certify saltcrete with legally defensible data is in progress.

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	10/1/91	11/9/91	11/9/91	11/9/91	11/9/91	11/9/91
	SAMPLE ID:	D884-10191	1-0118	1-0120	1-0124	1-0127	1-0130
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	152,000	157,000	140,000	175,000	149,000	152,000
2	Potassium	134,000	145,000	108,000	171,000	128,000	160,000
3	Calcium	20,500	16,800	26,600	13,200	12,900	16,000
4	Magnesium	3,660	6,170	5,200	3,590	2,970	3,990
5	Iron	1,130	718	1,650	817	811	896
6	Aluminum	911.00	545	1150	471	566	601
7	Zinc	173.00	57.4	297	143	161	87.6
8	Boron	230.00	177	159	186	161	162
9	Nickel	35	19	33	36	30	32
10	Chromium	60	18	91	52	55	39
11	Copper	34	29	39	41	31	38
12	Silver	58	35	74	52	46	56
13	Barium	26	22	35	19	19	22
14	Manganese	16	11	24	13	13	14
15	Vanadium	13	7	18	6	8	7
16	Lead	5	7	13 *		8	11
17	Cadmium	10	5	12	9	8	8
18	Cobalt	3	2	4	3	3	3
19	Selenium	*	12 *	*	*	*	*
20	Beryllium	1	1	1	1	1	1
21	Thallium	1 *	*	*	*	*	*
22	Arsenic	1 *	*	*	*	*	*
23	Mercury	0 *		0 *	*	*	*
24	Antimony	*	*	*	*	*	*
	* Below detectable limit						
	Brine samples are						
	marked with **						

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	12/4/91	12/5/91	1/5/92	1/6/92	2/22/92	2/23/92
	SAMPLE ID:	1-0122	1-0128	1-0315	1-0390	1-0422	1-0421
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	153,000	154,000	144,000	155,000	198,000	212,000
2	Potassium	133,000	134,000	155,400	141,000	72,900	72,700
3	Calcium	16,100	16,300	8,160	17,800	20,900	21,400
4	Magnesium	3,550	3,430	7,170	4,280	8,000	8,260
5	Iron	1,110	993	3,840	2,030	1,140	1,040
6	Aluminum	748.00	723	3,790.00	776	588.00	541
7	Zinc	198.00	175	345.00	173	336.00	345
8	Boron	212.00	168	183.00	208	232.00	216
9	Nickel	50	32	72	30	98	53
10	Chromium	74	58	30	51	60	32
11	Copper	38	34	36	39	42	36
12	Silver	62	52	25	38	30	29
13	Barium	23	22	91	23	26	26
14	Manganese	17	15	43	24	15	15
15	Vanadium	10	10	63	10	7	7
16	Lead	6	10	6	8	6 *	
17	Cadmium	10	9	4	8	4	5
18	Cobalt	3	3	4	3	4 *	
19	Selenium	*	*	*	*	15 *	
20	Beryllium	1	1	4	1	4	4
21	Thallium	1 *		1 *		1 *	
22	Arsenic	1 *		1 *		0 *	
23	Mercury	*	0 *		0	0 *	
24	Antimony	*	*	*	*	*	*
	* Below detectable limit						
	Brine samples are						
	marked with **						

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	2/28/92	4/23/92	4/24/92	5/11/92	5/12/92	6/15/92
	SAMPLE ID:	1-0423	1-0616	1-0618	1-0626	1-0627	1-0638
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	199,000	203,000	151,000	210,000	207,000	193,000
2	Potassium	73,300	93,100	147,000	86,100	83,900	99,100
3	Calcium	21,000	16,300	14,300	20,100	19,800	29,000
4	Magnesium	8,040	5,570	3,400	7,310	7,310	6,680
5	Iron	1,620	1,520	1,320	1,430	1,310	1,900
6	Aluminum	599.00	713.00	602.00	738.00	703.00	1,330.00
7	Zinc	338.00	238.00	163.00	326.00	329.00	298.00
8	Boron	237.00	285.00	233.00	252.00	232.00	269.00
9	Nickel	256	197	45	159	134	125
10	Chromium	180	131	62	101	82	79
11	Copper	65	53	36	51	48	44
12	Silver	31	21	57	29	27	25
13	Barium	27	22	21	27	26	38
14	Manganese	21	21	18	19	18	24
15	Vanadium	7	10	7	9	8	21
16	Lead	5	5	6	6	5	6
17	Cadmium	4	3	10	4	4	4
18	Cobalt	7	7	3	6	5	4
19	Selenium	2 *	*		2 *		2
20	Beryllium	4	2	1	3	3	2
21	Thallium	1	1	1	1	1	1
22	Arsenic	1	0	1	1	1	1
23	Mercury	0	0	0	0	0	0
24	Antimony	*	*	*	*	*	*
	* Below detectable limit						
	Brine samples are						
	marked with **						

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	6/16/92	7/10/92	7/11/92	7/16/92	10/8/92	10/31/92
	SAMPLE ID:	1-0639	1-0793	1-0703	1-0792	2-71475	2-71476
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	183,000	206,000	210,000	197,000	220,000	221,000
2	Potassium	85,300	113,000	98,600	115,000	87,600	78,600
3	Calcium	23,900	12,400	8,840	12,800	12,400	22,700
4	Magnesium	5,500	6,180	4,240	6,150	7,660	7,320
5	Iron	1,400	830	865	1,010	714	1,160
6	Aluminum	1070	545	442.00	623.00	450	941
7	Zinc	212	186	180.00	183.00	194	170
8	Boron	234	162	215.00	196.00	164	164
9	Nickel	34	23	87	79	24	20
10	Chromium	26	20	64	57	14	13
11	Copper	24	22	29	30	20	19
12	Silver	20	27	21	28	17	16
13	Barium	32	20	15	21	20	29
14	Manganese	18	12	11	13	19	39
15	Vanadium	18	8	4	9	5	12
16	Lead	*	*	4	4	*	*
17	Cadmium	3	2	3	2	2	2
18	Cobalt	*	*	*	4	*	*
19	Selenium	*	*	2	*	*	*
20	Beryllium	1	*	*	*	*	*
21	Thallium	*	*	1	1	*	*
22	Arsenic	*	*	0	1	*	*
23	Mercury	0	*	0	1	*	*
24	Antimony	*	*	*	*	*	*
	* Below detectable limit						
	Brine samples are						
	marked with **						

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	1/7/93	1/28/93	2/11/93
	SAMPLE ID:	2-71477	2-71932	2-71952
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	225,000	221,000	225,000
2	Potassium	74,500	72,000	74,000
3	Calcium	16,400	11,900	10,100
4	Magnesium	7,050	5,990	4,910
5	Iron	933	780	746
6	Aluminum	677	493	476
7	Zinc	143	116	101
8	Boron	162	154	144
9	Nickel	20	19	17
10	Chromium	12	12	11
11	Copper	18	17	19
12	Silver	17	15	12
13	Barium	22	18	16
14	Manganese	29	22	19
15	Vanadium	8	6	5
16	Lead	*	*	*
17	Cadmium	2	2	2
18	Cobalt	*	*	*
19	Selenium	*	*	*
20	Beryllium	*	*	*
21	Thallium	*	*	*
22	Arsenic	*	*	*
23	Mercury	*	*	*
24	Antimony	*	*	*
	* Below detectable limit			
	Brine samples are			
	marked with **			

Table 2.1-1
Analysis of Salt and Brine Samples, Cations

	DATE:	3/10/93	3/10/93	3/10/93	3/10/93
	SAMPLE ID:	44272**	44273**	44274**	44275**
	ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
1	Sodium	81,300	83,900	82,800	86,700
2	Potassium	29,300	29,400	29,000	27,300
3	Calcium	2,370	2,380	2,480	2,550
4	Magnesium	1,720	1,730	1,800	1,830
5	Iron	253	252	262	263
6	Aluminum	118	117	128	124
7	Zinc	53.3	53.7	55.8	55.3
8	Boron	45.4	47	44.8	44.8
9	Nickel	6	7	7	7
10	Chromium	5	4	5	5
11	Copper	8	8	8	8
12	Silver	4	4	4	4
13	Barium	*	*	*	*
14	Manganese	4	4	5	5
15	Vanadium	*	*	*	*
16	Lead	*	*	*	*
17	Cadmium	1	1	*	1
18	Cobalt	*	*	*	*
19	Selenium	*	*	*	*
20	Beryllium	*	*	*	*
21	Thallium	*	*	*	*
22	Arsenic	*	*	*	*
23	Mercury	*	*	*	*
24	Antimony	7	*	*	*
	* Below detectable limit				
	Brine samples are	**BRINE	**BRINE	**BRINE	**BRINE
	marked with **	SAMPLE	SAMPLE	SAMPLE	SAMPLE

Table 2.1-2
Analysis of Salt and Brine Samples, Anions

DATE:	10/1/91	11/9/91	11/9/91	11/9/91	11/9/91	11/9/91	12/4/91	12/5/91	1/5/92
SAMPLE ID:	D884-10191	1-0118	1-0120	1-0124	1-0127	1-0130	1-0122	1-0128	1-0315
ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Nitrate	217,021	246,888	164,592	181,737	174,879	181,737	217,021	174,879	234,736
Chloride	130,000	77,000	170,000	110,000	150,000	89,000	150,000	150,000	93,000
Sulfate	90,000	97,000	100,000	110,000	110,000	110,000	93,000	110,000	65,000
Carbonate	51,600	92,000	74,000	120,000	89,000	130,000	48,000	94,000	54,000
Acid Insoluble Matter	39,000	NA	NA	NA	NA	25,000	38,000	NA	69,000
Fluoride	10,000	8,300	12,000	14,000	9,500	14,000	10,000	11,000	8,000
TOC	8,700	9,600	11,000	11,000	11,000	9,500	10,000	11,000	9,300
Hydroxide	3,000	*	*	*	*	*	3,000	*	3,000
Phosphate	150						68		110
Cyanide	20	NA	NA	NA	NA	NA	16	NA	9
*Below Detectable Limit									
Brine samples are									
marked with **									

Table 2.1-2
Analysis of Salt and Brine Samples, Anions

DATE:	1/6/92	2/22/92	2/23/92	2/28/92	4/23/92	4/24/92	5/11/92	5/12/92	6/15/92
SAMPLE ID:	1-0390	1-0422	1-0421	1-0423	1-0616	1-0618	1-0626	1-0627	1-0638
ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Nitrate	181,737	239,166	185,166	234,737	190,447	221,450	239,166	248,024	181,589
Chloride	110,000	100,000	100,000	99,000	110,000	110,000	110,000	110,000	100,000
Sulfate	110,000	82,000	83,000	80,000	140,000	97,000	99,000	95,000	110,000
Carbonate	87,000	52,200	90,000	51,600	30,600	57,600	47,400	50,400	35,400
Acid Insoluble Matter	NA	39,000	NA	33,000	42,000	34,000	33,000	35,000	43,000
Fluoride	12,000	11,000	10,000	10,000	12,000	14,000	8,200	7,800	9,100
TOC	11,000	9,400	11,000	7,800	6,600	5,900	9,200	8,400	6,400
Hydroxide	*	3,000	*	3,000	3,000	3,000	3,000	3,000	3,000
Phosphate		67		68	570	66	97	69	49
Cyanide	NA	5	NA	30	6	10	9	15	10
*Below Detectable Limit									
Brine samples are									
marked with **									

Table 2.1-2
Analysis of Salt and Brine Samples, Anions

DATE:	6/16/92	7/10/92	7/11/92	7/16/92	10/8/92	10/31/92	1/7/93	1/28/93	2/11/93
SAMPLE ID:	1-0639	1-0793	1-0703	1-0792	2-71475	2-71476	2-71477	2-71932	2-71952
ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Nitrate	133,731	205,740	159,444	248,024	236,601	243,459	240,030	226,314	192,024
Chloride	95,000	140,000	110,000	130,000	140,000	130,000	130,000	140,000	150,000
Sulfate	130,000	91,000	170,000	84,000	110,000	110,000	110,000	120,000	130,000
Carbonate	61,000	55,000	21,600	23,400	41,000	50,000	44,000	49,000	49,000
Acid Insoluble Matter	NA	28,000	14,000	31,000	NA	NA	NA	NA	26,000
Fluoride	9,400	8,600	38,000	8,400	7,200	6,000	5,400	6,700	8,300
TOC	7,700	9,100	4,900	8,000	6,900	6,800	8,200	7,700	8,500
Hydroxide	*	*	3,000	3,000	*	*	*	*	*
Phosphate			1,600	660					
Cyanide	NA	NA	4	7	*	*	*	*	*
*Below Detectable Limit									
Brine samples are									
marked with **									

Table 2.1-2
Analysis of Salt and Brine Samples, Anions

DATE:	3/10/93	3/10/93	3/10/93	3/10/93
SAMPLE ID:	44272**	44273**	44274**	44275**
ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Nitrate	54,864	58,293	58,293	58,293
Chloride	52,000	53,000	54,000	53,000
Sulfate	41,000	41,000	42,000	45,000
Carbonate	13,000	12,000	12,000	13,000
Acid Insoluble Matter	NA	8,200	10,000	NA
Fluoride	2,100	2,000	2,200	3,000
TOC	3,700	3,800	3,800	3,700
Hydroxide	*	*	*	*
Phosphate				
Cyanide	*	*	*	*
*Below Detectable Limit				
Brine samples are	** BRINE	** BRINE	** BRINE	** BRINE
marked with **	SAMPLE	SAMPLE	SAMPLE	SAMPLE

Figure 2.1-1
Major Cations in Spray Dried Salt

Figure 2.1-2
Chloride and Carbonate Anions
in Spray Dried Salt

.

Figure 2.1-4
LDR Metals
in Spray Dried Salt

2.2 Petrology

The purpose of the petrology study was to determine the reason why the saltcrete expands.

2.2.1 Experimental

The approach was to compare samples from saltcrete crates that expanded to saltcrete crates that did not. In addition, samples of saltcrete that were generated in the laboratory and subjected to freeze/thaw testing were examined to determine if the expansion observed in the laboratory was due to the same mechanism as for the crates.

A core was taken from the center and from one end of seven crates with a 2½-inch core bit. Crates that expanded were cored at the end where the expansion was observed. An unexpanded crate produced during the same production run was cored for a comparison.

Three methods were employed to examine the microstructure: optical microscopy, scanning electron microscope (SEM), and x-ray diffraction (XRD). Optical microscopy was used to identify cement, the degree of cement hydration, porosity, homogeneity, salt crystals, and structural flaws. SEM and XRD were used to identify crystals. The analysis was performed on-site with oversight from consultants. Halliburton Energy Services contracted by EG&G and the Army Corps of Engineers contracted by DOE advised EG&G personnel about examining the waste form samples. Their reports are in Appendix 3.

2.2.2 Conclusions

The conclusions resulting from this study are:

1. The expansion is largely due to darapskite, which is a nitrate-sulfate hydrate $[\text{Na}_3(\text{NO}_3)(\text{SO}_4) \cdot \text{H}_2\text{O}]$.
2. Porosity, salt crystal formation, and expansion occur together.
3. Laboratory samples did not produce darapskite.
4. Calcium-chloro-alumina hydrate is a possible cause of expansion. However, it is not likely to be significant.
5. Expansion is finite, and the rate of expansion will decrease the longer a crate is in storage.

The consensus of opinion among those who analyzed the data is that the expansion of the saltcrete is due to the formation of darapskite. The components of darapskite are derived from the waste rather than the cement. Since the formation of this salt is liable to occur no matter what type of cement is used type cement, type I/II cement, type V cement, or a blend of cement and Class F flyash is suitable for the saltcrete treatment. It is also recommended that the waste loading be reduced from 35 wt% to 30 wt% since saltcrete containing less waste will have less darapskite. Waste loading of 30 wt% is recommended because production history shows that expansion is dramatically less when the waste loading is 30 wt% or less.

It was also observed that high porosity, crystal formation, and microfractures existed in the crates that expanded. Since porosity is higher in crates that expand, reducing the porosity of the saltcrete matrix may reduce expansion. Three possible causes of expansion are gas generation,

air entrainment, and excess water. Air entrainment is the only one of these three that has a simple remedy. Gas generation is caused by chemicals in the waste, and the water content has been reduced as much as possible for the existing mixing system.

The maximum amount of expansion and the time when the expansion stops are of concern while the saltcrete is stored at Rocky Flats. The petrology studies provided estimates but not definite quantitative answers. Some of the core samples had darapskite concentrations of 20 wt%. Since the waste loading was 35 wt%, and since nitrate and sulfate ions comprise less than half of the waste, a reasonable estimate is that maximum expansion has occurred in those samples. Considering that the core samples were chosen to represent the crates with the most expansion, maximum expansion can be expected to be approximately two to three inches after one year. Section 2.6 addresses the expansion measurements of the entire saltcrete inventory.

Variation of the darapskite concentration was noted in the petrology study (Appendix 3). The cause could be poor mixing which could be the result of short residence time in the mixer or the formation of large, unmixed cement lumps. Large lumps of cement have been observed during mixing when the viscosity limitation of the mixer is exceeded at the same time as a large amount of cement enters the mixer. The mixer is then unable to agitate the contents of the tank.

2.3 Time-of-Set

The time-of-set of saltcrete formulations is a consideration for choosing a cement/admixture composition. This experiment had two objectives. The first objective was to compare the time-of-set for waste forms made with type I/II cement (currently produced) to waste forms produced using a blend of type V cement and Class F flyash (V-F blend). The second objective was to compare the time-of-set of lab-scale samples to full-scale containers. Typically, type I/II Portland cement mixed with the Building 374 salts typically requires seven to 21 days to harden in crates. Both type V cement and Class F flyash generally take longer to set than type I/II. This has been qualitatively observed in the lab on previous occasions.

2.3.1 Experimental

The approach was to compare the time-of-set in the full-scale saltcrete blocks made with type I/II cement to lab-scale saltcrete blocks made with type I/II cement and lab-scale saltcrete blocks made with V-F blend by recording the respective temperature profiles. One full-scale block and four lab-scale blocks made with type I/II, plus one full-scale and four lab-scale blocks made with V-F blend were monitored. The lab-scale block was insulated in a polystyrene foam box to reduce heat loss to the atmosphere (as in the August 1993 report). The temperature profile was recorded to monitor the exothermic cement hydration reaction. One full-scale crate of 35 wt% type I/II saltcrete was available for testing and serves as the baseline for the lab-scale tests. The 30 wt% V-F blend full-scale block was monitored for comparison. Table 2.3-1 gives the composition of the blocks and lab-scale samples that were monitored.

The saltcrete crate made with the V-F blend hardened in approximately the same amount of time (15 days) as the currently produced saltcrete (35 wt% salt) made type I/II cement. In fact, the

crate of V-F blend set three days sooner than the crate of type I/II that was monitored for temperature, but other crates in the production run set sooner than either of the crates that were monitored. It is typical for the set times of the crates in a production run to vary by two to three days.

The full-scale V-F crate set sooner than was expected due to the accumulation of heat energy from the cement hydration reaction. Previous experience was with lab-scale samples which took much longer to set than type I/II lab-scale samples. The difference between type V and type I/II cement is in the concentration of tricalcium aluminate which reacts more quickly with water than the other cement components. Type I/II has a higher concentration of tricalcium aluminate than type V. Apparently, the type I/II samples generated early heat quickly enough to accelerate the hydration of the other cement components. The type V lab samples generated heat more slowly so more heat it was lost to the environment and was not available for accelerating the other cement components. The type V crate, however, accumulated the heat due to its size so the hydration reaction was accelerated in the crate. The lab-scale samples of V-F blend took approximately three times as long to set as the crate of V-F blend. The lab-scale samples of type I/II took 1½ times as long as the crate of type I/II.

TABLE 2.3-1

SAMPLE	SALT, WT%	SCALE	TYPE OF CEMENT	CEMENT + FLYASH, WT%	WATER, WT%	TIME OF SET, DAYS
1	35 %	Lab	I/II	36 %	29 %	17
2	35 %	Lab	I/II	36 %	29 %	18
3	35 %	Lab	I/II	36 %	29 %	16
4	35 %	Lab	I/II	36 %	29 %	18
Crate	35 %	Full	I/II	36 %	29 %	13
H04747						
6	30 %	Lab	V-F blend	42 %	28 %	29
7	30 %	Lab	V-F blend	42 %	28 %	28
8	30 %	Lab	V-F blend	42 %	28 %	30+
9	30 %	Lab	V-F blend	42 %	28 %	30+
Crate	30 %	Full	V-F blend	42 %	28 %	10
H04749						

The temperature profiles are shown in Figures 2.3.1-1, 2.3.1-2, and 2.3.1-3. A detailed table of temperatures is in Appendix 6.

Figure 2.3.1-1
Temperature vs Elapsed Time
Type I/II Cement

Figure 2.3.1-2
Temperature vs Elapsed Time
Type V Cement, Class F Flyash Blend

Figure 2.3.1-3
Temperature vs Elapsed Time
Type V Cement-Class F Flyash Blend Compared to Type I/II Cement

2.4 Freeze/Thaw Cycling

The objective of this experiment was to evaluate the durability and stability of saltcrete formulations using actual waste from the treatment process.

Lab-scale samples of saltcrete prepared with various proportions of type V cement, type I/II cement, and Class F flyash were cured in an oven then subjected to freeze/thaw cycling. The dimensions and mass of the samples were measured before and after the freeze/thaw cycling.

2.4.1 Experimental

Samples of saltcrete were prepared by adding the dry cementitious constituents to the brine. The ratio of water to salt to cement/flyash was 30.5 to 29.5 to 40.5 percent by weight. The cement to flyash ratio was 3:1. The water concentration in this test is slightly higher than in the recommended operating envelope (by 0.7 wt%) to provide a harsh freeze/thaw test. Cylindrical samples one inch in diameter by two inches high were weighed and measured before and after freeze/thaw cycling. The diameters were measured at three points and the length at two points. The samples were poured into sealed plastic molds then cured in a lab oven at 60°C for 2½ days. The ten different cement dry blends shown in Table 2.4.1-1 were evaluated.

Table 2.4.1-1 Freeze/Thaw Tests

Sample no.	Water wt%	Salt wt%	Cement type, wt%	Flyash wt%	Free H2O?
2 A 1-94	30.8	28.7	I/II 20.3	20.3	
2 B 1-94	30.8	28.7	I/II 20.3	20.3	
3 A 1-94	30.8	28.6	I/II 30.4	10.2	
3 B 1-94	30.8	28.6	I/II 30.4	10.2	
4 A 1-94	30.9	28.7	I/II 36.3	4.1	yes
4 B 1-94	30.9	28.7	I/II 36.3	4.1	
5 A 1-94	30.8	28.7	I/II 38.4	2.0	yes
5 B 1-94	30.8	28.7	I/II 38.4	2.0	yes
1 A 1-94	30.8	28.7	I/II 40.5	0.0	yes
1 B 1-94	30.8	28.7	I/II 40.5	0.0	yes
7 A 1-94	30.7	28.6	V 20.3	20.4	
7 B 1-94	30.7	28.6	V 20.3	20.4	
8 A 1-94	30.7	28.6	V 30.4	10.3	
8 B 1-94	30.7	28.6	V 30.4	10.3	
9 A 1-94	30.9	28.8	V 36.2	4.1	yes
9 B 1-94	30.9	28.8	V 36.2	4.1	
10 A 1-94	30.9	28.7	V 38.2	2.2	yes
10 B 1-94	30.9	28.7	V 38.2	2.2	
6 A 1-94	30.7	28.6	V 40.6	0.0	yes
6 B 1-94	30.7	28.6	V 40.6	0.0	yes

An unexpected benefit of this test was the observation that flyash immobilizes water when the flyash concentration was between 5 wt% and 10 wt% in the final waste form (see Table 2.4.1-1). This concentration of flyash is commonly used in waste treatments (Conner, 1990). The correlation of free water to flyash concentration lead to the recommendation that flyash be used in the treatment at 10 wt% of the final waste form.

The freeze/thaw tests showed that the type of cement did not affect the expansion nearly as much as the concentration of flyash. The previous study showed that the type of cement had a significant effect on the expansion. The different results suggest that the freeze/thaw test is not a reliable predictor of expansion. The petrology study in Section 2.2 indicates that the expansion mechanism in the lab-scale samples is different from the mechanism in the full-scale crates.

2.4.2 Conclusions

The freeze/thaw test is not a reliable predictor of the expansive properties of a cement formulation.

Flyash helped immobilize water in lab-scale samples.

2.5 Instrumentation

There are two reasons for recommending more instrumentation for the saltcrete process. The first is to provide documentation that the process is operated within a set of specifications, the second is to improve the accuracy and consistency of measurements.

2.5.1 Rationale

Documentation of the process will help provide evidence that the waste is treated according to the standard operating procedure (SOP), which is a certification requisite for the Nevada Test Site (NTS). The necessity for documentation is derived from NVO-325 (an NTS document). Envirocare of Utah, another disposal site, has no requirements for process documentation, but relies on chemical analysis of the treated waste. Currently, the weight of the components in saltcrete (brine, salt, and cement) are manually recorded. A method to automatically record this information would provide confirmation of the manual transcription.

The process parameters of interest are:

1. The water content of the untreated brine.
2. The weight of each component, brine, salt, and cement, added to a batch of saltcrete.
3. When the saltcrete is set.

Currently the water content of the untreated brine is calculate from its specific gravity as measured by a hydrometer. The precision of the hydrometer is ± 0.01 specific gravity units and an error of 0.02 specific gravity units has been observed in practice. This amounts to an error of approximately 1% by weight of the final waste form (3 wt% of the untreated brine). Since the process has a 2 wt% range, the hydrometer error can be significant. Technology Development

personnel have used a moisture balance to make water content determinations. The moisture balance has consistently produced results that are 0.2 % by weight of the final waste form (0.5 wt% of the brine).

The weights of the saltcrete components are measured by load cells on the mixing tank. A digital display of the weight is manually transcribed after each component is transferred to the tank. The weighing system has no automated recorder, but data acquisition instruments are on-site and will be installed soon to provide an automatic redundant record.

Currently, the completion of the cement hydration reaction is determined by inspection. Visual observation is used to determine that there is no free water and no free particulate matter. The waste form is poked with a rod to determine if the waste form is hard. A method to record the completion of the hydration reaction would help demonstrate whether the treatment of a given container of waste is successful.

2.5.2 Recommendations

Two Hydra Data Buckets, manufactured by Fluke, are recommended to record data. One recorder dedicated to monitoring the weights of the saltcrete components and the specific gravity of the brine will provide documentation of composition of the waste form. A second recorder to monitor the temperature of the crates while they are curing will provide documentation of the cement hydration.

A nuclear densitometer to continuously monitor the specific gravity of the brine and provide data for documentation of waste certification is recommended. A Texas Nuclear model 5201 is available from plant inventory. The densitometer data can be recorded by a Data Bucket.

The letter report prepared by A. A. Marlowe, included as Appendix 8, gives more detail about the recommended instrumentation.

A moisture balance should be used for determining the water content of the untreated brine.

2.6 Measurement of Expanded Crates

Saltcrete crates produced since April 1990 with noticeable bulges were measured for expansion in April 1993 and again January 1994. Approximately one out of seven crates in inventory were bulged. The average expansion in April 1993 was 0.84 inches. When those same crates were measured the second time the average expansion was 1.03 inches. Since the difference was less than the estimated accuracy of the measurements, the expansion during the period was considered negligible.

2.7 DOT Oxidizer Test

The test to determine if a material is an oxidizer (49 CFR 173 Appendix F) according to the Department of Transportation (DOT) was performed on samples of spray-dried salt. (A letter report is in Appendix 1.) Salt waste generated from Building 374 liquid waste treatment containing

less than 31 wt% nitrate ion is not an oxidizer by this test. However, this does not imply that salt waste generated in the future will not be. Higher nitrate concentrations and the combined effects of the other constituents in the waste may cause the salt to fail the oxidizer test.

Since the test is simple to perform, the determination can be made on each saltcrete production run if the decision is made to store untreated salt.

3.0 Formulation

3.1 Operating Envelope, Lab-Scale Tests

The objective was to determine the proportions of water, salt, and cement that exhibit the properties that allow the full-scale mixer to stir the paste and not produce free water.

3.1.1 Experimental

Tests were performed in the laboratory to find the minimum and maximum concentrations of water with a 30 wt% waste loading (30 wt% salt) and a 26 wt% waste loading. The maximum waste loading of 30 wt% was chosen because it was found that the likelihood of waste form expansion greatly increases at higher waste loading due to the darapskite formation (see Section 2 in the August 1993 report). The minimum waste loading of 26 wt% was chosen because it allows reasonable room for process variation. Once the bounding water and salt concentrations were found, the bounding cement concentration was calculated.

A high concentration of water in the paste reduces viscosity which allows better mixing. If the water concentration is too high, free water accumulates on the top surface of waste form. The free water must then be removed for the waste to be certifiable because it is a violation of the WAC (removal of free water can be included in the standard operating procedure). Once the proportions were determined in the laboratory, the formula was tested with the full-scale equipment.

Detailed data, graphs and explanations of them are in Appendix 4. A summary of the results is presented in Table 3.1.1-1 and Figure 3.1.1-1.

Table 3.1.1-1

	Water wt%	Salt wt%	Cement wt%
Maximum water at maximum salt loading	29.7	30.0	40.3
Minimum water at maximum salt loading	29.0	30.0	41.0
Minimum water at 26 wt% salt	27.2	26.0	46.8
Maximum water at 26 wt% salt	28.3	26.0	45.7

Figure 3.1-1
Lab-Scale Operating Envelope

3.1.2 Conclusions

When the salt concentration is 30.0 wt%, the laboratory-scale tests indicate that the maximum and minimum concentrations of water in the final waste form are 29.7 and 29.0 wt% respectively. When the salt concentration is 26.0 wt%, the maximum water concentration is 28.3 wt% and the minimum water concentration is 27.2 wt%. (See the next section for the full-scale test of these concentrations.)

The minimum cement concentration (40.3 wt%) was calculated from the maximum salt concentration (30.0 wt%) and the maximum water concentration (30 wt%). The maximum cement concentration (46.8 wt%) was calculated from the minimum water concentration (27.2 wt%) and the minimum salt concentration (26.0 wt%).

The information from lab-scale tests was used to develop the tests for the full-scale tests. The lab-scale tests indicated that the bounding conditions were very restrictive. Since there was very little difference between the maximum and minimum water concentrations and "problems with scale-up are legion" (Uhl, 1986), there was concern that there would be problems when this formulation was used with the full-scale mixer. However, the saltcrete paste is a shear-thinning fluid and there is a greater average shear rate in the full-scale mixer (Oldshue, 1983). This means that saltcrete paste with less water would exhibit acceptable viscosities in the full-scale mixer, as was shown in the full-scale tests (refer to Section 3.2).

3.1.3 Contingency Formulation

Tests were also performed on brine with no spray-dried salt added. The results from this test can be used as an emergency formulation in the event that the spray-drier fails. At 16 wt% salt, the range of water concentration was 25 wt% to 29 wt%. This water-content range has not been tested on the full-scale equipment. Verification of this water-content range should be tested on the full-scale equipment for free water formation and viscosity during the early part of a production run in the event the spray-drier fails.

3.2 Operating Envelope, Full-Scale

The objective was to determine the proportions of water, salt, and cement that exhibit the properties that allow the full-scale mixer to stir the paste and not produce free water. The tests used were the same as laboratory-scale tests. The limiting conditions established in this test can be used by LWTO to produce certifiable waste.

Explanation of terms used in this section:

Production run - One run produces approximately fifteen crates during a two day period. Production runs are made approximately once per month.

Batch - Three 1,200-pound batches are poured into one halfcrate.

Halfcrate - A plywood box 7' X 4' X 2' lined with fiberboard and plastic.

Bleed water - A layer of water that forms on the top of the saltcrete before the paste hardens. Bleed water must be removed because waste containing free water cannot be disposed.

Predicted water content - results from the laboratory-scale test.

Actual water content - results from the full-scale test.

Viscosity limitation of the mixer - saltcrete paste with viscosity values greater than the line in equation (1) is too viscous to agitate. A semi-solid mass forms that must be pushed out of the mixer with hand tools.

$$\theta = 60 + \frac{1}{2}(\text{rpm}) \quad (\text{equation 1})$$

Where θ is the angle of deflection, and rpm is the rotation speed of the viscometer. If the vortex is observed for a visual determination, the limitation of the mixer is where the vortex is less than two inches. (Markers on the mixer shaft may help make visual determinations.)

3.2.1 Experimental

The boundary conditions were based on the waste loading and water content. The maximum waste loading was established by reviewing historical production records (August 1993 report). The maximum water content was based on formation of bleed water. Formulations that produced bleed water were judged to have too much water. The minimum water content was established by the limitations of the mixer (the lower the water content, the higher the viscosity).

The approach was to test the corners of the envelope that was developed in the laboratory. To find the maximum water concentration the full-scale mixer could tolerate, the lab-scale maximum was tested. Two test crates were made to test for free water, one at the highest water concentration with 30.0 wt% salt concentration and one at the highest water concentration with 26.0 wt% salt concentration. These crates were visually monitored for formation of bleed water. Samples of these batches were placed in 50 ml graduated cylinders and were monitored for free water formation. To find the minimum water concentration that the full-scale mixer could tolerate, high-water-content batches were made first and then cement was added. Several tests were made to test for high viscosity by adding cement until the viscosity reached the limitations of the mixer.

Several steps were taken to ensure the accuracy of the test. During the test, the vacuum line (for dust control) to the mixer was closed, and the mixer motor was stopped after each component was added to minimize forces extraneous to the mixer weighing system. The digital weight readout was zeroed after the brine was added, after the salt was added, and after each batch was poured into a crate. This was done to prevent carrying over error from one weight determination to another. For example, an over run on the brine weight was not carried over to the salt measurement. The mixer load cells were calibrated with certified weights prior to the production run. The moisture balance, an instrument for thermal gravimetric determinations, was calibrated

with certified weights prior to the test. The viscometer was calibrated with the manufacturer's calibration kit before and after the test.

The parameters measured were the water content of the brine, the weight of the components in the saltcrete, the specific gravity and temperature of the brine, and the viscosity of the saltcrete slurry. Visual observations were made for free water in the crates. Observations for free water were also made by collecting samples in 50 ml test tubes. The test tubes were checked over a period of several hours.

The results are presented in Table 3.2-1 and in Figures 3.2-1, 3.2-2, and 3.2-3. The minimum and maximum water content lines were derived by performing linear regressions on the respective data points.

The full-scale test validated the laboratory-scale tests. The actual maximum water content was similar to the predicted value, but the predicted minimum water content was lower than the actual water content. see Figure 3.2.4 The fact that the full-scale envelope is larger than the lab-scale envelope is not surprising since the saltcrete paste is a shear-thinning fluid and the full-scale mixer has greater range of shear rate than the lab-scale mixer. The lab-scale impeller rotates at 400 rpm and has a diameter of one inch while the full-scale impeller rotates at 360 rpm and has a diameter of 12.6 inches. The higher shear rate produces more shear thinning, or in other words, the full-scale mixer thins the fluid more than the lab-scale mixer.

The full-scale envelope was found to have $1\frac{1}{2}$ times the water content latitude as the lab-scale envelope. The lab-scale tests indicated that for a given salt concentration, the water concentration can vary by approximately $1\frac{1}{2}$ wt%. The full-scale tests indicated that the water concentration can vary by approximately $2\frac{1}{4}$ wt%. This is significant because the size of the envelope is small, compared to the inherent variation of the process, such as the accuracy of the measuring system ($\frac{1}{4}$ wt% to $\frac{1}{2}$ wt%). Also consider that the pneumatic transfer systems deliver salt and cement in increments of 12 and 25 pounds respectively. These weights correspond to 1 wt% and 2 wt% of a batch.

Table 3.2.1																												
Cement Type	Flyash Class	Date	Time	Crate	Run	Specific Grav.		Wt % Water	Pounds In Saltcrete			Wt % In Saltcrete			Viscometer Readings												Free H2O ?	
						Measured by			Brine	Salt	Cmt	Water	Salt	Cement	rpm	degrees of deflection												
						LWTO	TD	In Brlne								1	2	3	6	10	20	30	60	100	200	300		600
100% I/II		12/8/93	11:24	4683	1	1.32	1.32	59.5	608	114	478	30.1	30.0	39.8		10	10	11	11	15	18	21	30	41	67	89	143	trace
100% I/II		12/8/93	13:00	4683	2	1.32	1.325	59.5	608	107	469	30.6	29.8	39.6		9	9	9	9	10	12	14	20	26	43	58	97	
100% I/II		12/8/93	13:45	4683	3	1.32	1.32	59.6	608	124	484	29.8	30.4	39.8		14	20	21	20	21	24	26	33	41	62	80	124	
100% I/II		12/8/93	16:50	4682	1	1.32	1.32	60.6	577	129	514	28.7	29.2	42.1		15	20	19	19	20	24	28	37	49	75	97		
100% I/II		12/8/93	16:50	4682	1	1.32	1.32	60.6	577	129	535	28.2	28.7	43.1		13	16	14	15	17	21	24	34	45	72	97		
100% I/II		12/8/93	16:50	4682	1	1.32	1.32	60.6	577	129	580	27.2	27.7	45.1		14	20	20	20	22	26	30	42	56	89	112		
100% I/II		12/8/93	16:50	4682	1	1.32	1.32	60.6	577	129	636	26.1	26.6	47.4		20	26	30	31	35	38	44	60	78	120	156		
100% I/II		12/8/93	16:50	4682	1	1.32	1.32	60.6	577	129	674	25.3	25.8	48.8		25	31	35	43	43	50	56	76	99	155	207		
100% I/II		12/14/93	8:05	4663	1	1.32	1.32	60.8	563	99	554	28.2	26.3	45.6		15	20	20	20	20	20	25	30	37	56	75	125	
100% I/II		12/14/93	8:45	4663	2	1.32	1.32	60.8	587	100	580	28.2	26.1	45.8		8	10	9	10	11	13	15	21	29	47	64	110	
100% I/II		12/14/93	9:20	4663	3	1.32	1.32	60.8	562	104	558	27.9	26.5	45.6		12	12	12	12	13	15	18	25	34	54	74	121	
100% I/II		12/14/93	10:30	4663	1	1.32	1.32	60.8	554	112	560	27.5	26.8	45.7		15	16	15	16	16	19	22	30	41	65	88	152	
100% I/II		12/14/93	11:00	4663	2	1.32	1.32	60.8	594	112	560	28.5	27.2	44.2		11	12	11	11	12	14	17	23	31	51	69	115	
100% I/II		12/14/93	11:05	4663	3	1.32	1.32	60.8	556	105	561	27.7	26.4	45.9		11	12	12	12	13	16	18	24	34	55	74	122	
100% I/II		12/8/93	10:55	4689	1	1.32	1.325	60.5	565	104	584	27.3	26.1	46.6		30	40	42	60	67	80	92	125	160	235	290	300	
100% I/II		12/8/93	14:35	4689	2	1.32		60.5	529	124	560	26.4	27.4	46.2		22	27	27	25	26	32	36	47	61	93	120	192	
100% I/II		12/8/93	15:45	4689	3	1.32		60.5	537	98	568	27.0	25.8	47.2		15	18	18	18	19	23	27	38	52	82	110	182	
100% I/II		12/8/93	15:45	4689	3	1.32		60.5	537	98	592	26.5	25.3	48.2		17	19	19	18	20	25	30	42	58	94	126	212	
100% I/II		12/8/93	15:45	4689	3	1.32		60.5	537	98	611	26.1	24.9	49.0		19	22	22	22	23	29	34	49	66	108	143	239	
100% I/II		12/8/93	15:45	4689	3	1.32		60.5	537	98	643	25.4	24.3	50.3		21	27	30	30	33	40	47	65	87	134	173	280	
100% I/II		12/14/93	13:00	4687	1	1.32		59.6	691	166	500	30.3	32.8	36.8		60	75	80	100	100	100	100	105	125	205	255	300	
75% V 25% F		4/27/94		4749	1	1.32		60.7	544	114	460	29.5	29.3	41.1						15	15	15	20	30	40	67		
75% V 25% F		4/27/94		4749	2	1.32		60.7	508	130	462	28.0	30.0	42.0									28	44	53	86		
75% V 25% F		4/27/94		4749	3	1.32		60.7	472	159	481	25.8	31.0	43.3												>300	>300	

Figure 3.2-1
Full-Scale Test

Figure 3.2-2
Full-Scale Envelope

Figure 3.2-3
Full-Scale Envelope and
Contingency

Figure 3.2-4
Comparison of
Lab-Scale to Full-Scale

Table 3.2-2

	Minimum		Maximum	
	Water		water	
	Salt	Water	Salt	Water
	wt%	wt%	wt%	wt%
Normal Conditions				
Maximum salt	30.0	27.9	30.0	30.4
Minimum salt	26.0	25.7	26.0	28.0
Contingency				
Saturated brine	14.0	25.0	17.3	28.2

3.2.2 Conclusions and Recommendations

The operating envelope reported here can be used as an effective formulation for treating the Building 374 salt and brine because waste acceptance criteria (WAC) are satisfied. WAC are met because the waste form has no free water, less than 1 wt% particulate matter (to satisfy NVO-325 only), and it is assumed from the chemical analysis that the LDR treatment standards will be met (sampling and analysis is in progress to gather the legally defensible data to support this assumption).

There are different reasons for recommending each minimum and maximum, yet no waste form should be rejected solely because it was produced outside the envelope. The process can be operated such that operating outside of the envelope should be the exception rather than the rule. An explanation of the limits follows:

- The maximum water content line was recommended because adding more water will cause bleed water to form. Bleed water can be removed before the container is sealed. So if the maximum water content is exceeded, the waste form can still be certified for disposal if the bleed water (if any) is removed and the other WAC are satisfied. Waste forms with less than the minimum water content can be certified with no further testing or treatments as long as the WAC are satisfied.
- The minimum water line is recommended because on the full scale tests, the viscosity limitation of the mixer was nearly exceeded. However, it is generally true that the less water there is in a waste form, the better. So if Liquid Waste Treatment Operations (LWTO) is able to effectively mix saltcrete with less water than is recommended here, then that practice should be adopted.
- The maximum salt content line was selected because the risk of waste form expansion is greater above that line. Waste forms with greater than the maximum recommended salt concentration have been expanding and damaging containers. However, these waste forms can still be certified as long as the WAC are satisfied.
- The minimum salt content line was selected arbitrarily. The only problem with waste forms with less than 26 wt% salt is lower waste loading efficiency.

The operating envelope can be used for type I, type I/II, or type V cements with or without Class F flyash because saltcrete paste made with these cements and the flyash have very similar viscosities. The fluid properties are important because they affect whether the waste form meets the WAC (specifically free water) and the compatibility of the paste with the existing equipment. The chemical properties of these cements are of less importance because the chemical nature of the waste lends itself to satisfying the WAC.

The recommended approach for mixing waste forms that lies within the operating envelope is to produce a paste that is 30 wt % water, 30 wt% salt and 40 wt% cement/flyash. Mix this thoroughly (five minutes of mixing is recommended) , then add cement in 40 to 50 pound increments until the paste is at the viscosity limitation of the mixer. The limitation can be determined with a viscometer or by observing the vortex in the mixer. If the viscometer is used to determine the limitation of the mixer, the viscosity of the paste should not exceed:

$$\theta = 60 + \frac{1}{2}(\text{rpm}) \quad (\text{equation 1})$$

Where θ is the angle of deflection, and rpm is the rotation speed of the viscometer. The vortex that is formed in the mixer is used by chemical operators as an indication of the viscosity of the saltcrete paste. When only salt and brine are in the mixer, the vortex is 12" to 18" deep. When the viscosity limit of the mixer is reached, the vortex is less than a few inches. If the vortex is observed for a visual determination, the limitation of the mixer is where the vortex is less than two inches. (Markers on the mixer shaft may help make visual determinations.)

The purpose for doing lab-scale tests was to predict how the full-scale process would behave. The lab-scale tests for free water agreed with the full-scale tests for the determination of the maximum water content. However, the minimum water content determinations differed significantly. The full-scale minimum water content is 2 wt% less than the maximum water content, whereas the predicted minimum from the lab-scale studies was 1 wt% less. Enough information can be obtained from the first three batches of a production run to establish a new operating envelope.

3.2.3 Contingencies

Contingencies for two improbable events were considered: first the failure of the spray-drier, and second, the unlikely lack of a disposal site for a long period of time. These represent the extremes in the water content of the formulation. In the event that the spray-drier fails and requires repairs lasting several months, saltcrete can be made with saturated brine and cement (the formulation is given in Table 3.2-2 and Figure 3.2-3). In the event that no disposal site is available for several years, there are alternatives to making saltcrete such as the storage of concentrated brine or compacted spray-dried salt (see Appendix 9). Both the pure salt and the concentrated brine can be made into saltcrete. These alternatives require the purchase of capital equipment and changes to RCRA permits.

4.0 Conclusions and Recommendations

4.1 Conclusions

The general conclusion is that the current process needs very little change to produce a well-documented, certifiable product. The recommendations are meant to make minor improvements to the testing, documentation, and operation of the process. The methods to cope with waste that does not meet waste acceptance are also included. Another conclusion is that the waste will change with time. Means to adapt the process to a changing waste stream are also recommended.

4.1.1 Cementation is an Adequate Treatment

Cementation is an adequate treatment for the solidification of Building 374 salt because the waste acceptance criteria (WAC) for disposal at the Nevada Test Site (NTS) and Envirocare of Utah are satisfied. The WAC that are affected by the saltcrete mixing process are free water, particulate matter, and EPA treatment standards. The EPA treatment standards are met according to a report by HNUS (HNUS, 1992). This report is scientifically valid though not legally defensible because some of the documentation and data validation were not performed. No free water has been observed in any of the sampling efforts (petrology study, and HNUS sampling). No significant amounts of dust or particulate matter have been reported either (petrology study, HNUS sampling).

Alternatives to treating the waste, such as storing the untreated brine or the untreated salt, were evaluated (Appendix 9). Storing the untreated waste is feasible if no disposal site is available or possibly if the wastes were reclassified from low level mixed waste (LLMW) to strictly low level waste (LLW).

4.1.2 The Untreated Waste Nearly Meets EPA Treatment Standards

Chemical analysis of the pure, untreated salt shows that the untreated waste nearly meets treatment standards and does not have the toxic characteristic. (Lockheed data, Appendix 2) These analyses were not done for the purpose of providing legally defensible data, so definitive statements cannot be made about legal issues. When the toxicity characteristic leaching procedure (TCLP) was performed on two samples, nickel was the only metal above the treatment standard with an average concentration of 0.380 mg/l in the TCLP leachate. The TCLP limit is 0.320 mg/l in the leachate.

4.1.3 Expansion is the Main Technical Issue

A portion of the saltcrete wasteforms expands after the cement has hardened and the container is sealed. The expansion can cause the plywood containers to bulge and breach the caulked seal. Containers with breached seals do not meet the Rocky Flats Plant (RFP) standard SX-211, and thereby do not meet the criteria for "strong, tight containers", a DOT requirement, in the judgment of plant personnel.

The observations by personnel in charge of storing the waste indicate that expansion occurs three to six months after treatment. Measurements of the waste forms indicate that expansion from year to year is insignificant after the initial expansion.

There are two phenomena that occur in conjunction with the expansion, porosity and the formation of darapskite. Porosity can be controlled to an extent by minimizing water content. The formation of the darapskite is a complex chemical process which can be reduced by limiting the waste loading to 30 wt% and thereby limiting the chemicals required to form darapskite. Controlling the chemical reactions that cause darapskite to form is more complex than making allowances for the expansion.

4.1.4 Documentation and Test Procedures Need Improvement

- Determining the water content of the brine by using a hydrometer leads to errors in the water content of the final waste form. The hydrometer error has been observed to be approximately 0.67 wt% of the final waste form. Since the minimum water content of the waste form is 2 percent less than the maximum water content, the hydrometer error can amount to 1/3 of the range.
- Setting of the final wasteform is qualitatively tested by resistance to penetration of a steel rod that is pressed against the waste by hand. Since all of the sampled wasteforms were solid, this method does not detract from the quality of the wasteform. However, no record is made of the test.
- No record of observation for free water of particulate material is made either.
- All records are generated manually. This does not compromise the quality of the data, but a data acquisition system for the key parameters would lend credence to the records by providing a redundant set of records.

4.1.5 The Waste Forms Are Not Always Homogeneous

Some cores extracted from the saltcrete were not well mixed based on the darapskite concentration and visual observations. However the sampling and analysis shows that the waste meets WAC for NTS and Envirocare, so this is not critical as long as concentrations of hazardous chemicals remains low.

4.1.6 The Chemical Nature of the Waste will Change

The chemical constituents of the waste have changed since the mission of the plant has changed. Since the plant operations will change in the future, the chemistry will likely change again.

4.1.7 The Optimum Formulation May Change

The best treatment may change as the chemistry of the waste changes.

4.2 Recommendations

4.2.1 Solidify the waste with cement using the formulation given here as a baseline treatment.

Water	30 percent by weight of the final waste form
Salt	30 percent by weight of the final waste form
Type I/II cement	30 weight percent of the final waste form
Class F flyash	10 weight percent of the final waste form

Mix this thoroughly (five minutes of mixing is recommended) , then add cement in 40 to 50 pound increments until the paste is at the viscosity limitation of the mixer. The limitation can be determined with a viscometer or by observing the vortex in the mixer. If the viscometer is used to determine the limitation of the mixer, the viscosity of the paste should not exceed:

$$\theta = 60 + \frac{1}{2}(\text{rpm}) \quad (\text{equation 1})$$

Where θ is the angle of deflection, and rpm is the rotation speed of the viscometer. If the vortex is observed for a visual determination, the limitation of the mixer is where the vortex is less than two inches. (Markers on the mixer shaft may help make visual determinations.)

4.2.2 Modify the piping in Building 374 to allow two tanks, tank 826-C and 826-A, to be isolated as independent feed tanks for the saltcrete process. A full tank is enough to supply the process for approximately eight months.

4.2.3 Lab-scale tests.

Perform lab-scale tests for saltcrete water content, viscosity, and set time once for each tank of brine that is treated. Then test the formulation with full-scale equipment. The methods for the recommended tests are in Appendix 11. The results from these can be used to confirm the baseline formulation or to modify it slightly.

4.2.3.1 Determine the maximum water content by testing for the formation of bleed water. If no visible layer of water forms in a 50 ml test tube, then water will not likely form in the full-scale crates. Perform this test with the following .

Component	Wt %	Wt %	Wt %	Wt %	Wt %
Water	29.0	29.5	30.0	30.5	31.0
Salt	30.0	30.0	30.0	30.0	30.0
Cement + Flyash	41.0	40.5	40.0	39.5	39.0

Cement + flyash is 3 parts cement, 1 part flyash.

Estimate the minimum water content by subtracting 2% from the maximum water content.

To determine the true minimum water content, a full-scale test is necessary.

4.2.3.2 Perform the set time test to estimate the time required for the full-scale crates to harden. Lab-scale samples of type I/II cements require 1½ times as long as the full-scale crates. Lab-scale samples of type V cement require 3 times as long as the full-scale crates. Perform the set time test with three samples made with the maximum amount of water.

4.2.3.3 If the lab-scale tests indicate the formulation will effectively solidify the waste, perform a full-scale test. Mix two batches with the maximum water content, then add cement until the viscosity limitation of the mixer is reached. Mix one batch at the minimum water concentration and one at the maximum salt concentration for verification.

4.2.3.4 If the lab-scale tests indicate problems, test other formulations varying the concentrations of salt, water, cement, flyash, and by using type V cement. A maximum waste loading of 30 wt% is strongly recommended.

4.2.4 Recommendations to improve the mixing operation.

4.2.4.1 Base the amount of the individual components on the solids content of the brine. Currently, the components are based on a calculation of the solids content of the brine. A direct determination of the solids content is more accurate. Perform this test once per shift.

4.2.4.2 Mixing can be improved by lengthening the mixing time and by adding the last 100 - 200 pounds in stages. Add the baseline formula to the mixer. Mix this thoroughly (five minutes of mixing is recommended), then add cement in 40 to 50 pound increments until the paste is at the viscosity limitation of the mixer. Mix thoroughly after each addition of cement.

4.2.4.3 Install a larger motor and impellers to improve mixing.

4.2.5 Recommendations to improve documentation and testing.

4.2.5.1 A hydrometer can be used to detect changes in the solids content of the brine. Perform this test once per crate.

4.2.5.2 Use an in-line nuclear densitometer to detect changes in the specific gravity of the brine. This instrument can be used to continuously.

4.2.5.3 Since the moisture balance is more accurate than the densitometer and the hydrometer, but requires several minutes to obtain data, the recommendation is to rely on it for accuracy, but perform the test once per shift. Since the densitometer monitors specific gravity continuously and can be used to provide a permanent record when used in conjunction with a data acquisition device, it is intended to provide a means to detect changes in solids content and to provide data to verify the written records. The hydrometer is recommended to provide redundant information.

- 4.2.5.4 Use a data logger to record the weight of the saltcrete components to provide documentation of the process and to provide a redundant record.
- 4.2.5.5 Manually record the weight of the saltcrete components, as is currently done so the process will have two sets of records.
- 4.2.5.6 Zero the saltcrete mixing system weight indicator after each component is added. This is so over runs or under runs of one component are not compensated by the next component to be added.
- 4.2.5.7 Monitor the temperature of the crates to determine when the cement has hydrated. Wait three days after the temperature peak or until the temperature returns to 40°C whichever takes longer. This is to provide a record that the treatment was complete. It also is a better indicator of the condition of all three batches in a crate than testing the hardness of the top layer as is currently done. Testing the hardness of the top layer is recommended to provide redundant records.
- 4.2.6 Recommendations to reduce the effects of wasteform expansion.
- 4.2.6.1 Place a 2-inch spacer in each end of the crates. The spacer (engineering drawing # 51224-0001) allows the saltcrete to expand without damaging the ends of the box.
- 4.2.7 Recommendations to improve out-of-specification wasteforms.
- 4.2.7.1 If bleed water collects on the top of the wasteform during the curing period, use a vacuum to remove the excess water.
- 4.2.7.2 If more than one percent of the total weight of the wasteform is fine particulate matter, use a vacuum to remove the particulates.
- 4.2.7.3 If the crate is damaged, repair or overpack the crate.
- 4.2.8 If wasteform expansion continues to be a problem perform another petrology study.
- 4.2.9 Sample Collection
- 4.2.9.1 Install a sample splitter in a pneumatic transfer line for collecting spray-dried salt.
- 4.2.9.2 Install a sample splitter in a pneumatic transfer line for collecting cement.
- 4.2.9.3 Implement the sampling and analysis plan #1-100000-EWQA-1.6.1 Addendum 2, Rev. 2 to determine LDR compliance.

5.0 References

Oldshue, J. Y., "Fluid Mixing Technology," McGraw-Hill Publications, New York, 1983

Uhl, V. W., and Von Essen, J. A., Mixing Theory and Practice Vol III," Academic Press, 1986

Conner, J. R., "Chemical Fixation and Solidification of Hazardous Wastes," Van Nostrand Reinhold, 1990

HNUS report "Saltcrete Waste Characterization Report, deliverable 224C-Rev.)", October 1992

U. S. Department of Energy Nevada Field Office and Reynolds Electric & Engineering Co., Inc., "Nevada Test Site Defense Waste Acceptance Criteria, Certification, And Transfer Requirements, NVO-325 (Rev. 1)," June 1992

Code of Federal Regulations 40 CFR 261

APPENDICES

APPENDIX 1	Department of Transportation (DOT) Oxidizer Determination
APPENDIX 2	Lockheed Analytical Laboratory, Table of Chemical Data
APPENDIX 3	Petrology Study, Reports from: D. A. Armentrout, EG&G, Halliburton Energy Services, and U. S. Army Corps of Engineers
APPENDIX 4	Lab-Scale Operating Envelope Data
APPENDIX 5	Full-Scale Operating Envelope Data
APPENDIX 6	Time of Set Data
APPENDIX 7	Freeze/Thaw
APPENDIX 8	Recommended Instrumentation
APPENDIX 9	Saltcrete Alternatives Study
APPENDIX 10	Measurements of Expanded Crates
APPENDIX 11	PUBLISHED UNDER A SEPARATE COVER
TEST METHODS	A Draft Procedure for Determining: Specific gravity by hydrometer Moisture content of brine using a moisture balance Viscosity Free water formation Time of set Freeze/thaw cycling Monitoring the deformation of wooden crates Department of Transportation Oxidizer Test

APPENDIX 1

DEPARTMENT OF TRANSPORTATION (DOT) OXIDIZER DETERMINATION

INTEROFFICE CORRESPONDENCE

DATE: November 18, 1993

TO: E. C. Garcia, Technology Development, Bldg. T130C, X5980

FROM: R. H. Getty, Materials and Surface Technology, Bldg. 881, X4632 *RLK*
S. C. Jorgensen, Waste Projects, Bldg. 881, X5393 *SCJ*

SUBJECT: SALTCRETE DOT OXIDIZER TEST - SCJ-024-93

INTRODUCTION

The salt waste stream generated by Building 374 liquid waste treatment using a spray-drying process was found to be a Department of Transportation (DOT) oxidizer when the plant was in production. Recent characterization of the waste since curtailment of production operations indicates it has a lower concentration of nitrate ion, the constituent that caused the salt to be an oxidizer. The DOT test (Appendix F to 49 CFR 173 - Guidelines for the Classification and Packing Group Assignment of Division 5.1 Materials) was performed to see if the salt waste is still an oxidizer. The reason for the oxidizer determination is to see if the material will promote combustion if there were a transportation accident that caused a fire.

The implication of the test is two-fold. If the salt is an oxidizer, the untreated material must be stored in a special building. If the salt is a DOT oxidizer, then it is considered by EPA to have the reactive characteristic under RCRA. The option to store the untreated salt could save storage space if a disposal site does not open.

EXPERIMENTAL

The official DOT determination has been changed since the last time that the spray-dried salt was tested. The oxidizer test reported in RFP-3919, "Nitrate Salt Immobilization Process Development and Implementation, November 1986," is not the official test now. The previous test required a five pound mixture and a flame source. The current official DOT test is a scaled down version. The current test is performed by igniting a 30 gram mixture of material and sawdust with an electric hot wire. The rate at which a reference material and sawdust burns is compared to the rate at which the salt waste mixed with sawdust burns. The reference material is mixed 1:1 by weight with the sawdust, while the salt waste is mixed at 1:1 and at 4:1. Each mixture is tested three times, for a total of nine tests. The ambient temperature and relative humidity have bounds for the test to be valid.

DOT OXIDIZER TEST

Test Number	Material Tested	Material Wt: Sawdust Wt	Duration of Burn	Nitrate Ion, %	Sample Number	Sample Date	Date Tested	Dry Bulb deg. C	Wet Bulb deg. C	Relative Humidity, %	Comments
1	Ammonium persulfate	1:1	1:43	--	Reference	--	10/19/93	22	15	48	Sawdust, ref. material not well mixed.
3	Ammonium persulfate	1:1	1:05	--	Reference	--	10/19/93	22	15	47	Better mix, smaller particle size ref. matl
5	Ammonium persulfate	1:1	1:00	--	Reference	--	10/20/93	21	14	47	Better mix, smaller particle size ref. matl
	Mean		1:16								
2	Spray-dried salt	1:1	4:00	31	2-71952	2/11/93	10/19/93	22	15	48	Highest known recent nitrate conc.
4	Spray-dried salt	1:1	2:00	31	2-71952	2/11/93	10/20/93	21	14	47	Highest known recent nitrate conc.
6	Spray-dried salt	1:1	2:00	31, est	2-71933	2/11/93	10/20/93	21	14	47	Est. from sample collected same day
	Mean		2:40								
7	Spray-dried salt	4:1	3:30	22	D-884	10/1/91	10/20/93	21	14	47	Used this sample for quantity availability
8	Spray-dried salt	4:1	2:25	22	D-884	10/1/91	10/20/93	21	14	47	Used this sample for quantity availability
9	Spray-dried salt	4:1	2:50	22	D-884	10/1/91	10/20/93	21	14	47	Used this sample for quantity availability
	Mean		2:55								

Relative humidity calculations from Brent Bowen, X3222, RFP climatologist

APPENDIX 2

LOCKHEED ANALYTICAL LABORATORY, TABLE OF CHEMICAL DATA

FIRST SAMPLE SET																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											</
------------------	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	----

[illegible]

COMPARISON OF MASS SPECTROSCOPY TO ATOMIC EMISSION SPECTROSCOPY									
MS MINUS AES	DATE:	1-0116	1-0120	1-0124	1-0127	1-0128	1-0130	1-0390	1-0421
SAMPLE ID:	11/9/91	11/9/91	11/9/91	11/9/91	12/5/91	11/9/91	11/9/91	1/6/92	2/23/92
ANALYTE	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Sodium	-600	-1900	-1500	-310	-100	250	470	200	350
Calcium	610	640	-1900	-310	-100	250	470	200	350
Magnesium	610	640	-1900	-310	-100	250	470	200	350
Iron	-63	10	-151	84	-112	-26	-820	-182	-131
Aluminum	-20	10	-20	40	-5	88	24	220	616/92
Zinc	-8.1	-14	-22	45	-22	3.5	-31	-30	-29
Boron	0.3	-0.4	-2.8	22.3	-1	3.8	-4.7	-1.6	-3.4
Nickel	-0.1	-3.6	-7	42	-1.1	1.6	-2.2	-3.9	-2.2
Chromium	-0.1	-3.6	-7	42	-1.1	1.6	-2.2	-3.9	-2.2
Copper	-1.1	-1.4	-5	15.4	0.2	2.7	-1.2	-2.3	-2.3
Silver	6	6.7	1.3	6.8	6.2	74.9	5	1.2	2.7
Barium	-0.1	-0.8	0.8	19.7	1.6	2.1	1.1	-0.1	0.6
Manganese	0.5	-0.2	8.2	19.7	0.6	1.4	-7	-0.2	-0.5
Vanadium	0.5	-0.7	6.7	6.7	0.2	0.7	0.1	-0.3	3.7
Lead	-2.1	-3.6	-2.6	-4	-0.1	-0.7	-1.5	-0.1	-0.7
Cadmium	0.1	-0.1	-0.3	1.4	-0.1	0.7	-1.1	0.4	0.6
Cobalt	-0.2	-0.4	-0.2	1.3	0	-0.2	-0.2	0.5	0.2
Selenium	-7.8	-0.2	-0.2	1.4	-0.1	0.7	-1.1	0.4	0.6
Beryllium	-0.01	-0.1	-0.1	0	0	0.1	-0.04	0	0.03
Thallium									
Arsenic									
Mercury									
Antimony									
Silicon									
Strontium	-1	-2	-15	22	-5	11	3	-13	-1
Average difference MS minus AES									
Sodium									
Calcium	-285.283								
Magnesium	88.421								
Iron	-98.421								
Aluminum	35.053								
Zinc	-8.442								
Boron	1.700								
Nickel	1.895								
Chromium	0.478								
Copper	8.047								
Silver	0.827								
Barium	1.732								
Vanadium	0.713								
Lead	-3.017								
Cadmium	0.234								
Cobalt	0.014								
Selenium	-7.800								
Beryllium	0.088								
Thallium									
Arsenic									
Mercury									
Antimony									
Silicon									
Strontium									

APPENDIX 3

PETROLOGY STUDY, REPORTS FROM:

D. A. ARMENTROUT, EG&G,

HALLIBURTON ENERGY SERVICES,

AND,

U.S. ARMY CORPS OF ENGINEERS

Technology Development

ANALYSES OF SALTCRETE

by

D. L. Armentrout

TD94-DDT-001

August 16, 1994

EG&G Rocky Flats

ANALYSES OF SALTCRETE

by

D. L. Armentrout

TD94-DDT-001

August 16, 1994

EG&G Rocky Flats

Prepared Under Contract No. DE-AC34-90RF62349
Rocky Flats Operations Office U.S. Department of Energy

Approved: _____

D. J. Santi
(Manager, D&D Technology)

Date: _____

8-16-94

Distribution

J.M. Connell
E.C. Garcia
S.C. Jorgensen
J.C. Petersell
D.J. Santi
Library

KWIC Index

Saltcrete
X-ray Diffraction
Scanning Electron
Microscope

UNLI
REVIEWED FOR CLASSIFICATION

BY GLENN W BENETSON

DATE 8/16/94

INTRODUCTION

The Building 374 evaporator at Rocky Flats Environmental Technology Site (RFETS) processes low level mixed waste solutions to produce a slightly contaminated mixed waste salt. The mixed waste brine produced by the evaporator contains a mixture of many different salts that change in concentration from day to day. Some of the brine is further processed in a spray drier. For disposal, the brine, spray dried salt, and cement are mixed together to form saltcrete in concentrations that are approximately equivalent to 30% water, 35% salt and 35% cement. The saltcrete is poured into half-crates and allowed to cure. The cement binds together both the RCRA and the radioactive waste components. Contamination is not smearable from the surface of this waste form.

A problem has occurred during the curing process of some of the saltcrete. In a few instances, saltcrete expands and breaks the seals on half-crates. Decontamination and Decommissioning Technology (DDT) personnel were asked to perform analyses on this waste form. This report will describe the findings of the optical microscope analysis, the X-ray diffraction (XRD) analysis and the scanning electron microscope (SEM) analysis.

SPECIMEN PREPARATION

Sixteen core samples were taken from seven half-crates. Samples were obtained from three half-crates without a bulge, three half-crates with a bulge in the side, and one half-crate bulged at one end on the bottom. The cores are approximately 2.75" diameter by 15" long. A total of 54 sections were removed from the sixteen cores since the cores could not be removed in one piece from the half-crates. The samples were taken from three different batches, poured on October 7-8, 1992, January 4-5, 1993, and January 11-12, 1994.

In addition to the 16 core samples, eight lab-scale samples were received. Salts were used in approximately the same salt loading as used in the full-scale process. Samples were made from three different types of cement and two different types of fly ash. The lab-scale samples were poured into 1" diameter by 2" high cylindrical molds and cured at 55° C for 2.5 days. These samples were then subjected to either wet/dry cycling or freeze/thaw cycling.

Optical Specimen Preparation

Core samples were cut on a diamond wafering saw using methanol for a coolant. Specimens were cut about 2-5 mm thick. Outer edges of the core slices were usually removed to avoid damaged areas from the original coring process. Glass microscope slides were labeled and then the specimens were mounted on the slides with super glue. Specimens were allowed to cure for several minutes before the start of grinding and polishing. The petrographic specimen mounts were ground in a grinding machine with a 15 μ m diamond plate for a few minutes, using anhydrous ethanol as coolant. Specimens were ground down to a thickness of about 30 μ m (rough approximation since no accurate measuring system was available). Specimens were cleaned with ethanol and polished with 6 μ m diamond paste on a nylon polishing cloth. Polishing time was about 15 minutes or until visible scratches were mostly removed. Specimens were cleaned with ethanol. Final

polish was with 1 μm diamond paste on a nylon polishing cloth until fine scratches were not observed in the microscope

Specimens were cleaned with ethanol after the final polish and were etched for 60 seconds with a CDTA-ethanol solution (cyclohexanediaminetetraacetic acid disodium salt) and rinsed immediately with ethanol and dried. The CDTA solution chelates or reacts with the calcium to form a colored film over the specimen that greatly enhances the visibility of the cement crystals and non-crystalline phases. The samples were stored in a desiccator until ready for microscopic examination.

XRD Specimen Preparation

Core samples were cut on a diamond wafering saw using methanol for a coolant. A small piece from the center of the core was crushed with a mortar and pestle into sand size pieces. The saltcrete specimen was allowed to dry in a hood for several hours. After the specimen was dry, it was crushed again until no grit could be felt through surgeon's gloves. The specimen was packed into a glass sample holder for the Rigaku rotating anode X-ray diffractometer. A thin cover was used to prevent contamination of the instrument by saltcrete dust from the specimen. Either a mylar or a Teflon cover was placed carefully over the specimen to minimize the interference with the X-rays caused by the cover.

Two different conditions were used for the XRD data given in this report. For a general scan the following conditions were used:

- Copper target (rotating anode), 40 kV, 40mA, line focus
- Graphite diffracted beam monochromator
- Scintillation counter
- One degree divergence and scatter slits
- 0.034 degree receiving slit
- Mylar cover 3.6 μm thick
- Step scan 2-65° at 0.05° increments 2.0 sec/step

A number of peaks were observed between 20 and 40° two theta. Detailed scans were made between 20 and 40° two theta under the following conditions:

- Copper target (rotating anode), 40 kV, 80mA, line focus
- Graphite diffracted beam monochromator
- Scintillation counter
- One degree divergence and scatter slits
- 0.034 degree receiving slit
- Teflon cover 5 μm thick
- Step scan 20-40° at 0.02° increments 4.0 sec/step

SEM Specimen Preparation

Core samples were cut on a diamond wafering saw using methanol for a coolant. A rectangular piece from the center of the core was cut and labeled. The saltcrete specimen was allowed to dry in a vacuum of better than $1 \cdot 10^{-3}$ Torr overnight. The rectangular

specimen was fractured in two pieces, and one of the fracture surfaces was etched in a maleic acid and methanol solution. The two fracture surfaces were mounted side by side for examination in the SEM. After mounting, the samples were coated with a thin layer of gold in a sputter coater. All specimens were stored under a vacuum of better than $1 \cdot 10^{-4}$ Torr.

The SEM has an energy dispersive X-ray (EDX) detector that can be used for obtaining semi-quantitative elemental analysis for elements with an atomic number higher than nine. The EDX detector was used to identify phases in the field of view and to obtain the element compositions of the specimens. The EDX elemental composition analysis program assumes that the specimen is flat. In order to obtain an accurate elemental analysis the flat powder sample from XRD analysis was used for the elemental analysis. A conductive foil was placed around the outside of powder sample to improve electrical conduction, and no cover was used. Containment of the specimen was achieved by packing the powder in a glass slide and examining the specimen in a secured horizontal position.

RESULTS

The three different types of analyses used in this report were decided upon as reasonable for evaluating the expansion problem by DDT, Halliburton Energy Service, and U.S Army Engineer Waterways Experiment Station scientists and engineers. These methods compliment each other to provide a detailed description of the cement hydration and identification of expansive phases. Optical microscopic examination can reveal amounts of cement hydration, presence of microcracking and micropores, and the identification of some crystalline phases. XRD is used strictly for phase identification. The SEM can identify crystalline phases in cracks, which is very helpful in recognizing expansive phases. Results from each type of analysis will be discussed separately below.

Optical Microscope Results

Microscopic examination of the specimens generally consisted of two methods, polarized transmitted light and reflected light. Both of these examinations were performed on the same microscope that was equipped with both types of light systems. Polarized transmitted light examination uses a polarizer above the specimen and another below the specimen in the transmitted light path. Reflected light examinations were used with the vertical illuminator that projects a focused beam of high intensity light through the objective lens onto the surface of the specimen. This technique is particularly useful for examining the degree of hydration of the cement and showing some of the microcracks or micropores in the sample.

Microscopic examinations of 22 specimens were performed with photomicrographs taken of most specimens. Photomicrographs were taken with a video camera mounted on the phototube of the microscope. The video camera sends the signal through a computer with image processing and character generator to a video printer and a monitor. Photomicrographs were prepared by the video printer and images were also stored in the

computer. Magnifications were calibrated yielding images on the video printer that were approximately twice the microscope magnification.

A large number of color micrographs from saltcrete were presented and discussed in Reference 1. Polished sections of saltcrete showed some degree of cement hydration in all of the specimens. The amount of cement hydration appeared to increase with the age of the saltcrete half-crates. None of the samples showed complete hydration of the cement. Many microcracks were also observed in the saltcrete sections. Inside many of the cracks were crystalline phases that appear to be the cause of the cracks. Many microvoids and micropores were found in the specimens.

XRD Results

Although care was taken to minimize the effects of the two different covers used, there were some diffraction peaks resulting from the covers. A diffraction pattern from just the Teflon cover is shown in Figure 1. The two small peaks in Figure 1 overlapped two peaks from the saltcrete. For all data a correction was made for the two Teflon peaks by subtracting the intensities from the saltcrete data. A diffraction pattern from just the mylar cover is shown in Figure 2. There is a large mylar peak at approximately 26° two theta. Since this peak overlaps several saltcrete peaks, data from a Teflon cover was used instead of 20 - 40° two theta data using a mylar cover. X-ray diffraction patterns of a specimen from a bulging half-crate with pour date of October 7, 1992 are shown in Figures 3 & 4. Table 1 contains a summary of the XRD peaks observed and their intensities for a number of different half-crates and lab-scale samples. The D-spacing values are given in Angstroms and the intensity values are given in counts/second referenced to 40 mA. Identification of most of the XRD peaks is included in Table 1. No match was found for the minor peaks with no identification listed in Table 1.

One of the most common expansive phases in cement is ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_3, \text{SiO}_4, \text{CO}_3)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$]. Ettringite has a large D-spacing peak at $9.67\text{\AA}$ and XRD is particularly sensitive to this phase. No ettringite was observed in any of the XRD patterns obtained from the saltcrete half-crates or lab-scale samples.

Figure 1 - X-ray diffraction pattern of a Teflon cover used in this report. The two peaks are labeled with D-spacing values and intensities.

Figure 2 - X-ray diffraction pattern of a mylar cover used in this report. The two peaks are labeled with D-spacing values and intensities.

Figure 3 - X-ray diffraction pattern from a bulged area of a half-crate made 10/7/92. A mylar cover was used and the peaks are labeled with D-spacing values.

Figure 4 - X-ray diffraction pattern from a bulged area of a half-crate made 10/7/92. A Teflon cover was used and the peaks are labeled with D-spacing values.

Table 1

X-ray Diffraction Lines for Saltcrete Samples

D-space	SCR	SC-35	SC-25	SC-50	SC-48	SC-13	SC-10	SC-17	SC-40	SC-37	SC-31	LS-7c	LS-1	LS-4c	Phases	D-sp	<I>
10.340	659.0	375.3	630.1	544.0	584.2	459.2	233.3	388.4	900.2	369.3	460.1				Darapskite	10.301	100
7.940	385.8	253.0	332.6	441.4	403.2	402.2	261.6	344.5	272.5	241.3	196.4	216.1	495.5	313.3	Ca ₄ Al ₂ O ₆ Cl ₂ · 10H ₂ O + ()O ₄ (	7.891	100
4.913	1215.3	1855.3	1358.3	1577.1	1605.5	1197.7	683.8	1565.3	2273.2	1318.1	1478.4		718.4		Ca (OH) ₂	4.900	74
4.667								51.3				170.8	91.5	140.4	Na ₂ SO ₄	4.667	73
4.265												96.7		86.2	Na SO ₄	4.270	20
4.145	100.1	90.7	101.9	93.6	116.2	112.8	68.9	94.3	82.1	80.7	76.3				Darapskite	4.130	20
3.963				113.8	105.7				85.5	67.4	61.5		109.1		Na ₂ S ₅ O ₁₆	3.960	75
3.945	151.7	101.2	102.9			118.2	69.6	108.3				57.9		166.8	Ca ₄ Al ₂ O ₆ Cl ₂ · 10H ₂ O	3.940	80
3.890				40.4	43.6			47.5							Na NO ₃	3.890	6
3.871																	
3.837	114.8	79.4	79.9	86.7	77.7	89.4	52.6	78.6	68.3	57.5	51.7	63.6	99.9		Ca SO ₄ ?	3.840	13
3.776	96.0	75.9	87.1	87.5	104.3	78.3	92.3	64.3	96.9	139.6	105.4	74.8	39.0		K NO ₃	3.780	100
3.743	47.3	32.5	42.2	49.2	54.3	38.4	49.6	31.1	45.2	73.7	53.1				K NO ₃	3.730	56
3.673												37.1					
3.612									35.6		25.8						
3.589	70.9	44.9	38.3	58.0	70.7	57.6	55.3	50.6		53.7					Darapskite	3.590	12
3.528	195.1	126.4	102.5	115.9	129.0	150.0	105.8	113.6	107.7	94.3	75.3				Darapskite	3.530	18
3.465	134.9	116.0	112.5	141.3	174.3	175.3	109.1	119.7	142.5	128.9	79.9				Darapskite	3.460	35
3.392												33.7					
3.350												610.9		555.1	Na ₂ S ₅ O ₁₆	3.350	100
3.264	125.3	102.1	125.9	110.0	110.9	122.1	96.9	112.6	116.2	91.7	76.8	58.8	40.2	85.6	Na Cl + Darapskite	3.260	13
3.213									38.6								
3.204													35.6				
3.195	76.7	40.8	54.8	52.4	64.4	60.9	50.6	45.1		32.9	21.7				Darapskite	3.190	12
3.184												85.2		148.3	Na ₂ SO ₄	3.178	51
3.113	165.4	181.8	168.8	124.8	127.2	147.7	105.5	111.0	127.7	121.0	80.6		63.8		Ca (OH) ₂	3.112	23
3.074	143.7	98.2	98.6	76.4		79.8		51.1	75.4	71.0	39.2	146.6	49.8	291.5			
3.041	518.0	346.0	371.9	742.1	702.9	313.6	390.1	317.4	378.5	382.0	383.8	757.1	322.8	1320.3	Calcite +Na NO ₃ + K NO ₃	3.035	100
2.997	73.4	77.1	83.6						62.1		25.2						
2.976				100.9	84.6	66.5	136.2					64.4	49.9	148.7			
2.959	77.3	61.4	62.3			62.6			49.4	54.6							
2.932			45.6						44.5								
2.900	142.8												81.6	197.8	Ca SO ₄ ?	2.949	30
2.881	153.8	190.3	164.5	150.9	136.4	168.7	125.0	108.7	130.2	123.8	84.1	74.5			Ca ₄ Al ₂ O ₆ Cl ₂ · 10H ₂ O + ()O ₄ (	2.870	50
2.858	126.2	124.7	119.7	105.5	124.9	138.9	100.1	87.9	102.7	82.4	56.6				Darapskite	2.856	30
2.821	1022.4	849.5	882.9	881.4	795.6	882.0	659.0	597.1	712.9	826.8	698.4	497.3	314.8	1161.7	Na Cl	2.821	100
2.786	153.6	228.9	127.4	366.9	339.9	269.2	157.5	147.3	148.4	204.9	161.7	314.3	301.6	1426.3	Na ₂ SO ₄	2.783	100
2.751	79.0	118.1	241.4	235.2	199.5	150.6	183.8	80.7	92.1	185.2	90.8	198.1	320.2	322.6			
2.728													64.0				
2.718	71.6	74.4	68.8				59.0	39.7	59.9	60.5		62.1					
2.694														171.4			

Table 1 Continued

D-space	SCR	SC-35	SC-25	SC-50	SC-48	SC-13	SC-10	SC-17	SC-40	SC-37	SC-31	LS-7c	LS-1	LS-4c	Phases	D-sp	<I>
2.669	75.1	76.2	75.6	68.2	78.3	77.2	72.3	50.7	68.4	70.5	63.2				Darapskite	2.667	8
2.653												136.8	107.2	223.2	K NO3 + Na2 SO4	2.647	55
2.630	904.4	923.3	856.6	684.5	606.6	738.3	500.7	619.2	731.0	605.1	463.8		376.6		Ca (OH)2	2.628	100
2.613												248.2	223.3	266.1			
2.596	89.4	97.2	78.4	97.8	110.4	95.4	87.1	72.6	67.6	66.7	45.3				Darapskite	2.594	30
2.577	47.9		58.8	51.9				27.0	86.5								
2.544											31.7						
2.536	66.1	42.4	48.5	63.2	65.5	47.0	41.9	39.6	34.9	45.3		46.3		90.3	Na NO3 + Darapskite	2.530	10
2.500												48.7		104.6			
2.448	128.4	99.0	101.3	91.5	91.1	91.9	88.1	85.7	88.6	87.3	88.6	73.8	94.1	277.7	Ca (OH)2 + Darapskite	2.447	3
2.333	152.1	99.1	97.5	77.2	81.1	107.3	87.7	76.8	69.7	78.7	71.7	103.0	172.5	222.8			
2.314	92.8		69.7	126.3	114.5	58.4	58.6	66.1	81.2	70.4	66.6	97.6	54.5		Na NO3	2.311	25
2.288												83.4	45.8	185.8	Calcite	2.285	18
2.190	61.9	72.1	146.1	150.7	153.1	99.4	105.4	78.7	129.8	117.0	168.1	125.3	175.4	88.2	K NO3	2.192	41
2.136												47.1		57.9	Na NO3	2.125	10
2.102												65.9		143.0	Calcite	2.095	18
2.050							41.0		39.2	52.8					Darapskite ?	2.072	12
1.995	409.7	359.4	417.8	382.3	327.7	337.0	255.3	280.1	331.8	311.6	314.9	205.0	144.9	228.9	Na Cl	1.994	55
1.939			213.5				143.4							65.1	Darapskite	1.938	10
1.932												62.7					
1.928	380.4	412.5	374.1	405.8	297.8	287.1	218.7	285.5	358.8	309.6	238.2		186.0		Ca (OH)2	1.927	42
1.912													96.8				
1.904									58.7								
1.877														73.8	Na2 SO4	1.864	31
1.797	225.3	215.2	217.2	158.2	132.3	182.3	136.7	149.4	185.1	155.7	123.6		104.1		Ca (OH)2	1.796	36
1.777		72.4	40.4		104.2	73.8			55.7	56.0					Darapskite	1.774	12
1.768				141.2			444.3	57.8		66.1		157.3	118.8	78.1			
1.760											63.8						
1.736				67.5		60.8			90.7						Darapskite	1.728	10
1.686	115.5	126.6	131.1	103.0	85.9	111.0	78.0	108.2	102.3	91.5	68.6		69.4		Ca (OH)2	1.687	21
1.630	138.4	150.4	169.7	214.8	145.3	123.6	126.2	111.8	112.2	121.0	110.2	142.5	93.7	102.1	Na Cl	1.628	15
1.551						70.5	87.7				65.1						
1.490		135.8										75.2		79.8	Na NO3	1.488	2
1.484	72.6	90.9	87.4	92.7	66.9	63.1	59.3	59.2	68.0	54.3	54.4		46.6		Ca (OH)2	1.484	13
1.448	108.2	121.7	122.8	84.5	74.8	81.3	53.0	77.4	90.8	75.0	54.2		51.5		Ca (OH)2	1.449	13
* DW Int	18.4	14.8	17.2	17.4	20.3	18.4	11.8	14.4	19.4	13.6	12.2	0.0	0.0	0.0			
Cre. Date	Oct-92	Oct-92	Oct-92	Jan-94	Jan-94	Jan-93	Jan-93	Jan-93	Oct-92	Oct-92	Oct-92						
Core Dis.	Scrap	G Cen	B End	B End	G Aft B	B End	B Opp	G Cen	B End	B Cen	G Cen	V - F	I/I	I - C			
Samp. #	SCR	SC-35	SC-25	SC-50	SC-48	SC-13	SC-10	SC-17	SC-40	SC-37	SC-31	LS-7c	LS-1	LS-4C			

* Darapskite weighted intensity from four strong non-interfering darapskite lines.

SCR = Top scrapings from a crate, G cen = Non-bulged half-crate from center, B end = Core from bulged area of half-crate,

G Aft B = Core from non-bulged half-crate but bulged after removing from crate, B Opp = Core taken from the opposite end of the bulge

B Cen = Core from center of half-crate with a bulge in one end, V - F = Type V cement with class F fly ash, I/I = Type I/I cement no fly ash,

I - C = Type I cement with class C fly ash.

SEM Results

The SEM has a high resolution capability with a large depth of field that makes it well suited for examination of fracture surfaces. The EDX detector on the SEM allows for identification of phases from the elemental composition. Examination of saltcrete focused mainly on: 1) identifying phases in microcracks on the fracture surface, 2) locating some of the phases identified with XRD, and 3) performing elemental analysis on flat powder specimens used in XRD. The first part of the examination showed repeatedly that the mineral phase Darapskite $[\text{Na}_3(\text{NO}_3)(\text{SO}_3) \cdot \text{H}_2\text{O}]$ could be found in many microcracks Figures 5-7. Darapskite could also be found growing in microvoid caused by small pockets of unmixed brine shown in Figure 8. Microvoids from brine formed crystals along the surface of the microvoid while microvoids from gas generation had no crystal growth in the void. In some cases Darapskite was found with potassium nitrate (KNO_3) shown in Figures 9 and 10 or with calcium aluminate chloride hydrates ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ or $\text{Ca}_4\text{Al}_2\text{O}_4\text{Cl}_2 \cdot 10\text{H}_2\text{O}$) shown in Figure 11. Other phases found include $\text{Ca}(\text{OH})_2$ in Figure 12, NaCl in Figure 13, and CaSiO_4 in Figure 14. Results from the elemental analysis on flat powder specimens used in XRD is given in Table 2.

Analyses of the lab-scale specimens were also important since these samples were expansive and no Darapskite was found in these samples. The calcium aluminate chloride hydrates ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ or $\text{Ca}_4\text{Al}_2\text{O}_4\text{Cl}_2 \cdot 10\text{H}_2\text{O}$) are suspected to cause the expansion in the lab-scale specimens. These two phases cannot be distinguished with the EDX since oxygen is not detected. Figure 15 shows calcium aluminate chloride hydrates in a lab-scale specimen. In Figure 16 a microvoid is shown in a lab-scale specimen with a large number of cracks. Microvoids in the saltcrete can either be trapped water or gas. If the microvoid contain salt crystals then it probably contained a water salt mixture.

Figure 5 - The center of this picture shows darapskite crystals growing in a cement matrix. The micrograph is an secondary electron images from an SEM.

Figure 6 - The same area as Figure 5 is shown in this sulfur X-ray map. The darkness of the dots increases as more sulfur is detected in a region. The majority of the dots away from the darapskite are a result of background radiation.

Figure 7 - In this secondary electron image many cracks are shown in the cement matrix around some darapskite.

Figure 8 - Darapskite, shown in this secondary electron image, has grown into a microvoid that was once filled with brine.

Figure 9 - Darapskite crystals are shown with some potassium nitrate crystals growing in a cement matrix. The micrograph is an secondary electron images from an SEM.

Figure 10 - The same area as Figure 9 is shown in this potassium X-ray map. The darkness of the dots increases as more potassium is detected in a region. The map shows the location of the potassium nitrate phase.

Figure 11 - Darapskite is shown on the left with some flakes of calcium aluminates chloride hydrates on the right. This sample was etched with maleic acid.

Figure 12 - The plate like crystals shown in this micrograph protruding out of the surface are calcium hydroxide crystals.

Figure 13 - A microvoid is shown in this micrograph that is completely lined with sodium chloride. The void shown was once filled with a sodium chloride brine that later formed these crystals.

Figure 14 - The round particle in the center of this micrograph is a calcium silicate particle.

Figure 15 - The stick like structures in this micrograph are calcium aluminate chloride hydrates in a lab-scale 4c sample.

Figure 16 - The microvoids in the lab-scale sample 4c were full of shrinkage cracks as shown in this micrograph.

Table 2

Whole Sample Energy Dispersive X-ray (EDS) Analysis

Spray Dried Salt Apr 28, 94		SC-25 Bulged Area Oct 8, 94		SC-35 Non-bulging Oct 8, 94		SC-48 Non-bulging Jan 11, 94		SC-13 Bulged Area Jan 4, 93	
Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %
Na >	56.0	Ca	33.7	Ca	34.1	Ca	35.1	Ca	33.4
Cl >	23.9	Na	31.9	Na	31.8	Na	33.0	Na	33.0
K >	10.3	Cl	11.0	Cl	10.5	Cl	10.2	Cl	10.5
S >	6.1	Si	8.6	Si	9.2	Si	7.9	Si	8.5
Ca <<<<	2.2	K	6.6	K	6.0	K	5.3	K	6.0
Si <<	0.6	S	4.5	S	4.5	S	4.2	S	5.0
P >>	0.5	Al	1.3	Al	1.4	Al	1.4	Al	1.4
Al <<	0.2	Fe	0.9	Fe	0.8	Fe	1.1	Fe	0.9
Mg <	0.2	Mg	0.8	Mg	0.9	Mg	1.1	Mg	0.7
		P	0.7	P	0.8	P	0.7	P	0.7
SC-10 Opp. End Bulged Jan 4, 93		SC-17 Non-bulging Jan 5, 93		SC-40 Bulged Area Oct 7, 92		SC-37 Away from Bulge Oct 7, 92		SC-31 Non-bulging Oct 8, 92	
Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %	Element	Atomic %
Ca	33.6	Ca	34.8	Ca	33.8	Ca	34.3	Ca	35.5
Na	32.8	Na	32.0	Na	31.8	Na	31.3	Na	30.5
Cl	10.4	Cl	10.3	Cl	10.7	Cl	10.7	Cl	10.2
Si	8.7	Si	8.8	Si	8.8	Si	8.5	Si	9.3
K	5.6	K	5.5	K	6.3	K	6.6	K	6.0
S	4.9	S	4.8	S	4.7	S	4.5	S	4.5
Al	1.5	Al	1.4	Al	1.3	Al	1.4	Al	1.5
Fe	0.9	Fe	0.9	Mg >	1.0	Mg >	1.0	Mg >	0.9
Mg	0.9	Mg	0.8	Fe <	0.8	Fe <	0.9	Fe <	0.9
P	0.7	P	0.7	P	0.8	P	0.7	P	0.8
LS-7c Type V With Class F Fly Ash		LS-1 Type I/II Without Fly Ash		LS-4c Type I With Class C Fly Ash					
Element	Atomic %	Element	Atomic %	Element	Atomic %				
Na >	28.6	Ca	47.2	Na >	32.5				
Ca <	26.9	Na	20.6	Ca <	25.2				
Si >	15.2	Si >	11.8	Si >	12.4				
Cl <	8.1	Cl <	6.7	Cl <	8.8				
Al >>	6.7	K	3.8	Al >>	6.2				
K <	5.8	S	3.6	S	5.0				
S <	4.4	Al	2.4	Mg >>	3.7				
Mg >	2.5	Mg >	1.7	K <<<	3.6				
Fe <	1.1	Fe <	1.5	Fe <	1.2				
P	0.7	P	0.7	P	0.8				
				Ti +	0.4				

One ">" symbol is included with an element for each increase in element rank from the average rank.

One "<" symbol is included with an element for each decrease in element rank from the average rank.

The "+" symbol is included if the element is new and is not in average element analysis.

DISCUSSION

The optical analysis performed by Halliburton Energy Services and the SEM and XRD analyses performed by DDT agreed very well with one another. Microvoids, micropores, crystal growth in cracks, and crystal growth away from cracks were observed both in the optical microscope and the SEM. A considerable portion of the Portland cement had hydrated based on observations of thin sections in the optical microscope and XRD analysis. Phases observed with XRD analysis were also found in the SEM with the EDS detector.

The amount of hydration that occurred in the saltcrete is difficult to quantify with optical and XRD analyses. There are several reasons that support a considerable amount of Portland cement hydration. Optical microscope observation showed a number of partially hydrated grains of cement. Further evidence of hydration came from the identification of $\text{Ca}(\text{OH})_2$, CaCO_3 , and $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ and the absence of large amounts of unhydrated cement phases in the XRD analysis. Complete hydration was not observed in any of the thin sections analyzed with the optical microscope. The amount of hydration appeared to increase with the age of the saltcrete half-crates.

An expansive phase has a volume increase or a density decrease when it forms. Density alone is not enough to identify expansive phases that can bulge a half-crate. There must be additional evidence that the phase change occurred when the saltcrete had sufficient strength to bulge the half-crate. If the saltcrete does not have sufficient strength to bulge the crate, the saltcrete will expand upward in the unconfined direction. The expansive phase can form either during the curing process as water is absorbed by new phases, with a temperature change, or with a change in humidity of the environment.

The first expansive phase that was investigated was darapskite $[\text{Na}_3(\text{NO}_3)(\text{SO}_3) \cdot \text{H}_2\text{O}]$. Darapskite, as shown in Table 1, is generally present in higher concentrations in the cores taken from bulging area in the half-crates. Darapskite has a density of 2.20 g/cm^3 [2] while the three components of darapskite, sodium nitrate (NaNO_3), sodium sulfate (NaSO_4), and water (H_2O) in the proper ratios to form darapskite have a density of 2.28 g/cm^3 . Darapskite then will expand approximately 3.6% as it forms. Additional expansion can be caused by voids that are created as the darapskite forms. Darapskite can be made easily by mixing together the three components with an excess of water and allowing the mixture to dry. Darapskite is also the only double salt that can be formed from nitrate and sulfate. Figures 5 and 7 show that darapskite has been located in a region where there is a cracking in the matrix.

Cracking can only occur after the material has some set strength and it is caused by either expansion or contraction. Expansion cracking will have radial cracks emanating from an expansive phase, while contraction cracking will form either concentric rings around a contracting phase or crack as a dried up river bottom. Contraction cracking is shown in the microvoid in Figure 16, while expansive cracking can be seen in Figures 5 and 7 around the darapskite.

From Table 1, no darapskite was found in the lab-scale samples. There are other phases in the lab-scale samples that could cause expansion in these samples. In an earlier report done by the Waste Programs group where the lab-scale samples were originally investigated [3], a small expansion was observed during the wet/dry cycling while a large expansion occurred during the first freeze of freeze/thaw cycling. Two similar phases that could explain this type of expansion are calcium aluminate chloride hydrates ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ or $\text{Ca}_4\text{Al}_2\text{O}_4\text{Cl}_2 \cdot 10\text{H}_2\text{O}$). The $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ phase is stable only below 28 °C. During the first freeze/thaw cycling, the lab-scale samples were taken from the curing temperature of 55 °C measured for volume and then subjected to freeze cycle of -12 °C. If $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ is an expansive phase this would explain the volume increase during the first freeze cycle and the reason not much increase in volume was obtained during the wet/dry cycling at temperatures above 28 °C. The calcium aluminate chloride hydrates were present in both the lab-scale and core sample. They would have a tendency to break up the saltcrete as it cycles though the transformation temperature of 28 °C.

In Figure 13 a large amount of silicone was also detected. Silicone from an unknown phase appeared to be mixed in with the calcium aluminate chloride hydrates. The form of this phase and whether it could be expansive is not known. Table 3 summarizes the amount of expansion with the amount of calcium aluminate chloride hydrates, silicon, and aluminum. No trait was found that matched the behavior of expansion in the lab-scale samples. During collection of the XRD data, the room temperature was not measured. Since $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ changes phase near room temperature the amount of this phase is highly dependent on the temperature of the sample during analysis. The amount of the calcium aluminate chloride hydrates observed with XRD also did not follow amount of the limiting element aluminum in this phase. Because of this complicated behavior, a complete explanation for expansion in the lab-scale specimens is not known. Other phases could exist in the saltcrete that could cause harmful expansion.

Table 3
Expansion Comparison of the Lab-Scale Samples

Samp. #	Binder Composition	Expansion [3]	Calcium Aluminate Chloride Hydrates	Silicon Conc.	Aluminum Conc.
LS-7c	Type V with Class F fly ash	Small	Small conc.	Large	Large
LS-1c	Type I/II with no fly ash	Medium	Large conc.	Small	Small
LS-4c	Type I with Class C fly ash	Large	Medium conc.	Medium	Medium

Expansion of the saltcrete is finite and will decrease with time. The formation of darapskite requires the presence of sodium sulfate, sodium nitrate and water in equal molecular concentrations. If anyone of these three molecules is not present then darapskite cannot form. Darapskite cannot form in an excess of water since it is soluble in water. After enough of the cement has cured, absorbing excess water, darapskite can form. Once darapskite has started to form it will continue to form until it depletes the supply of one of the required constitute molecules. During the darapskite formation, any

addition of moisture through a high humidity environment will impede the growth of darapskite. The calcium aluminate chloride hydrates will form when the temperature is below 28 °C. Cycling of the temperature near 28 °C will cause the creation of some additional cracks and voids. After a few temperature cycles the expansion will decrease to zero.

CONCLUSIONS

- 1) The optical analysis performed by Halliburton Energy Services and the SEM and XRD analyses performed by DDT agreed very well with one another.
- 2) A considerable portion of the cement is hydrating in these cores.
- 3) Darapskite $[\text{Na}_3(\text{NO}_3)(\text{SO}_3) \cdot \text{H}_2\text{O}]$ causes much of the expansion in the saltcrete.
- 4) Calcium aluminate chloride hydrates ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ or $\text{Ca}_4\text{Al}_2\text{O}_4\text{Cl}_2 \cdot 10\text{H}_2\text{O}$) are phases that could expand and fatigue the saltcrete structure.
- 5) Other phases could exist in the saltcrete that could cause harmful expansion and damage the half-crates.
- 6) Expansion of the saltcrete is finite and will decrease with time.

RECOMMENDATIONS

A new capability has been established at Rocky Flats Environmental Technology Site to examine saltcrete and other cemented waste forms for hydration and expansive phase identification. The next logical step to take is to utilize this new capability to optimize the saltcrete process. The understanding that was gained during this study can be used to maximize the amount of waste salt placed in a half-crate and minimize the number of rejected half-crates.

REFERENCES

1. W.J. Caveny report, Cementing Method and Materials, Halliburton Energy Service, CCX-2102-94, May 18, 1994.
2. M.J. Redden, Master Thesis, The Crystal Structure of Darapskite, Massachusetts Institute of Technology, June, 1968.
3. J.M. Connell, A.M. Faucette, S.C. Jorgensen, J.H. Oldham, and K.M. Swan-Bogard report, Saltcrete Evaluation.

Note: The report by Halliburton Energy Services includes over 40 pages of color micrographs. Neither the black-and-white or the color copies of the micrographs were of sufficient quality to be included. Only the summary of the Halliburton report is included.

HALLIBURTON ENERGY SERVICES

DUNCAN TECHNOLOGY CENTER - DUNCAN, OKLAHOMA
A HALLIBURTON COMPANY

CEMENTING METHODS AND MATERIALS

PROJECT REPORT

This report is the property of Halliburton Energy Services and neither it nor any part thereof nor a copy thereof is to be published or disclosed without first securing the express written approval of laboratory management; it may however, be used in the course of regular business operation by any person or concern and employees thereof receiving such report from Halliburton Energy Services.

To: Mr. J.M. Connell
Mr. S.C. Jorgensen
Technology Development
EG&G Rocky Flats Plant
Golden, CO

CCX-2102-94
Final Report

July 26, 1994

Title: Solidified Waste Samples at Rocky Flats Plant, Colorado

Prepared by: Bill Caveny, Jerry Childs, Gant McPherson

PURPOSE

The purpose of this project was to perform microscopic examination on the solidified waste to determine cement hydration reaction with the waste materials.

CONCLUSION

A meeting was held at Halliburton Technology Center in Duncan, Oklahoma, July 6, 1994. Those present at the meeting were Dan Armentrout EG&G, Gant McPherson, Jerry Childs, and Bill Caveny, all with Halliburton Energy Services. The purpose of the meeting was to evaluate X-Ray diffraction (XRDA) and scanning electron microscopy (SEM) data collected from the cement solidified waste samples that have been cored for analysis in this project. The data evaluated had been collected by Dan Armentrout of EG&G.

General conclusion based on the X-Ray diffraction analysis and Scanning Electron Microscopy analysis generated by Dan Armentrout EG&G, and the Microscopy Analysis by polarized transmitted light, and reflected light microscopy, generated by Bill Caveny of Halliburton are as follows:

1. A considerable portion of the Portland cement has hydrated (based on formation of $\text{Ca}(\text{OH})_2$, $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, CaCO_3 , presence of amorphous cement gel phase pattern, absence of large amounts of unhydrated cement phases such as tricalcium silicate, etc., and microscopical observation and photograph of partially hydrated grains of cement).

LIMITATION OF LIABILITY: This report was prepared by and is the property of Halliburton Energy Services, a Division of Halliburton Company; the data reported is intended for the private information of the above named party; accordingly, any user of this report agrees that Halliburton shall not be liable for any loss or damage, regardless of cause, including any act or omission of Halliburton, resulting from the use of the data reported herein; and Halliburton makes no warranties, express or implied, whether of fitness for a particular purpose, merchantability or otherwise, as to the accuracy of the data reported.

2. Darapskite ($\text{Na}_3\text{NO}_3\text{SO}_4 \cdot \text{H}_2\text{O}$) may be responsible for some of the expansion of the cement solidified waste in the halfcrates (based on the XRDA identification and the tentative SEM and Light microscopy identifications of this material in core samples that had significant expansion).
3. $\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10(\text{H}_2\text{O})$ appears (by XRDA) to be more abundant in the samples exhibiting greater expansion. Possibly this compound may be contributing to the expansion (further investigations would be needed).
4. Due to the extremely complex and variable nature of the waste material and the numerous possible reactions with the hydrating cement, it is difficult to arrive at a set of positive conclusions and quantitative data.
5. Based on the observations in this investigation, it appears that the present solidification formulation may be improved for some of the nitrates wastes at the Rocky Flats Plant. In future projects, some changes which should be considered are:
 - (a) Determination of the water ratio where recrystallization of the nitrate and other salts is minimized. Controlled porosity and permeability systems can be formulated through the informed use of dispersants and adjustments in the particle size distributions of the solids involved.
 - (b) Evaluation of latexes in combination with Portland cement, high aluminate cement and/or ultra fine cement as solidification media.
 - (c) Evaluation of non-cement systems based on the cross-linking and vulcanization of latexes to encapsulate the nitrate salts in a rubber or plastic type environment.

cc: Ralph Voss
Larry Watters
Joe Sandy - ERC
Fred Sabins - Houston

Respectfully submitted,

Laboratory Analyst

HALLIBURTON ENERGY SERVICES

By Bill Caveny
Bill Caveny

By Jerry Childs
Jerry Childs

By Gant McPherson
Gant McPherson

js

LIMITATION OF LIABILITY: This report was prepared by and is the property of Halliburton Energy Services, a Division of Halliburton Company; the data reported is intended for the private information of the above named party; accordingly, any user of this report agrees that Halliburton shall not be liable for any loss or damage, regardless of cause, including any act or omission of Halliburton, resulting from the use of the data reported herein; and Halliburton makes no warranties, express or implied, whether of fitness for a particular purpose, merchantability or otherwise, as to the accuracy of the data reported.

SUBCONTRACTOR: Halliborton Energy ServicesACCRUAL MONTH AND YEAR: 7-94

1. EGAO SUBCONTRACT NUMBER	2. SUBCONTRACT STATEMENT OF WORK TITLE	3. TASK NUMBER (if Applicable)	4. AUTHORIZED FUNDS	5. TOTAL INCURRED COSTS THROUGH END OF PREV. MONTH	6. TOTAL INCURRED COSTS THROUGH END OF CUR. MONTH	7. FEE'S AT REP FACILITIES	8. FEE'S AT SUBCONTRACTOR FACILITIES
ASC38210 PA3	Saltcrete Petrology Study CIMP Treatment Systems		25181.00	22245.63	200.00	0-	0.0115
	Jerry Childs 2 hrs @ \$100/hr (Meeting in Dymally OK with Dave)	\$200.00		Mike, This closes out the cost for this project.			
	Armetroot of EG+G about progress of project.			Thanks for the business			
	Anticipate costs through end of month.	0-		Refers to Subcontract			
				Jerry Childs			
		200.00					

SUBCONTRACTOR'S SIGNATURE:

08/14/91

J. D. Childs