1 of 2

Technology Development

TECHNOLOGY DEVELOPMENT SALTCRETE EVALUATION

August 16, 1993

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Executive Summary

The objective of the project was to identify, define, and resolve the issues pertaining to the production of a certifiable cemented salt waste form ("saltcrete") using the existing cementation equipment in the Building 374 liquid waste treatment facility. This report describes the saltcrete process, issues precluding waste form certification, issues resolution where appropriate, and formulation optimization results. This report summarizes acceptance criteria, waste characterization, problem assessment, and formulation study results for the period October 1, 1992, to June 30, 1993.

The only certification issue related solely to the waste form is the long term integrity of the saltcrete containers. A portion of these containers no longer meet Department Of Transportation (DOT) standards for "strong, tight" containers. These containers were damaged by swelling of the saltcrete which, in turn, broke the seal made by the caulking in the nailed seams of the crates. A statistical analysis of the inventory produced since January 1990 revealed that:

- There was a 1 1/2 year period when the portion of swelling boxes was approximately 2%.
- This period coincided with the time when the target waste loading was 30 wt%.
- Higher waste loading increases the likelihood of bulging.
- Increasing water content increases the likelihood of bulging.
- Increased bulging coincides with higher waste loadings and with the replacement of the saltcrete load cells.

It is worth noting that much of the saltcrete was produced based on the premise that the solidified waste would have to be reprocessed; thus, Liquid Waste Treatment Operations took the most expeditious approach to solidifying the waste by increasing the waste load. Most of the saltcrete produced meets Nevada Test Site waste form acceptance criteria when the waste loading was maintained at 30 wt%.

Formulation studies indicate that different types of cement and fly ash influence the durability of the final waste form. Results of freeze/thaw testing showed that:

- Type I cement with class C fly ash caused swelling of 5% in length, (more than was observed for the halfcrates in storage).
- Type I/II cement, the type currently used in saltcrete production, swelled 2% in length (about the average of the swelling crates).
- Type V cement with class F fly ash reduced or eliminated swelling.
- Class F fly ash reduced or eliminated swelling.

The swelling of the saltcrete is likely due to a chemical reaction between sulfates and nitrates in the waste and tricalcium aluminate and calcium oxide in the cement. The swelling is aggravated by large temperature changes but is not influenced by changes in humidity. Cements with high tricalcium aluminate concentrations exhibited more swelling in the freeze/thaw test.

Many of the control parameters necessary for the certification, such as waste loading and water to cement ratio, may be determined from a statistical evaluation of historical data. These evaluations are scheduled for completion in fiscal year 1993. In the mean time, the target waste loading should be reduced to 30 wt% rather than the current 35 wt% waste loading because the lower waste loading consistently produced a certifiable product in the past. Once the operating range is established, the waste loading percentage may be readjusted.

Documentation and control of the process parameters are necessary for certification of the saltcrete. Process parameters that impact the operations or product quality, such as waste loading or water content, must be maintained within established control boundaries in order to certify saltcrete. The key process parameters identified in this study are:

- Waste loading;
- Water content;
- Tricalcium aluminate concentration in cement; and
- Calcium oxide concentration in fly ash (if recommended for production operations).

Waste load and water content are currently controlled by measuring the specific gravity of the brine using a hydrometer and measuring the component weights using load cells on the mix tank. In addition to the current documentation, the weight of the empty crates, the weight of the crates just after filling, the cumulative zero readout, and data acquisition systems to provide a confirmation of transcribed data are recommended. This will help establish process control and improve documentation. Currently, all of the data is manually transcribed.

Calibration of process instrumentation is also necessary for certification. Hydrometers, the saltcrete weighing system, and the floor scale should be calibrated regularly to provide defensible data and process control. In the case of the saltcrete weighing system, control of the process was lost and is the suspected cause of a number of swelling crates due to inaccurate waste loading. The hydrometers and the floor scale are currently calibrated, but the saltcrete weighing system remains uncalibrated.

Documentation of the waste treatment process can be improved by retaining an analysis of the cement (known as the mill run sheet) on file and by collecting a sample of the cement for bench scale testing and verification of vendor specifications. More stringent specifications need to be added to ensure consistent behavior of the cement.

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1.0 INTRODUCTION

1.1 OBJECTIVE

The objective of this project was to identify, define, and resolve the issues pertaining to the production of a certifiable cemented salt waste form ("saltcrete") using the existing cementation equipment in the Building 374 liquid waste treatment facility. This report describes the saltcrete process, issues precluding waste form certification, issues resolution where appropriate, and formulation optimization results. Waste characterization results are also presented. Results from process variability studies in support of development of a process control plan will be reported separately.

1.2 BACKGROUND

1.2.1 Description of Process

The Rocky Flats Plant (RFP) treats relatively large volumes of aqueous waste generated from various sources, including laboratories, laundry, production operations, and incidental waters from runoff, solar evaporation ponds, and interceptor trenches. Plutonium processing operations have historically produced large quantities of nitric acid waste which, upon neutralization, results in a high volume waste stream containing predominantly nitrate compounds. The cessation of plutonium processing at RFP, however, has significantly reduced the concentration of nitrates in the aqueous wastes.

Aqueous wastes are mixed and treated in Building 374. Radioactive wastes are treated by flocculation and precipitation to remove actinides. The agglomerated waste is concentrated in a clarifier. The clarifier underflow goes to radioactive sludge treatment and the overflow is sent to a holding tank where it is mixed with low specific activity wastes prior to concentration in a quadruple effect evaporator. The effluent from the evaporator is a 35% solids brine solution, a portion of which is taken to dryness using a spray dryer. The spray dried salt, 35% brine, and Portland type I/II cement are combined to produce the "saltcrete" waste form.

The existing saltcrete process was developed as a short-term corrective action to meet Department of Transportation (DOT) regulations promulgated in the early-1980's. This eight-year-old equipment that was installed in 1985 was designed for a five-year life. The cementation equipment consists of a 350 RPM Lightning Mixer with two 13.6 inch diameter A-310 impellers. One impeller is connected at the bottom of the shaft and the other is connected 12 inch above the lower impeller. The mix tank has a PVDF inner liner with a fiberglass dual laminate exterior. The mixer is capable of mixing and pouring only very low viscosity formulations.

1.2.2 History

The original saltcrete process went into use with a formulation of 55 wt% salt, 18 wt% cement, and 27 wt% water to form a pourable, high waste loaded grout which met the Nevada Test Site (NTS) requirements in effect during the mid-1980's (1). The saltcrete process consistently produced certifiable product until late 1988, when shipping delays necessitated extended outdoor storage. During this period, the saltcrete product was stored in cardboard triwall containers unprotected from the environment. As a result of this environmental exposure, some saltcrete blocks crumbled and some triwall containers degraded, broke open, and spilled waste onto the storage pad.

In June 1989, Waste Operations changed the formulation to 51 wt% salt, 22 wt% cement, and 27 wt% water. However, the swelling problem continued. Waste Operations replaced the cardboard triwalls with reinforced plywood half-boxes (2'x4'x7'). The improved boxes appeared to alleviate the swelling problem.

In December 1989, RFP ceased plutonium production operations and, as a result, stopped shipping the large quantities of neutralized nitric acid to Building 374 for treatment. Building 374 continued to process large quantities of waste from other areas on plantsite. However, the chemical composition of the waste processed was much lower in nitrates without the input from production operations.

In June 1990, some of the saltcrete halfcrates began swelling while still in the staging area. Observations of these blocks showed light and dark swirling patterns, indicating that the salt blocks were poorly mixed and inhomogeneous. Bench-scale mixing tests indicated that formulations that mixed well prior to the December 1989 production curtailment were now extremely viscous and difficult to mix. To compensate for the increased viscosity, operators were adding additional water to the formulation.

Technology Development (TD) conducted formulation studies using salts generated during June 1990 to identify a formulation that would consistently mix and pour in the existing cementation equipment and that would not swell during extended storage (2). TD recommended a 30 wt% salt formulation that was used for production beginning in September 1990. This formulation appeared to eliminate the swelling problem.

In spite of the quality improvements, the saltcrete product could not be certified because of a lack of waste characterization data and inadequate process controls. Halliburton anticipated reprocessing all of this saltcrete as part of the Solar Ponds Project. As a result Waste Operations was encouraged to maximize waste loading to reduce the amount of saltcrete generated, and subsequently increased the waste loading to 35 wt% during the fall of 1992. Occasionally swelling of saltcrete halfcrates is still being noted.

The objective of this study was to identify and recommend solutions to issues precluding certification of the newly generated saltcrete product. This includes optimization of the saltcrete formulation and collection of pertinent data for the preparation of a process control plan. This report summarizes acceptance criteria, waste characterization, problem assessment, and formulation study results for the period October 1, 1992 to June 30, 1993.

1.2.3 Future Salt Solidification Processes

Polyethylene extrusion is being investigated as a potential final treatment technology for the salt waste stream. Encapsulation of the salts in polyethylene results in a less permeable and more durable waste form than cementation. This is currently a fiscal year 1997 capital project.

The existing spray dryer, evaporator, and cementation equipment may be replaced as part of the Waste System Evaporator (WSE) Project. Title II design for Phase I is complete and construction is on hold pending project reviews. The TSDD will contain recommendations to proceed with either cementation or polymer encapsulation of the salt waste stream.

Given the maturity of the WSE project, developing upgrades or improvements to the existing saltcrete cementation equipment would result in a duplication of effort and inefficient use of resources. Therefore, development efforts focused on utilizing the existing equipment where possible.

2.0 PROCESS CHARACTERIZATION

2.1 WASTE ACCEPTANCE CRITERIA

2.1.1 Regulatory Acceptance Criteria

The saltcrete waste form is a low level mixed (LLM) waste that is currently destined for disposal at the Nevada Test Site (NTS). Thus, the saltcrete product must meet NTS waste acceptance criteria (WAC), including Department of Transportation (DOT) regulations and regulatory requirements for land disposal restricted (LDR) wastes.

A summary of the NTS WAC is presented in the following text:

- Waste activity must be <100 nCi;
- the waste requires immobilization if,
 - 1 wt% of the waste has a particle diameter of < 10 μm , or
 - 15 wt% of the waste has a particle diameter of < 200 μm ;
- low level mixed waste (LLM) disposed at NTS must not contain free liquids;
- no characteristic hazardous wastes are allowed;
- where practical, waste shall be treated to reduce volume and provide a more physically and chemically stable waste form;
- wastes shall not react significantly with the packaging during normal storage, shipping, and handling time;
- mixed wastes prohibited from land disposal under 40 CFR § 268 will not be accepted unless treated as specified under 40 CFR § 268, Subpart D (see Table 2.1.1-1); and
- cyanide or sulfide-bearing wastes in concentrations greater than 10 wt% as CN^- or S^{2-} will not be accepted.

The WAC are from the September 1991 version of Draft NVO-325 (rev.1).

**Table 2.1.1-1: Constituent Concentration in Waste Extract
(CCWE) Standards for Saltcrete**

ORGANIC COMPOUNDS

Waste codes F001-F005

<u>CONSTITUENT</u>	<u>Maximum Allowable CCWE mg/L</u>
Acetone	0.59
n-Butyl alcohol	5.0
Carbon disulfide	4.81
Carbon tetrachloride	0.96
Chlorobenzene	0.05
Cresols (and cresylic acid)	0.75
Cyclohexanone	0.75
1,2-Dichlorobenzene	0.125
Ethyl acetate	0.75
Ethylbenzene	0.053
Ethyl ether	0.75
Isobutanol	5.0
Methanol	0.75
Methylene chloride	0.96
Methyl ethyl ketone	0.75
Methyl isobutyl ketone	0.33
Nitrobenzene	0.125
Pyridine	0.33
Tetrachloroethylene	0.05
Toluene	0.33
1,1,1-Trichloroethane	0.41
1,1,2-Trichloro	
1,2,2-Trifluoroethane	0.96
Trichloroethylene	0.091
Trichlorofluoromethane	0.96
Xylene	0.151

**Table 2.1.1-1: Constituent Concentration in Waste Extract
(CCWE) Standards for Saltcrete**

ORGANIC COMPOUNDS

Waste codes F001-F005
(continued)

METALS

Waste codes F006, F007, and F009

<u>CONSTITUENT</u>	Maximum Allowable <u>CCWE mg/L\</u>
Cadmium	0.066
Chromium	5.2
Lead	0.51
Nickel	0.32
Silver	0.072

LABORATORY TESTS

1. EPA Method 9095. This is the paint filter test for free liquids. A measured amount of solid waste is placed in a paint filter (60 mesh) for 5 minutes. If any portion of the material passes through the filter, the material is deemed to contain free liquids.
2. ASTM 4359. This is the paint can test for liquid/solid determination. The ASTM standard procedure states that this is a method to be applied to viscous materials. For this test, material is placed in a 1-quart paint can, the can is sealed and heated to 100°F for 24 hours. Then the can is opened and inverted. If the solid waste deforms significantly, (begins to run out of the can) or if more than one ml of water condenses on a watch glass below the can, the material fails.
3. TCLP, the Toxicity Characteristic Leaching Procedure. This is an EPA method where the waste is size-reduced to less than 9.5 mm (3/8") and digested in a mild acid. The digestant (or extract) is then analyzed for a specific list of hazardous metals and organic compounds.

The Building 374 salt is not officially identified with EPA waste codes at this time. Waste Identification and Characterization (WIC) assumes that the applicable waste codes will be F001, F002, F003, F004, F005, F006, F007, and F009. The F039 code may be added later. Therefore, TCLP analyses may be required for all of the constituents listed in Table 2.1.1-1. Some may be eliminated from the list if characterization efforts prove that they are not present in the waste. The maximum allowable constituent concentration in the waste extract (CCWE) is given in mg/L.

There is no specific test for stability of the final waste form. Since a permitted disposal site is not currently available to accept mixed wastes, however, the saltcrete waste form must be able to withstand extended storage at RFP prior to shipment. A reasonable approach for evaluating the relative stability of waste forms is to subject the waste to ASTM 559 (wet/dry cycling) and ASTM 560 (freeze/thaw cycling), and measure compressive strength and dimensional and weight changes. For Class B and C wastes, the Nuclear Regulatory Commission (NRC) recommends using a modified ASTM 560 to assess the stability of cemented waste forms.

2.1.2 Process Criteria

The saltcrete formulation must have the following characteristics to satisfy Waste Operations requirements:

- (1) The formulation must have rheological properties that allow Waste Operations to adequately mix and pour using the existing equipment. This means that the formulation must have a fairly low viscosity.

- (2) The formulation must cure in a reasonable period of time. One to five days for curing is desirable, since this period avoids delays in subsequent production runs. This time period also avoids undesirable effects associated with premature setting, such as flash setting while still in the mix tank or degradation of the final waste form integrity. Recent production runs indicate significant retardation, with hydration occurring between seven and ten days. Prior production runs hydrated within 3 days. It is possible that changes in the chemical composition of the salt affects the time to set of the saltcrete product.
- (3) The formulation must be capable of producing an acceptable waste form for a wide range of chemical compositions. Alternatively, bench-scale tests could be conducted prior to each production run to ensure that the formulation produces an acceptable product. This approach would require extremely quick turnaround to avoid production delays.
- (4) The formulation should use the maximum feasible waste loading in order to minimize storage requirements and disposal costs. Prior formulation studies conducted at RFP indicate that the maximum waste loading is approximately 30 wt% (1).
- (5) The process should be as simple as possible. Complicating parameters, such as the use of additives, must result in substantial process improvements in order to justify the associated increase in expense and effort.

2.2 WASTE CHARACTERIZATION

Twelve samples of the spray dried salt were shipped to Lockheed Analytical Laboratory (LAL), Las Vegas, NV for analysis. The samples were collected over a one-year time span to provide information on variations in waste stream chemistry. Sample numbers and corresponding sample dates are presented in Table 2.2-1.

The objective of the characterization was to identify the chemical components of the final solidified waste. Obtaining legally defensible data for permit compliance or certification of the final waste form was not an objective of this characterization. As such, samples were analyzed in accordance with Contract Laboratory Program (CLP) protocol, but the rigors (and expense) of the legally defensible CLP data package were not employed.

The salts were analyzed for major cations and anions, TAL metals, and total organic content. The analytical techniques employed are listed in Table 2.2-2.

The results of the major anion analysis are tabulated in Table 2.2-3. The variability of the major waste constituents over time is graphically represented in Figure 2.2-1. Of particular interest is the relatively large variations in waste chemistry over short time periods. It is also interesting to compare the current waste chemistry to the chemistry of the salt prior to the curtailment of plutonium operations in 1989 (Table 2.2-4). The nitrate concentration has decreased, while the chloride concentration has increased significantly.

Major cation and target heavy metal concentrations are tabulated in Table 2.2-5. The variability of target heavy metals over time is graphically represented in Figure 2.2-2.

The reported metals results were obtained by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Three of the samples from the group were redigested and analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to investigate the accuracy of the chromium and nickel results for samples showing anomalously high results.

The ICP-MS analysis consisted of two parts. The first part was a quantitative analysis for the metals reported initially. The results of this analysis show a considerable high bias for chromium and nickel in the original ICP-AES results for two of the samples. High bias was also reported for copper and iron, with a slightly high bias for manganese. The ICP-MS results for the third sample agree with the original ICP-AES results. Dilutions of the samples analyzed by ICP-AES confirm the high bias for the indicated elements. The ICP-AES and ICP-MS results for the analytes showing bias are summarized in Table 2.2-6.

The ICP-MS results for the remainder of the analytes compared well with the initially reported ICP-AES results. Therefore, LAL believes that the original results for the major cations are accurate.

The second part of the ICP-MS analysis was a qualitative ICP-MS scan of all masses to determine the source of the high bias by ICP-AES for the affected analytes. This scan indicated the presence of some unusual elements, including erbium, gold, neodymium, thorium, tungsten, and zirconium. Spectral interferences (overlap) from one or more of these elements caused the bias results.

The ICP-AES results were reported because the CLP method quality control measures used to assess interference and interelement correction problems did not indicate that the data were questionable. The CLP criteria and checks are not designed to deal with the interferences present in the RFP salt waste. All future and previously analyzed samples will be analyzed by ICP-MS to avoid spectral interference problems.

TCLP analysis was conducted on one sample of salt (not saltcrete). Results for target heavy metals are presented in Table 2.2-7. Cadmium and nickel were the only two analytes to exceed LDR limits, although nickel results show a significant high bias (as previously discussed). All organics were below detection level.

Table 2.2-1:
LAL Analytical Data from Report#1214211 Sample Sequence

SAMPLE SEQUENCE	SAMPLE NUMBER	SAMPLE DATE	DAYS
1	D884-101911	10/01/91	1
2	1-0122	12/04/91	65
3	1-0315	01/05/92	97
4	1-0422	02/22/92	145
5	1-0423	02/28/92	151
6	1-0616	04/23/92	206
7	1-0618	04/24/92	207
8	1-0626	05/11/92	224
9	1-0627	05/12/92	225
10	1-0638	06/15/92	259
11	1-0792	07/11/92	285
12	1-0703	07/16/92	290

Table 2.2-2: Analytical Techniques

<u>Parameter</u>	<u>CAS Number</u>	<u>Method Detection Limits (mg/L)</u>	<u>Method Ref.*</u>
Chloride	7647-14-5	5	EPA 325 Series or 300.0
Nitrate	10-28-6	0.1	EPA 353.1 or 353.2
Sulfate	7778-80-5	5	EPA 375.4 or 300.0
Fluoride	10-72-0	0.1	EPA 340 Series
Carbonate	10-14-0	10	EPA 310.1
Total Dissolved Solids	10-33-3	10	EPA 160.1
Total Suspended Solids	10-32-2	5	EPA 160.2
pH	10-29-7	0.1 pH Unit	EPA 150.1
Specific Conductance	10-34-4	1 uS	EPA 120.1
Sulfide	7783-06-4	1	EPA 376 Series
Phosphorus, Total	7723-14-0	0.05	EPA 365
Ammonia	7764-41-7	0.05	EPA 350 Series
Cyanide	74-90-8	0.05	EPA 335.2 or 335.3
Silica	7740-21-3	2	EPA 370.1
Hexavalent Chromium	7740-47-3	EPA 218.5	
TOC		1	EPA 415.1 or ASTM D4129-82
Free Chlorine	7782-50-5	1	S.M. 4500 - Cl
Americium	7440-35-9		HASL-300
Plutonium	7440-07-5		HASL-300
Uranium	7440-61-1		HASL-300

*All equivalent USEPA SW846 methods, Standard Methods, and other methods used or referenced require permission from EG&G Rocky Flats.

TABLE 2.2-3: MAJOR ANIONS

ANALYTE	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	SAMPLE ID	AVERAGE	AVERAGE
	DBB4-10191	1-0122	1-0315	1-0422	1-0423	1-0616	1-0618	1-0626	1-0627	1-0638	1-0703	1-0792	CONC	CONC
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(%)	(mg/kg)
Nitrate	217021	217021	234736	239166	234737	190447	221450	239166	246024	181589	159444	248024	21 9235417	219235 417
Chloride	130000	150000	93000	100000	99000	110000	110000	110000	110000	100000	110000	130000	11.2666667	112666 667
Sulfate	95000	93000	65000	82000	80000	140000	97000	99000	95000	110000	170000	84000	10.0416667	100416 667
Carbonate	51600	48000	54000	52200	51600	30600	57600	47400	50400	35400	21600	23400	4.365	43650
Insoluble Mat.	39000	38000	69000	39000	33000	42000	34000	33000	35000	43000	14000	31000	3.75	37500
Fluoride	10000	10000	8000	11000	10000	12000	14000	8200	7800	9100	38000	8400	1.22083333	12208 3333
TOC	8700	10000	9300	9400	7800	6600	5900	9200	8400	6400	4900	8000	0.78833333	7883 33333
Hydroxide	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	0.3	3000
Phosphate	150	68	110	67	68	570	66	97	69	49	1600	660	0.02978333	297 833333
Cyanide	20	16	8 6	5 4	30	6 3	10	9 3	15	10	3 9	6 8	0.0011775	11 775
Total Anions	549491	569105	536154 6	535838 4	519235	535223 3	543026	549072 3	557708	488548	522547 9	536490 8	53 6870025	536870 025
Total Cations	312866 19	308213 67	296709 5	302407 25	304746 09	321200 05	318286 06	326674 28	320946 12	331953 82	323624 66	333210 62	31 6736526	316736 526
Total	862357 19	877318 67	832864 1	838245 65	823981 09	856423 35	861312 06	875746 58	878654 12	820501 82	846172 56	869701 42	85 3606551	853606 551
Remander	137642 81	122681 33	167135 9	161754 35	176018 91	143576 65	138687 94	124253 42	121345 88	179498 18	153827 44	130298 58	14 6393449	146393 449

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MAJOR ANIONS, WT. % CONCENTRATION

FIGURE 2.2-1

Table 2.2-4:
Approximate Concentration of Building 374 Salt
Prior to Operations Shutdown, Based on 1989 Characterization

<u>COMPOUND</u>	<u>SYMBOL</u>	<u>% COMP</u>
Sodium Nitrate	NaNO ₃	53.9
Potassium Nitrate	KNO ₃	33.9
Sodium Chloride	NaCl	3.2
Potassium Chloride	KCl	2.2
Sodium Sulfate	Na ₂ SO ₄	2.8
Potassium Sulfate	K ₂ SO ₄	1.8
Sodium Phosphate	Na ₃ PO ₄	0.9
Potassium Phosphate	K ₃ PO ₄	0.6
Sodium Fluoride	NaF	0.4
Potassium Fluoride	KF	0.3
SUM		100.0%

TABLE 2.2-5: MAJOR CATIONS AND TARGET HEAVY METALS

ANALYTE	SAMPLE ID D884-10191 (mg/kg)	SAMPLE ID 1-0122 (mg/kg)	SAMPLE ID 1-0313 (mg/kg)	SAMPLE ID 1-0422 (mg/kg)	SAMPLE ID 1-0423 (mg/kg)	SAMPLE ID 1-0616 (mg/kg)	SAMPLE ID 1-0618 (mg/kg)	SAMPLE ID 1-0626 (mg/kg)	SAMPLE ID 1-0627 (mg/kg)	SAMPLE ID 1-0638 (mg/kg)	SAMPLE ID 1-0703 (mg/kg)	SAMPLE ID 1-0792 (mg/kg)	AVERAGE CONC (%)	AVERAGE CONC (mg/kg)
Sodium	152000	153000	144000	198000	199000	203000	151000	210000	207000	193000	210000	197000	18 4750	184750.0
Potassium	134000	133000	55400	72900	73300	93100	147000	86100	83900	99100	98600	115000	9 9283	99283.3
Calcium	20500	16100	81600	20900	21000	16300	14300	20100	19800	29000	8840	12800	2 3437	23436.7
Magnesium	3660	3550	7170	8000	8040	5570	3400	7310	7310	6680	4240	6150	0 5923	5923.3
Iron	1130	1110	3840	1140	1620	1520	1320	1430	1310	1900	865	1010	0 1516	1516.3
Aluminum	911	748	3730	588	599	713	602	738	703	1330	442	623	0 0982	982.3
Zinc	173	198	345	336	338	238	163	326	329	298	180	183	0 0259	259.0
Boron	230	212	183	232	237	285	233	252	232	269	215	196	0 0231	231.3
Nickel	35.2	50	72.1	97.5	256	197	44.8	159	134	125	87	79	0 0111	111.4
Chromium	60	73.6	30	60.4	180	131	62	101	82.4	78.6	64.4	56.9	0 0082	81.7
Copper	33.6	37.8	36.3	41.5	64.8	52.8	36.1	51	48.1	44.4	29	29.5	0 0042	42.1
Silver	58.2	61.9	25.3	30.1	31.4	21.4	56.7	28.8	27	25	20.6	27.9	0 0035	34.5
Barium	26	23.3	91.4	25.5	26.7	21.9	20.8	26.5	26	37.5	15.2	20.8	0 0030	30.1
Manganese	16.3	16.6	42.9	15.4	21.1	20.7	18.3	19.2	17.7	24.4	11.4	13.4	0 0020	19.8
Vanadium	12.9	10.2	62.9	8.7	7.4	10.4	7.3	9.2	7.6	21	3.8	8.7	0 0014	14.0
Lead	5.1	6.3	5.7	5.6	5.4	5.4	6.4	5.7	5.4	6.1	4.1	3.6	0 0005	5.4
Cadmium	9.5	9.9	4.3	4.2	4.3	3.3	9.9	4.2	3.9	4.4	3.1	2.2	0 0005	5.3
Cobalt	2.9	3	3.8	4.1	7	6.8	2.5	6.2	4.6	3.8	3.9	3.9	0 0005	4.9
Selenium	*	*	*	14.7	2	*	*	2.2	*	2.2	2	*	0 0005	4.6
Beryllium	0.8	0.85	4.1	4	4.1	1.5	1	3.3	3.4	2.1	*	*	0 0003	2.5
Thallium	0.61	0.92	1.3	1	1.2	1.1	1.2	1.2	1.1	1.1	1.3	1.2	0 0001	1.1
Arsenic	0.98	1.3	1.4	0.43	0.53	0.49	0.87	0.52	0.63	0.91	0.4	1	0 0001	0.8
Mercury	0.1	*	*	0.12	0.16	0.26	0.19	0.26	0.29	0.31	0.36	0.52	0 0000	0.3
Antimony	*	*	*	*	*	*	*	*	*	*	*	*	0 0000	0.0
Total Cations	312866.19	308213.67	296709.5	302407.25	304746.09	321200.05	318286.06	326674.28	320946.12	331953.82	323624.66	333210.62	31.67	316737

* Below detectable limit

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LDR METALS, mg/kg CONCENTRATION

FIGURE 2.2-2

Table 2.2-6

ICP-AES AND ICP-MS FOR ANALYTES SHOWING BIAS RESULTS

CLIENT SAMPLE ID	LAS SAMPLE ID	CHROMIUM		COPPER		IRON		MANGANESE		NICKEL	
		ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS	ICP-AES	ICP-MS
D-884-10191	A47801	60.0	69.0	33.6	38.8	1130	1040	16.3	21.4	35.2	35.0
1-0423	A47793	180	30.2	64.8	33.6	1620	1134	21.1	15.7	256	49.8
1-0616	A47794	131	29.2	52.8	34.0	1520	934	20.7	20.6	197	61.2

Note: All results are in mg/kg, as received.

Table 2.2-7: TCLP Results on One Waste Sample

ANALYTE	CONCENTRATION, mg/l	LDR LIMIT, mg/l
Cadmium	0.36	0.066
Chromium	0.14	5.0
Lead	0.36	0.5
Nickel	1.22	0.3
Silver	0.04	0.072

2.3 RHEOLOGICAL REQUIREMENTS OF THE FULL-SCALE MIXER

The objectives of the study described in this section were to characterize the rheological behavior of the saltcrete paste in the Building 374 mixing vessel and to define the rheological requirements of the vessel. The reasons for performing the evaluations were to find the normal operating range of the present process equipment and the limiting conditions (maximum viscosity) that it can tolerate. This information was used to specify a key performance criterion for the formulation development. Also, a procedure for simulating the full-scale system on a laboratory-scale was developed.

2.3.1 Approach

The approach was to identify the normal and limiting conditions of the paste viscosity by taking samples during production runs. Grab samples of the saltcrete paste were collected from the halfcrates. In most cases, the samples were collected and evaluated immediately after the paste was poured into the crate. In some cases, the samples were collected and evaluated several hours after the paste was poured. Three rheological conditions were investigated: "normal", extremely viscous, and "normal" viscosity after several hours of quiescence.

Normal conditions were studied because these are considered tolerable and effective by Liquid Waste Treatment Operations. These conditions are then the target conditions for the optimum formulation. The extreme conditions represent the limitations of the mixing equipment. These conditions should not be exceeded when the variability of the waste feed, cement properties, and the mixing process are applied to the optimum formulation. The viscosity of waste that was several hours old was evaluated to get an indication what would happen if waste was left in the mixer due to failure or plugging of the dump valve.

Evaluating the viscosity that the mixing equipment can barely tolerate depended on the chance encounter of saltcrete paste too viscous (or nearly so) to pour out of the mixing vessel. When this unusual event did occur, a grab sample was taken from the crate as the paste was poured, or immediately thereafter. An EG&G Chandler Model 35 multispeed viscometer was used to measure the viscosity of the sample. This data was used in conjunction with the viscosity of normal saltcrete paste to define the rheological limits of the mixing equipment.

The viscosity of normal production-line saltcrete paste was evaluated in the same way. Grab samples were collected from the crate near the pour spout then immediately taken to the viscometer. The viscometer was in the production area, so the test could be completed five minutes after the paste was poured into the crate.

The viscosity of saltcrete paste several hours old was evaluated by collecting a grab sample from the top three inches of a waste crate. These samples were stirred slightly with a rubber spatula to get the sample level in the test cup. The same viscometer was then used to measure the viscosity.

2.3.2 Results

The viscometer readings of Type I/II cement mixed with Building 374 brine and salt on the production line are given in Appendix D. Deflection (dial reading) is a measure of shear stress and revolutions per minute (RPM) provides a measure of the shear rate. Figure 2.3.2-1 is the graphical representation of saltcrete viscosity.

The limiting conditions were encountered during the January 1993 run. The saltcrete paste would not pour out of the mixing vessel and mixing problems were observed. "Normal", "too thick", and "almost too thick" conditions are represented in Figure 2.3.2-1. "Too thick" means that the paste would not pour out of the mixer except with the aid of hand tools. The "almost too thick" batch appeared not to mix in the vessel for a few minutes. Lumps of cement stayed on the surface. Eventually a vortex formed and the cement lumps were churned in with the rest of the paste, and the paste poured out of the mixing vessel. "Normal" conditions occurred when the paste mixed and poured with no difficulty. The "normal" line in Figure 2.3.2-1 depicts an average of values from the January 1993 production run.

2.3.3 Discussion

The chemical and physical properties of saltcrete have changed since the last formulation studies were performed in 1990. In the past, the salt acted as a super plasticizer and no gelation was observed (the viscosity was qualitatively evaluated in the previous study). A commercial super plasticizer (Dowell D-19™) had no noticeable effect on the viscosity during the 1990 study, but since the salt had a thinning effect, this was of little concern. During the October 1992 and January 1993 production runs, the saltcrete paste exhibited gelation, shear thinning, and retarded set for every batch that was tested. The differences could be due to chemical changes in the waste stream.

The saltcrete paste is a non-Newtonian pseudoplastic (shear thinning) fluid, which means that it exhibits a lower viscosity at high shear rates than at low shear rates. In the case of saltcrete, the apparent viscosity is time dependent as well as shear-rate dependent. The apparent viscosity of the paste increases rapidly, but can be reduced with agitation. At low shear rates the apparent viscosity of the saltcrete was approximately 4,000 cP to 7,000 cP, whereas the apparent viscosity of saltcrete at high shear rates was 100 cP to 200 cP. Another phenomenon, gelation (or perhaps false setting due to the formation of plaster compounds), occurred when the paste was allowed to remain quiet for 5 minutes.

Gelation and high apparent viscosity at low shear rates are usually attributed to the attraction of particles to each other (5). This attraction can sometimes be reduced by adding thinners to the paste. However, thinners usually are less effective in slurries with high concentrations of salt.

The limiting conditions can be represented by drawing a line between the normal apparent viscosity at low rates, and the limiting apparent viscosity at high rates. The reasoning is that the apparent viscosity at low shear rates is about the same under all three conditions (normal, limiting and too thick), and that the apparent viscosity at high rates is noticeably different. This approach is somewhat conservative because the limiting conditions at low shear rates are not known. In other words, the line could be somewhat higher at the low shear rates. The formula of the line representing the limiting conditions is:

$$\text{deflection} = 60 + \frac{1}{2} (\text{rpm}).$$

Figure 2.3.2-1: Normal and Limiting Conditions of the Full-scale Mixer

The most probable use of the rheological data will be to compare it to other viscometer readings so that the units of shear rate and shear stress are quoted as the direct instrument readings. Standard units would be useful if the saltcrete paste were pumped through a pipeline or if friction calculations were necessary.

In the event that standard units are necessary, the conversions are given below. The apparent viscosity of a sample is proportional to the dial reading of the viscometer. The shear rate is proportional to the rotation rate of the cylinder.

$$\text{shear stress} = k_1 \times k_2 \times \theta, \text{ dynes/cm}^2$$

$$\text{shear rate} = k_3 \times N, \text{ sec}^{-1}$$

$$\text{viscosity} = \frac{\text{shear stress, dynes/cm}^2}{\text{shear rate, sec}^{-1}} \times 100, \text{ cP}$$

$$\text{viscosity} = \frac{k_1 \times k_2 \times \theta}{k_3 \times N} \times 100, \text{ cP}$$

where

- k_1 is the torsion spring constant, 386 dyne-cm/degree deflection
- k_2 is the shear stress constant for effective bob surface, 0.01323 cm^{-3}
- k_3 is the shear rate constant, $1.7023 \text{ sec}^{-1}/\text{RPM}$
- θ is the deflection (dial reading), degrees
- N is the cylinder rotation rate, RPM
- cP centipoise, the units of viscosity

2.3.4 Laboratory-Scale Simulation of Production Process

The rheology of the saltcrete was evaluated with a multi-speed rotational viscometer. Production-line samples were collected from halfcrates and evaluated in the production area. Lab-scale samples were evaluated using the same materials as in the full scale process but were mixed in an Osterizer blender. The samples had 1/454 the mass of a full-scale batch. The 2-quart blender had four one inch blades. The full-scale mixer (described in Section 1.2.1) had two 13.6 inch, 3-bladed impellers. A detailed description of the procedure is in Appendix C.

2.3.4.1 Experimental Procedure Using Actual Salt Waste

The lab-scale simulation was performed with constituents that match those of the saltcrete in crates HO4096 (3rd batch) and HO4097 (1st batch) in an Osterizer blender. The detailed procedure, given in Appendix C, was derived by an iterative approach. It was found that the mixing time affected the viscosity. The amount of time spent mixing was adjusted until the viscosity of the lab-scale saltcrete matched the viscosity of the full-scale saltcrete. The results are presented in Appendix D and in Figure 2.3.4.1-1.

Figure 2.3.4.1-1: Simulation of the Full-Scale Process

A 1/6-scale model of the Lightnin™ mixer was also used to mix samples. The impeller speed (rpm) was the same as what was used in the 1990 study (1). Although the mixer performed properly in the 1990 study, the mixer failed to mix the cement with the fluid in the 1993 study. The rpm's were increased to 600, but the mixer was still unable to mix the cement with the salt and the brine. Efforts to use the scale model to simulate the process were abandoned.

2.3.4.2 Results

The average of the full-scale viscometer readings was compared to the average of the viscometer readings from the lab-scale simulation. Figure 2.3.4.1-1 previously shown demonstrates that the simulation models the full-scale process at the higher shear rates, but is slightly higher at the lower shear rates. Since only two batches of saltcrete from the full-scale process were used as the baseline for the full-scale baseline, the variance at each viscometer RPM was not calculated. A relative difference at each RPM was calculated and then twice the standard deviation of the relative differences was used as a criterion for whether the lab-scale simulation modeled the full-scale process. This is described mathematically as follows:

$$\text{relative difference} = \text{absolute value of } \frac{(\text{reading} - \text{average})}{\text{average}}$$

When the full-scale process was evaluated, the apparent viscosity at the high shear rates proved to be more important than the apparent viscosity at the low shear rates. In fact, the y-intercept was nearly the same in all cases, regardless of whether the apparent viscosity was in the normal operating range or nearly too high for the mixer to tolerate. Thus, a small difference at low shear rates is acceptable.

In Figure 2.3.4.1-1:

- 1) the "Avg" curve represents the average of the full-scale measurements
- 2) the "Avg+2" curve represents the average of the full-scale measurements plus two times the relative standard deviation
- 3) the "Avg-2" curve represents the average of the full-scale measurements minus two times the relative standard deviation
- 4) the "Simulation" curve represents the average of the lab-scale measurements

2.3.5 Conclusions

- (1) The objectives of the study were met. The normal conditions of the process were evaluated to provide a representation of the process as it is now.
- (2) The maximum-viscosity paste that the mixer can tolerate was encountered and evaluated.
- (3) The rheology of samples collected immediately after mixing were comparable to the samples collected after a number of hours of quiescence.
- (4) An experimental procedure was developed for process simulation for laboratory-scale tests of saltcrete formulations.
- (5) Lab-scale rheological testing of saltcrete paste prior to production may be useful in avoiding production problems, as a means of Quality Control (QC) of the bulk cement, as a warning that the waste stream is changing, and in certification of the waste for disposal. Lab-scale testing is not done routinely at this time.

2.4 EVALUATION OF SALTCRETE INVENTORY

2.4.1 Waste Form Swelling

As discussed in the Introduction, swelling saltcrete containers have been reported at the Rocky Flats Plant since the Nevada Test Site stopped accepting mixed waste from Rocky Flats in late 1988. Swelling of the waste form is a certification concern because it can cause the container to bulge and lose its seal. If this happens, the crate is no longer a "strong, tight" container as required by Department of Transportation (DOT) regulations. Severe swelling can also lead to complete degradation of the waste form to the point that it no longer meets dispersible solid requirements.

In an attempt to quantify the extent and cause of the swelling problem, a detailed inventory of all of the saltcrete stored at Rocky Flats was conducted. A computer database was created incorporating available production data and the results of a visible inspection of the halfcrate population. When swelling was observed, the amount of swelling was measured and included in the database.

The amount of swelling measured varied from less than 1/4 inch to 2 3/8 inch on one face of the long dimension (84 inches) of the halfcrate. This corresponds to a maximum of 5% volume expansion using a conservative approach for calculating volume. A list of the bulged halfcrates and the amount of swelling observed is presented in Table 2.4.1-1.

Most of the halfcrates are stored in tent 12 on the 750 pad. Photograph 2.4.1-1 illustrates the general condition of the halfcrate population in tent 12. Recently produced saltcrete halfcrates are stored in tent 8 on the 904 pad. Photograph 2.4.1-2 illustrates the general condition of this population. The two worst halfcrates (in terms of bulging) are shown in Photographs 2.4.1-3 and 2.4.1-4. Although the degree of bulging is not severe, these two halfcrates are significantly more bulged than the other halfcrates showing signs of bulging. The discoloration and delamination of some of the halfcrates is due to outside weathering.

Statistical Applications conducted an evaluation of the database to identify possible trends associated with the swelling halfcrates. The percent of bulged halfcrates per week of production is plotted in Figure 2.4.1-1. Figure 2.4.1-2 compares waste loading to batch date.

Clearly, waste loading and date of production affect the likelihood of swelling during storage. The time period when the process was most effective coincides with the use of the 30 wt% waste loading formulation. Of the saltcrete halfcrates produced between December 9, 1990 and September 20, 1992, only 12, or approximately 2%, exhibited signs of swelling.

Statistical Applications is continuing to review the database to attempt to quantify a relationship between swelling halfcrates and waste loading, water to cement ratio, and individual component ratios. Preliminary results indicate that there may be a definite correlation between water to cement ratio, waste loading, and bulging crates. If successful, this data could help identify process boundaries and results could be incorporated into the process control plan.

**Table 2.4.1.-1
BULGED SALTCRETE HALF-CRATES LOG**

CRATE ID	ACCUMULATION DATE	HORIZONTAL MEASUREMENTS INCHES	LOCATION-750 PAD ROW
H03352	12/8/90	3/4	1
H02211	7/13/90	3/4	1
H03087	8/22/90	3/4	1
H03260	11/30/90	3/4	1
H02207	7/15/90	3/4	1
H03082	8/22/90	5/8	1
H00339	7/12/90	3/4	2
H03722	9/25/91	1/2	2
H00347	7/13/90	1/2	2
H02208	7/14/90	3/4	3
H00346	7/12/90	7/8	3
H02204	7/13/90	5/8	3
H03268	11/14/90	1 1/16	3
H03084	9/21/90	1	3
H03148	10/4/90	3/4	3
H00344	7/7/90	3/4	4
H03204	12/8/90	1 3/8	4
H00342	7/14/90	1/2	4
H03182	10/24/90	1/2	4
H03143	10/6/90	1/2	4
H03141	9/19/90	3/4	4
H03169	11/19/90	1/2	4
H00337	7/12/90	1/2	5
H02203	7/13/90	1 1/2	6
H00340	7/13/90	1/2	6
H02202	7/12/90	3/4	6
H03089	8/31/90	5/8	8
H03170	10/23/90	5/8	8
H03138	10/7/90	1/2	8
H03155	9/18/90	5/8	8
H03151	10/7/90	1	8
H03264	11/14/90	3/4	9
H03258	11/29/90	5/8	10
H03254	11/30/90	5/8	10
H03140	9/18/90	1	11
H03181	11/15/90	1/2	11
H03136	10/7/90	1/2	11
H03146	10/7/90	3/4	11
H03255	11/15/90	7/8	11
H03178	10/23/90	1	11
H03262	11/15/90	1/2	11

**Table 2.4.1.-1
BULGED SALTCRETE HALF-CRATES LOG**

CRATE ID	ACCUMULATION DATE	HORIZONTAL MEASUREMENTS INCHES	LOCATION-750 PAD ROW
H03091	9/20/90	1/2	12
H03096	9/18/90	7/8	12
H02210	7/12/90	1 1/8	13
H03185	10/23/90	3/8	13
H03139	9/17/90	1 1/4	13
H00280	4/10/90	3/4	13
H02205	9/14/90	7/8	13
H03092	8/20/90	3/8	13
H03094	8/22/90	1/2	13
H03101	8/31/91	7/8	13
H03100	8/20/90	1	13
H02201	6/16/90	7/8	13
H00261	6/16/90	1 1/4	13
H03184	10/24/90	1	14
H03180	10/23/90	1/2	14
H03083	8/22/90	1 5/16	14
H03093	8/22/90	1	14
H03261	11/29/90	1/4	14
H00283	6/16/90	1 1/2	14
H03080	8/21/90	1/2	14
H00281	4/10/90	1 1/4	14
H03602	7/9/91	1 1/4	14
H03175	10/24/90	1 1/4	15
H03179	11/15/90	1/2	15
H00274	7/4/90	5/8	16
H03152	10/7/90	1 1/4	17
H03145	9/20/90	1	17
H03187	11/30/90	1/2	18
H03095	9/20/90	< 1/4	18
H02206	7/14/90	3/4	19
H03090	8/20/90	3/4	22
H02209	11/7/90	1 1/4	23
H00341	7/14/90	3/4	23
H00270	4/11/90	3/4	23
H04424	6/19/91	3/4	24
H03661	8/22/91	3/4	4
H00338	7/12/90	1 1/2	5
H03270	11/15/90	3/4	5
H03097	8/22/90	5/8	5
H03629	7/23/91	< 1/4	6
H03099	8/20/90	7/8	6

Table 2.4.1.-1
BULGED SALTCRETE HALF-CRATES LOG

[illegible]

Table 2.4.1.-1
BULGED SALTCRETE HALF-CRATES LOG

[illegible]

Figure 2.4.1-1
374 Saltcrete Production Log Data
Percent of Bulged Boxes per Week of Production

Photograph 2.4.1.2-4: Bulged halfcrate—atypical damage.

Photograph 2.4.1.2-2: 904 pad with nailcrates.

Photograph 2.4.1.2-3: Bulged halfcrate—atypical damage.

2.4.2 HNUS Characterization Results

Halliburton NUS Environmental Services (HNUS) sampled and analyzed twelve halfcrates plus one duplicate as part of the solar ponds waste characterization program (2). The half crate analytical data are summarized in Table 2.4.2-1. None of the RCRA metals, volatile organics, or semi-volatile organics were above their respective LDR standards.

Two of thirteen half crate samples tested contained amenable cyanide at concentrations exceeding the constituent concentration in waste (CCW) standard. However, the amenable cyanide mean concentration is well below the LDR standard of 30 mg/kg. HNUS noted that "when the data are analyzed using the approach outlined in SW-846, the upper limit of the 80% confidence interval is below the LDR standard. Therefore, it is possible to predict with reasonable certainty that the halfcrate population as a whole is below the LDR standard for amenable cyanide."

In summary, it is probable that the entire halfcrate population meets all LDR standards.

Figure 2.4.1 -2: Building 374 Saltcrete Production Log Plot—4/90-2/93

Specific Gravity=1.29 was assumed for missing data.

TABLE 2.4.2-1

SUMMARY OF SALTCRETE CHARACTERIZATION DATA - HALF CRATES
 SOLAR POND/PONDCRETE PROJECT
 ROCKY FLATS PLANT, COLORADO

ANALYSIS	UNITS	FREQUENCY OF DETECTION	RANGE OF POSITIVE DETECTIONS	MEAN CONCENTRATION ⁽¹⁾	STANDARD DEVIATION ⁽¹⁾	% RELATIVE STANDARD DEVIATION ⁽¹⁾
VOLATILES⁽²⁾						
2-Butanone	ug/kg	9/13	4 to 45	16	14	88
Toluene	ug/kg	3/13	4 to 8	4	1	37
Freon 113	ug/kg	1/13	14	4	3	75
SEMI-VOLATILES⁽²⁾	ug/kg	0/13	ND	ND	ND	ND
ALCOHOLS⁽²⁾	mg/kg	0/13	ND	ND	ND	ND
INORGANICS						
Aluminum	mg/kg	13/13	6330 to 11900	8790	2240	25
Arsenic	mg/kg	1/13	9.9	4.3	1.7	39
Barium	mg/kg	13/13	134 to 276	190	59	31
Boron	mg/kg	13/13	87.1 to 164	121	25	20
Cadmium	mg/kg	13/13	1.5 to 5.5	3.7	0.9	25
Calcium	mg/kg	13/13	126000 to 282000	198000	57700	29
Chromium	mg/kg	13/13	30.2 to 118	51.7	24.9	48.1
Iron	mg/kg	13/13	6830 to 12500	8910	2160	24
Lead	mg/kg	0/13	ND	ND	ND	ND
Magnesium	mg/kg	13/13	1760 to 8490	3880	2480	64
Mercury	mg/kg	11/13	0.1	0.1	0.02	20
Nickel	mg/kg	13/13	22.4 to 45.8	30.7	7.5	24.3
Potassium	mg/kg	13/13	38900 to 164000	105000	44600	43
Selenium	mg/kg	0/13	ND	ND	ND	ND
Silver	mg/kg	13/13	16.0 to 57.8	32.6	12.6	38.5
Sodium	mg/kg	13/13	62300 to 133000	94300	26600	28

TABLE 2.4.2-1 (Cont'd.)

SUMMARY OF SALTCRETE CHARACTERIZATION DATA - HALF CRATES
 SOLAR POND/POND/CRETE PROJECT
 ROCKY FLATS PLANT, COLORADO
 PAGE 2

ANALYSIS	UNITS	FREQUENCY OF DETECTION	RANGE OF POSITIVE DETECTIONS	MEAN CONCENTRATION ⁽¹⁾	STANDARD DEVIATION ⁽¹⁾	% RELATIVE STANDARD DEVIATION ⁽¹⁾
TCLP LEACH						
Aluminum	ug/l	10/12	95 to 1090	410	390	97
Arsenic	ug/l	0/11	ND	ND	ND	ND
Barium	ug/l	12/12	840 to 1500	1180	230	19
Cadmium	ug/l	0/12	ND	ND	ND	ND
Calcium	ug/l	12/12	633000 to 3120000	1800000	940000	52
Chromium	ug/l	12/12	147 to 978	457	302	66
Iron	ug/l	0/12	ND	ND	ND	ND
Lead	ug/l	0/12	ND	ND	ND	ND
Magnesium	ug/l	1/12	191	64	44	68
Mercury	ug/l	2/12	1.0	0.2	0.4	180
Nickel	ug/l	12/12	31.0 to 199	84.9	45.3	53.3
Selenium	ug/l	0/12	ND	ND	ND	ND
Silver	ug/l	0/12	ND	ND	ND	ND
pH	Units	12/12	11.8 to 12.2	12.0	0.1	1.2
ASTM LEACHATE						
Chloride	mg/l	12/12	690 to 2600	1360	600	44
Nitrate	mg/l	12/12	900 to 2500	1360	560	41
Percent Recovery of Solids	%	12/12	27.2 to 56.0	42.5	10.5	24.8
Phosphate (ortho)	mg/l	0/12	ND	ND	ND	ND
Total Dissolved Solids	mg/l	12/12	12000 to 27000	20000	6200	30
Sulfate	mg/l	12/12	1100 to 4100	2150	980	46

TABLE 2.4.2-1 (Cont'd.)
SUMMARY OF SALTCRETE CHARACTERIZATION DATA - HALF CRATES
SOLAR POND/PONOCRETE PROJECT
ROCKY FLATS PLANT, COLORADO
PAGE 3

ANALYSIS	UNITS	FREQUENCY OF DETECTION	RANGE OF POSITIVE DETECTIONS	MEAN CONCENTRATION ⁽¹⁾	STANDARD DEVIATION ⁽¹⁾	% RELATIVE STANDARD DEVIATION ⁽¹⁾
MISCELLANEOUS						
Moisture-gravimetric	%	13/13	18.8 to 25.6	22.3	2.4	11.0
Ammonia	mg/kg	5/13	<10 to 22	6.6	8.9	135.3
Specific Gravity of Waste	---	12/12	1.67 to 1.95	1.86	0.08	4.31
Cyanide-soluble	mg/kg	13/13	-35 to 56	-0.054	31	57100
Cyanide-total	mg/kg	13/13	16 to 81	38	23	62
Free Swell Test	%	12/12	0 to 70	20	20	100
Gross alpha	pCi/g	12/13	<9 to 140+-20	63	40	63
Gross beta	pCi/g	13/13	49+-6 to 150+-20	110	33	31
TOC	mg/kg	13/13	560 to 5000	3500	1500	43
Percent Water (KF)	%	12/12	1.78 to 25.6	21.9	2.6	12.0
Viscosity	Cp	12/12	125 to 385	230	80	35
pH (in soil)	Units	13/13	12.7 to 13.3	13.1	0.2	1.7
Ammonia, Distillation	mg/kg	5/13	14 to 22	10	6	63
Unconfined Compressive Strength	PSI	---	INT	INT	INT	INT
Unit Weight of Shelby Tube	g/cc	---	INT	INT	INT	INT
Specific Gravity - Flt Cake	---	12/12	2.13 to 2.88	2.56	0.22	8.44
Specific Gravity - Salt Rinse	---	12/12	1.93 to 2.42	2.23	0.14	6.48
% Solids - Filter Cake	%	12/12	74.9 to 81.6	77.6	2.1	2.8
Pycnometer Fil - SG	---	12/12	1.028 to 1.058	1.044	0.011	1.063
Pycnometer Fil - TDS	mg/l	12/12	36000 to 78000	60000	15	24
Pycnometer Fil - pH	Units	12/12	12.3 to 12.9	12.7	0.2	1.7
Salt Rinse Fil - SG	---	12/12	1.043 to 1.088	1.068	0.017	1.577
Salt Rinse Fil - TDS	mg/l	12/12	69000 to 120000	93000	23000	25
Salt Rinse Fil - pH	Units	12/12	12.4 to 13.0	12.7	0.3	2.4

INT Interference
ND Not Detected
pCi/g Picocuries per gram

- (1) Values calculated using 1/2 detection limit for nondetects, based on guidance contained in the Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part A). Interim Final, December 1989.
- (2) Only compounds with positive detections are listed. The complete list of compounds analyzed is shown in Table 2-5. The complete database is included in Appendix B.

2.5 CERTIFICATION ISSUES

2.5.1 Process Controls

2.5.1.1 Program Controls

There are three phases of program control required to certify the saltcrete product. First, a Process Control Plan (PCP) is required to identify the success criteria to attain certification of the waste form. Second, a qualification test plan will be implemented to verify that the success criteria are met. Third, a waste certification plan is required to detail the documentation of the success criteria, including a plan for how the waste certification official will certify the product and package for disposal.

Completion of each of these tasks requires extensive coordination between several different organizations. To ensure adequate coordination, a Total Quality Management (TQM) Process Improvement Team (PIT) was established. The objective of the team is to prepare and implement a plan for certification of both the saltcrete in inventory and the saltcrete being generated. This involves identification of the steps required to certify the waste for disposal at NTS, identification of the groups at RFP necessary to accomplish certification, establishment of a communication network to expedite the process, coordination of activities that are already in progress, identification of any activities that are not scheduled or budgeted, and analysis of the potential for saving time and money. The following text describes in more detail the activities related to certification of the newly generated saltcrete product.

A process description must be prepared by a Liquid Waste Treatment Operations (LWTO) subject matter expert. This will include detailed actions of personnel and equipment to complete a process cycle. The PIT will evaluate each step of the operation and identify the actions that impact operations or product quality. These actions are pulse variables and each will have an operation limit. The process description must be regularly reviewed during the PIT process to verify that changes to procedure and/or operation are addressed.

Process and equipment qualification takes place in a sequence of development and implementation actions and is based on a current process description. Bench-scale and systems operations tests are conducted to identify the variables that have the greatest impact on the process. A statistical evaluation is conducted to measure the impact of changes to these variables. The results of these efforts are the limits of operation for the process. This report summarizes bench-scale and systems operations test results and identifies the key variables for control. Process limits are also identified where available. Some additional tests made be required to identify process limits for other key variables.

All personnel involved with the treatment or packaging of saltcrete must have sufficient training to satisfy the needs of the operation and process control. The details of training and qualification already exist.

The process control plan will identify selected control elements, the permitted variance for the control, the measurement control methodology, the frequency of measurement, and the method for recording measurements. The PIT is recommending electronic recording devices and/or measuring devices. All measure and test equipment must be part of a valid calibration program. Saltcrete prepared from an operation that exceeds the limits of control will be rejected. Rejected saltcrete will be reprocessed or tested for certification. Any operation that regularly stresses a control boundary should be stopped and the process reevaluated.

The records generated by this operation are the primary documents for certification. All records pertaining to the proper treatment and packaging of the waste form will be reviewed prior to certification.

The certification of the treated waste form will be based on three levels of verification. First, the existence of documentation must be verified that substantiates that operations produced the treated waste form in compliance with the process control plan. Second, the completion of adequate sampling to ensure that the waste form itself complies to regulatory requirements must be verified. The final level is verification that procedures and controls were in place and observed during the generation of the waste form.

Certification requirements identify the criteria and define how each will be achieved. Because many of the criteria are subjective, the generator must define a method to demonstrate compliance. Certification will rely on a comprehensive sampling and analysis plan to verify that the treated waste meets Treatment Storage and Disposal (TSD) requirements. In addition, Quality Control (QC) samples will be taken regularly.

Certain administrative activities are required for the control of any process. Each container offered for disposal must have individual evidence of acceptability. The generator must record empirical values existing at the time the waste package is filled and must have that data available for each waste container. The most feasible means of maintaining information that is not generated automatically is to provide a travel document for each container as it is filled. The following information was extracted from the proposed pondcrete certification plan.

1. Waste box number.
2. Date and time box is filled.
3. Batch number for the fill cycle.
4. Any notes that tie the crate to any of the certification tests applied.
5. Weight.
6. Fill time, elapsed.
7. Space for inspection approval.
8. Entry field for the data recorded in the preceding tables.
9. Pozzolan batch number.
10. Entry field for notes. Defect reports. Other observations.

2.5.1.2 Determination of Solids Concentration in Brine

Waste loading is one of the most important control parameters in any waste cementation process. The current saltcrete formulation incorporates approximately 35 wt% salt (from brine and spray dried salt), 28 wt% water (from brine), and 37 wt% cement. In order to calculate the amount of spray dried salt necessary to bring the total salt loading to 35 wt%, the salt concentration in the brine must be determined. The concentration of salt in the brine is determined from the specific gravity of the brine. The relationship between specific gravity and relative amounts of brine and spray dried salts were determined in a previous study (1).

Specific gravity is determined by collecting a 50 ml brine sample and reading the specific gravity using a hydrometer. The accuracy of this measurement determines the accuracy of the weights of salt and water.

Several problems inherent to the process could adversely affect the accuracy of the hydrometer reading. First, the brine in the 826C storage tank may not be homogeneous. A recirculation system draws brine from the bottom of the tank and returns it to the top of the tank. This keeps the brine tank fairly well mixed, but there is a possibility that the solids content may vary within the tank. If the inhomogeneity is significant, then the accuracy of the specific gravity measurement could be adversely affected.

Second, entrained air and suspended solids could cause errors in the specific gravity measurement. The entrained air causes frothing, which can cause problems with reading the hydrometer. Suspended particles influence the specific gravity reading when the particles are above the bottom of the hydrometer. However, the majority of suspended particles typically settle below the bottom of the hydrometer before the reading is taken.

Finally, the hydrometer cylinders are opaque and are occasionally difficult to read. If the hydrometer is not kept clean, the scale is barely legible. In order to evaluate the accuracy of the hydrometer method, specific gravity was determined by several methods and compared to the specific gravity determined using the hydrometer. Fourteen samples from 3 different processing runs were evaluated. These results are tabulated in Table 2.5.1.2-1. A statistical analysis was performed and is presented in Table 2.5.1.2-2.

Results indicate good agreement between the hydrometer and the other methods tested. However, some relatively simple improvements should be made to the procedure to ensure data accuracy. First, the specific gravity should be determined more frequently. Specific gravity is currently determined only once per shift. At a minimum, specific gravity should be determined prior to each batch run.

Second, the equipment currently in use to measure specific gravity should be replaced with equipment that will make it easier to accurately read the hydrometer. Specifically, the opaque 50 ml cylinder currently in use should be replaced by a clear plastic cylinder. Plastic coated and plastic shell hydrometers meeting ASTM specifications should be used.

Finally, certification of the production hydrometers must be maintained. The production hydrometers currently in use were recently certified. If they are replaced as recommended above, these hydrometers must be certified.

TABLE 2.5.1.2-1

1. SAMPLE NO	2. SAMPLE DATE	3. WO SpG	4. SPG GRAD	5. SpG HYDRO	6. SpG PIPETTE	7. TS x MOIST BAL	8. TS WT %	9. TS WT %
3994-3	10/6/92	1.22	1.25	1.25	1.24	30.6	28.7	31.0
3985-3	10/29/92	1.22	1.21	1.21	1.20	28.4	28.7	27.5
4019-1	10/29/92	1.22	1.21	1.21	1.22	28.2	28.7	27.5
4019-2	10/29/92	1.22	1.21	1.21	1.23	28.1	28.7	27.5
4019-3	10/29/92	1.22	1.22	1.21	1.23	28.4	28.7	27.5
4048-1	10/29/92	1.22	1.21	1.21	1.23	28.4	28.7	27.5
4048-2	10/29/92	1.22	1.22	1.21	1.23	28.4	28.7	28.7
4048-3	10/29/92	1.22	1.21	1.21	1.23	28.6	28.7	27.5
3930-1	8/11/92	1.33+	1.30	1.30	1.31	37.4	>40.3	37.4
3930-3	8/11/92	1.32	1.29	1.30	1.29	37.4	39.3	37.4
3931-1	8/11/92	1.33+	1.30	1.30	1.29	37.2	>40.3	37.4
3931-3	8/11/92	1.33+	1.29	1.30	1.30	37.2	>40.3	37.4
3937-1	8/11/92	1.32	1.30	1.30	1.30	37.2	39.3	37.4
3937-2	8/11/92	1.32	1.30	1.30	1.29	37.3	39.3	37.4

1. Sample number - half-date/batch number from which the Laboratory sample was obtained.
2. The batch processing date.
3. The SpG transcribed to the production log.
4. The SpG as determined in the Laboratory. Wt/Vol -100 ml graduate.
5. The SpG as determined in the Laboratory - hydrometer.
6. The SpG as determined in the Laboratory. Wt/Vol Oxford Pipette Volume.
7. Weight percent total solids as determined using the moisture balance.
8. Weight percent total solids derived from Figure 3 (TD92-001) using the production log SpG.
9. Weight percent total solids derived from Figure 3 (TD92-001) using the average SpG determined in the Laboratory.

TABLE 2.5.1.2-2

Oct 29, 1992

TS WT % (Column 7 Data)

28.1	Median = $(n+1)/2$ th value = $(7+1)/2 = 4$ th value
28.2	Median = 28.4
28.4	Mode = 28.4 (most frequent value)
28.4	Range = $28.6 - 28.1 = 0.5$
28.4	Mean = 28.4
28.4	s = 0.16
28.6	Variance = 0.026
	71% of data fall within 1 s
	100% of data fall within 2 s

Aug 11, 1992

TS WT % (Column 7 data)

37.2	Median = Av of 3 and 4 value
37.2	Median = 37.2
37.2	Mode = 37.2
37.3	Range $37.4 - 37.2 = 0.2$
37.4	Mean = 37.3
37.4	s = 0.10
	Variance = 0.01
	100% of the data fall within 1 s

2.5.1.3 Saltcrete Process Weighing Systems

Accurate component weights and accurate data transcription are two of the most important tasks necessary to produce a certifiable saltcrete monolith. The current saltcrete formulation incorporates approximately 35% salt (from spray dried salt and brine), 28% water (from brine) and 37% cement. The operator measures the specific gravity of the brine and determines the appropriate amount of brine, spray dried salt, and cement (measured according to Load Cell Units (LCU), required to give a mixable formulation for the selected waste loading. Load Cell Unit is the digital display relative to the load cell signal. The digital display will reflect the correct weight in pounds when the four load cells are functioning properly, are electronically balanced and the display unit properly calibrated. The relationships between specific gravity and component weights, were determined in 1990 bench tests (1).

The components are sequentially transferred to the mixer. The cumulative LCU, after each addition, is recorded in the production log. The brine LCU is displayed under static conditions. The salt and cement LCU's are displayed under dynamic conditions (mixer and vacuum pump running). The components are intimately mixed and then transported to the halfcrate. When the hydration process has proceeded to the point that the mass has solidified, qualitatively determined by attempting to force a welding rod into the mass with no success, the box is sealed, banded and weighed. The gross weight is transcribed in the production log book.

The mixer scale has never been calibrated, which virtually precludes certification of the saltcrete product without extensive sampling of the final waste form. The mixer scale will be calibrated by suspending weights below the mixer. A work order was initiated to obtain certified rigging. An attempt to certify the mixer hooks resulted in hook failure. New hooks have been on order for several months.

In 1990, a rough calibration curve was developed by pumping 100 pound quantities of water into the mix tank and recording the load cell reading. Fifteen data points were recorded and a calibration curve was generated (1). Sometime during 1991 or 1992, the load cells ceased to function properly. A repeat calibration of these load cells indicated a significant variation from the calibration curve. Moreover, the net weight of the halfcrates exceeded the sum of the constituent weights. Close inspection of the load cells indicated that the load cells were significantly damaged. All four load cells were replaced on September 29, 1992.

A rough calibration of the new weighing system was performed using a similar procedure. The data is tabulated in Table 2.5.1.3-1. Figure 2.5.1.3-1 compares the 1990 calibration curve with the 1993 calibration curve. A comparison of constituent weights and constituent weight percents of the 1990 and 1993 data is presented in Table 2.5.1.3-2

The load cells should be isolated from the environment to prevent damage. A work package was initiated but never completed because a suitable method of isolation has not yet been identified. Facilities Engineering is currently reviewing the work package for design of an adequate isolation device. In the meantime, LWTO is exerting care in the maintenance of load cells and associated instruments.

A preliminary study was conducted to determine the variability of the electronic digital indicator display during mixing as well as a possible base line drift. Water was pumped to the mixer at weights of 398 pounds and 698 pounds. The lower weight was selected to approximate the brine volume used in production. The higher weight was selected to simulate the brine mixed with spray dried salt. The results of this test are tabulated in Table 2.5.1.3-3 and indicate that no baseline drift exists and no significant error is introduced during mixing. The Fairbanks half crate weighing scale is certified on a yearly schedule. A review of the certification data from 1987 through 1992 indicates that the equipment is functioning properly and is accurate.

Table 2.5.1.3-1: 1993 MIXER SCALE COMPARISON

RUN 1		RUN 2	
POUNDS	LCU*	EQUIV POUNDS	LCU* EQUIV POUNDS
0	0	0	0
105	103	101	99
211	208	201	198
313	308	303	299
414	407	403	398
516	508	504	498
619	608	606	598
721	708	707	698
822	807	807	797
924	907	911	898
1026	1007	1014	998
1128	1107	1115	1099
1232	1209	1213	1196

y intercept = 0.49
 slope = 1.019
 correlation coefficient = 0.99999
 *LCU = Load Cell Units

y intercept = 0.31
 slope = 1.014
 correlation = 0.99999

**TABLE 2.5.1.3-2:
COMPARISON OF CONSTITUENT WEIGHTS AND WEIGHT
PERCENT OF 1990 AND 1993 CALIBRATION DATA**

<u>CONSTITUENT</u>	<u>LCU</u>	<u>POUNDS</u> <u>1993</u>	<u>POUNDS</u> <u>1990</u>
Brine	507	500	543
Brine and Salt	710	700	733
Brine/Salt & Cement	1100	1083	1200

<u>CONSTITUENT</u>	<u>POUNDS</u> <u>1993</u>	<u>POUND</u> <u>1990</u>	<u>WEIGHT %</u> <u>1993</u>	<u>WEIGHT %</u> <u>1990</u>
Salt	381.5	387.1	35.2	32.2
Water	318.5	345.9	29.4	28.8
Cement	<u>383.0</u>	<u>467.0</u>	<u>35.4</u>	<u>38.9</u>
TOTAL	1083.0	1200.0	100.0	99.0

Figure 2.5.1.3-1: Saltcrete Mix Tank Calibration Curve

TABLE 2.5.1.3-3

FAIRBANKS

POUNDS H ₂ O	LCU STATIC	LCU - SPAN MIXER	VAC	LCU - SPAN MIXER/VAC	DYNAMIC TIME	NOTES
398	403					
		408-409			2 Min	One Impeller
	403					
		408-410			2 Min	One Impeller
	403					
			390		2 Min	
	403					
				395-396	2 Min	One Impeller
	402					
				395-396	2 Min	One Impeller
398	403					
698	707					
		716-717			2 Min	Two Impellers
	707					
			695		2 Min	
	707					
				703-705	2 Min	Two Impellers
687	707					

2.5.2 Waste Sampling and Analysis

An effort is currently underway to characterize the saltcrete process inputs and determine if the newly generated saltcrete waste form meets the LDR treatment limits. This effort is described in the "Building 374 Process Waste (Saltcrete) Sampling and Analysis Plan," which is an addendum to the "Waste Stream and Residue Identification and Characterization (WSRIC) Quality Assurance Project Plan (QAPP)." The sampling and analysis plan will stipulate procedures to ensure that data will be of sufficient quality to meet NTS criteria.

2.5.3 Disposal Site Issues

The Nevada Test Site (NTS) does not currently have the necessary permits to accept waste for disposal. Since there is no approved alternative, the waste may have to remain at Rocky Flats for several years. Therefore, other sites should be considered.

The WAC were evaluated for two other sites, Envirocare in Utah and the Hanford Site in Washington. The packaging requirements of these sites are mutually exclusive with each other and the NTS. The Hanford Site could accept waste for storage if the waste were untreated and packaged in galvanized drums. Envirocare will likely receive a permit for disposal of plutonium contaminated mixed waste in the near future. Envirocare requires that waste be buried in layers no more than one foot thick. In contrast, the NTS requires that the waste be treated and contained in drums or 2' x 4' x 7' wooden crates.

The certification criteria defined for the saltcrete product assume that the disposal facility will be the NTS. If a different disposal facility is selected, then the certification criteria will change.

2.6 TIME OF SET OF SALTCRETE HALFCRATES

The set time of the saltcrete halfcrates is an important parameter for production operations. Saltcrete halfcrates are staged in the Building 374 waste treatment facility until the paste hardens, at which point the halfcrates are closed and transferred to interim storage. Due to space limitations, production operations cannot begin the next saltcrete run until the halfcrates produced by the previous run have been transferred out of Building 374. Since Liquid Waste Treatment Operations (LWTO) tries to operate at approximately two week intervals, saltcrete formulations that take longer than about 5 days to harden could delay operations. In order to establish a baseline, the set time of the full-scale production blocks was characterized. The time to the peak of the exotherm can be interpreted as the time to set.

Stainless steel-sheathed thermocouples were inserted into the saltcrete paste after the halfcrate was filled and moved to the staging area. Temperature and time were recorded with an Omega data logger until the exotherm peak was observed. Four production runs were monitored over a period of three months. Results for all of the monitored halfcrates are tabulated in Table 2.6-1. The temperature profiles for each production run are graphed in Figures 2.6-1, 2.6-3, 2.6-5, and 2.6-7. Average temperature profiles for each production run are graphed in Figures 2.6-2, 2.6-4, 2.6-6, and 2.6-8.

The saltcrete blocks hydrated between 5.8 and 11.5 days after they were poured. Variations in waste chemistry probably account for much of the differences in reaction time between the production runs, and probably also account for some of the differences in reaction time within the same run.

Table 2.6-1: Time to Set of Saltcrete Halfcrates

HALFCRATE #	POUR DATE	POUR TIME	DATE OF SET	TIME OF SET	ELAPSED TIME TO SET=DAYS
H0 4020	10/29/92	1902	11/5/92	2102	7.1
H0 4019	10/29/92	1250	11/6/92	0902	7.8
H0 4048	10/29/92	1610	11/7/92	0202	8.4
H0 3985	10/29/92	0854	11/7/92	0202	8.7
H0 3990	10/29/92	0404	11/7/92	1402	9.4
H0 4063	1/4/93	1950	1/10/93	1402	5.8
H0 4009	1/4/93	1720	1/11/93	1202	6.8
H0 4065	1/5/93	0215	1/12/93	0002	6.9
H0 4062	1/5/93	0430	1/12/93	1202	7.3
H0 4083	1/27/93	0440	2/2/93	1402	6.4
H0 4077	1/27/93	0245	2/3/93	0202	7.0
H0 4080	1/26/93	2200	2/3/93	0202	7.2
H0 4078	1/27/93	0800	2/4/93	0202	7.8
H0 4100	2/11/93	0825	2/20/93	1402	9.2
H0 4104	2/10/93	2030	2/20/93	1402	9.7
H0 4099	2/10/93	1835	2/21/93	0202	10.3
H0 4092	2/11/93	0208	2/22/93	1402	11.5

The production date and time corresponds to the date and time of the last batch poured into the the specified half crate.
Note the elapsed time variation between dates.

Figure 2.6-1 Temperature Profile for 10/29/92 Production

**Figure 2.6-2: Average Temperature Profile for
10/29/92 Production**

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FIGURE 2.6-3 Temperature Profile for 1/5/93 Production

Figure 2.6-4: Average Temperature Profile for
1/5/93 Production

Figure 2.6-5: Temperature Profile for 1/27/93 Production

Profile for 2.6-6: Average Temperature Profile for
1/27/93 Production

Figure 2.6-7: Temperature Profile for 2/11/93 Production

3.0 FORMULATION OPTIMIZATION

3.1 OBJECTIVES AND APPROACH

3.1.1 Objective

The objective of the study described in this section was to determine the optimum formulation for the existing saltcrete process in Building 374. The experiment was conducted in two phases. The first phase evaluated the rheology of ten formulations. The second phase evaluated the best 6 formulations from Phase I against 3 additional criteria.

3.1.2 Quality Objective

The data from this experiment will be used to identify the ratio and types of cement, admixtures, waste and water used to produce the saltcrete product. The intent of this experiment was to optimize the process, not to collect the data needed to certify the final waste form. Therefore, the quality objective is level 2 as defined in the TD-QAMP Draft Rev 2 (3). Formulation variability studies to gather information for input to the Process Control Plan will have a level 3 quality objective.

3.1.3 Approach

The experiment used both actual waste (salt and brine) and surrogate brine. Preparation of the surrogate waste is described in section 3.1.5. Surrogate wastes were tested to simulate waste chemistry. The optimum formulation was selected primarily from the results of tests using actual waste because of uncertainties inherent with the use of surrogates.

In order to minimize the number of samples generated, the experiment was conducted in two phases. In the first phase, the viscosity of ten formulations was measured. Six of the lowest viscosity formulations were then evaluated against three additional criteria (described in section 3.1.5). The low viscosity formulations were chosen because they require less water to meet the limitations of the mixer. There are advantages to low-water-content waste forms such as lower volume, better stability and better immobilization of hazardous chemicals.

For formulation studies using actual waste, cement (dry blend), brine and spray dried salts were mixed according to the proportions in SOP 374-30 Rev 0 (4). Samples of brine and spray dried salts were collected at the beginning of the experiment and these samples were used for all of the different tests applied to all formulations evaluated. This was done to ensure that variations in results between dry blends were due to the dry blends and not to variations in waste chemistry.

The following dry blends were tested:

1. 100% Portland type I cement
2. 50% Portland type I, 50% class C fly ash

3. 50% Portland type I, 50% class F fly ash
4. 100% Portland type I/II cement
5. 50% Portland type I/II, 50% class F fly ash
6. 50% Portland I/II, 50% Class C fly ash
7. 100% Portland type V cement
8. 50% Portland type V, 50% class C fly ash
9. 50% Portland type V, 50% class F fly ash
10. HNUS 207C pond formulation:
Portland type V, class C fly ash, lime at 1:2:0.75
water/pozzolan ratio at 0.42
11. HNUS 207C pond formulation:
Portland type V, class C fly ash, lime at 1:2:0.75
12. 85% Portland type I, 15% Dow latex solids
13. 40% Portland type V, 40% class F fly ash, 10% attapulgite clay

The water to pozzolan ratio was 0.78 except for formulation 7. Duplicates of each formulation were tested in random order.

Portland type I/II cement is currently used to produce the saltcrete product. Type I cement is a commonly used, general purpose cement that is usually the least expensive. Type II cement is also a general purpose cement that is commonly used where moderate sulfate attack is expected, or where moderate heat of hydration is required. Heat evolution may be required to overcome the retarding effect of the waste constituents.

Type V cement is recommended in situations where sulfate attack is expected. The Portland Cement Association recommends using Type V cement if the sulfate concentration in soils or water is between 1,500 to 10,000 ppm. HNUS selected Type V cement for the 207C pond water based on this recommendation, because the maximum sulfate concentration in the 207C pond is 18,000 mg/l. The average sulfate concentration in the spray dried salts exceeds 100,000 ppm. HNUS did not compare Type V cement to Type I/II cement for the 207C pond.

However, the Portland Cement Association's recommendation was based on external sulfate attack after much of the hydration reaction has been completed. Sulfates react with aluminates in the cement structure to form the expansive sulfoaluminate, ettringite. Ettringite usually forms early in hydrating

cement during its plastic stage and is responsible for initial set. Normally, sulfates are added to cements in the form of gypsum to control set time. Ettringite is thermodynamically unstable and subsequently decomposes in calcium silicate hydrate gel, which is the binding matrix of cement. If ettringite forms after the calcium silicate hydrate has formed a rigid structure, destructive expansion can occur. It is conceivable that excess water and sulfates in the mix could react with tricalcium aluminates in the cement to form expansive ettringite during the later stages of concrete cure. Cements with a tricalcium aluminate content of 7% give a rough division between cements of good and poor performance in sulfate waters (6). Thus, low aluminate cements (Type V and Type I/II) were selected for evaluation.

Sulfates also react with calcium hydroxide to produce gypsum, which can lead to expansive degradation of the cemented product. The addition of fly ash can improve sulfate resistance by removing free calcium hydroxide, thus rendering the alumina-bearing phases inactive. Fly ash also reduces the permeability of the final product, thereby increasing sulfate resistance, compressive strength and leach resistance.

The current saltcrete cementation requires a high water/cement ratio in order to produce a paste that will adequately mix and pour in the existing equipment. The excess water reduces the integrity of the final product and increases the risk of expansion. Pacific Northwest Laboratories (PNL) observed significantly reduced viscosities when attapulgite clay was added to the dry blend for a nitrate salt waste stream (7). Attapulgite clay and other thinners were tested to evaluate whether the use of these materials would allow reduced water content while maintaining low viscosities.

3.1.4 Assumptions

1. The ability of the formulation to pass the TCLP is independent of the dry blend formulation due to the inherent buffering capacity of cements and the low concentration of heavy metals in the waste stream. The HNUS characterization results on the half crate population indicated that Portland type I cement with waste loadings of up to 55% passed the TCLP (see section 2.4.2). The untreated salts also barely failed the TCLP (section 2.2). Therefore, since the TCLP is an expensive test, and since all formulations should easily pass the TCLP, the TCLP was not used as a criterion for formulation selection.
2. The brine and spray dried salt samples collected for the formulation studies are representative of the average salt waste chemistry. This will be confirmed by submitting salt samples to LAL and comparing these results to previous characterization data on the salts.
3. The target component ratio for formulation studies is 38% dry blend, 32% salt, and 30% water.

3.1.5 Success Criteria

Each formulation was evaluated against the following criteria:

Phase I:

1. Rheology: The formulation must produce a grout that falls below the line defined by $YP = 60$, $PV = 150$, or dial reading = $60 + rpm/2$ on a Chandler Model 35 viscometer (see section 2.3). Formulations producing viscosities above this point are unacceptable. Lower viscosity grouts are preferred. Two samples for each formulation were tested for viscosity and an average value calculated.

Phase II:

Six of the formulations evaluated in Phase I were further evaluated in Phase II against the following criteria:

2. Time to set: For the purposes of this experiment, time to set is defined as the time to the peak of the hydration exotherm. Shorter time to set values are preferred.
3. Free liquids: The presence of free liquids on the samples after curing is unacceptable. Samples were visually inspected for the presence of free liquids.
4. Durability: The relative durability of each formulation was evaluated using a modified ASTM D559-82 wet/dry cycle test and a modified ASTM 560 freeze/thaw cycle test. Neither test is required for low level wastes, but ASTM 560 is recommended by the NRC for Class B and C wastes. The NRC recommends using right circular cylinder molds with a length to diameter ratio of 2:1. For these experiments, 2 inch by 1 inch molds were used. Small samples were chosen because they are more susceptible to degradation during environmental cycling tests. In order to complete the effort on schedule, the number of cycles was reduced to 4. The time interval between cycles was extended from 36 hours to 48 hours to accommodate work schedules.

3.2 VISCOSITY MEASUREMENTS OF FORMULATIONS

The objective of the study described in this section was to evaluate ten formulations for compatibility with the existing mixing equipment as described in Section 2.3. The formulation must not have viscosities that lie above the "nearly too thick" line defined in Section 2.3 which defines the limitations of the mixer (Figure 2.3.3-1). Formulations that have viscosities below the "normal" line are preferred because lower viscosities imply that they require less water than the current formulation. Using less water improves waste form properties such as stability and hazardous constituent immobilization.

The actual waste (brine and salt) from Building 374 was used for comparison with the limitations of the mixing equipment. Surrogate salts were tested to see if the process could be simulated with nonradioactive, nonhazardous material for finding cause and effect of waste components (see Section 3.2.2).

The viscosity of the saltcrete was evaluated with a multi-speed rotational viscometer. Production-line samples were collected from halfcrates and evaluated in the production area (see Section 2.3). Lab-scale samples were evaluated using the same materials as in the full scale process but were mixed in an Osterizer blender. A detailed description of the procedure is in Appendix C.

3.2.1 Actual Salts

The viscosities of individually prepared, duplicate lab-scale samples of ten formulations were evaluated to eliminate those that would not be compatible with the existing mixer. The waste loading was the same as the newly generated saltcrete to make a comparison to the full-scale process. (These samples were 28 wt% water, 32 wt% salt, and 38 wt% cement to match the composition of the full-scale paste used for the process evaluation. This differs slightly from the intended composition in the Liquid Waste Treatment Operations SOP of 28 wt% water, 35 wt% salt, and 37 wt% cement). The formulations and additives tested were:

Type I/II

Type V

50% type I/II, 50% class C

50% type V, 50% class C

50% type I/II, 50% class F

50% type V, 50% class F

85% Portland type I/II, 15% Dow latex solids

Type V, class C fly ash, lime, 1:2:2.275 with water to pozzolan ratio of 0.74

Type V, class C fly ash, lime, 1:2:0.075 with a water to pozzolan ratio of 0.42

40% type V, 40% class F, 10% attapulgite

In addition, seven superplasticizers were tested using type I/II cement. The superplasticizers were:

Dowell D-19

Dowell D-65

Protex PSP-L

Sodium acid pyrophosphate (SAPP)

Drilling specialties, Inc., Disco

The samples were randomly selected by assigning each formulation and duplicate a number from 1 to 20. The numbers were written on small slips of paper, placed in a beaker, and drawn at random. The same approach was taken for the plasticizers. Individually prepared, lab-scale samples of the seven plasticizers and duplicates were randomly selected by drawing numbers from a beaker.

3.2.1.1 Procedure

The laboratory procedure used to evaluate the viscosities of the formulations was the same as the one used to simulate the full-scale process (see Section 2.3.2) modified to allow for cement admixtures and plasticizers.

3.2.1.2 Results

None of the cement blends showed improved viscosity but two plasticizers did improve the viscosity. The viscosities of type I/II cement, type V cement, and 50:50 blends with class C and class F fly ash were nearly the same as the viscosity of the currently generated saltcrete slurry. The other miscellaneous formulations were generally worse than the current saltcrete slurry.

The viscometer readings of cement and admixtures mixed with Building 374 brine and salt on a lab-scale are given in Table 3.2.1.2-1. Deflection (dial reading) is a measure of shear stress and revolutions per minute (rpm) provides a measure of the shear rate. Figures 1 through 9 represent the viscosities of the cement formulations. The narrative in this section addresses the graphs. In Figures 1 through 9 "Limit" is the most viscous paste the mixer can produce, "Too High" is beyond the capability of the mixer and "Normal" is typical for saltcrete paste. The midpoint of the curves (the dial readings at 300 rpm) are compared to make the comparisons simple. All of the viscometer data is presented in Table 3.2.1.2-2.

The viscosities of type I/II and type V cement were virtually the same as the full-scale process when mixed the actual waste. Both were significantly less than the limitations of the mixer (see Figures 3.2.1.2-1 and 3.2.1.2-4). The average dial reading at 300 rpm for type I/II was 78.5, and for type V it was 83.

Fly ash had very little effect on viscosity. When class C was mixed with type I/II and type V cement, the waste slurry was virtually the same as type I/II alone mixed with the full-scale equipment. Neither of the class C formulations were near the limitations of the full-scale mixing equipment (see Figures 3.2.1.2-2 and 3.2.1.2-5). The average dial readings at 300 rpm for class C mixed 50/50 with type I/II and type V were 75 and 79 respectively. When class F was mixed with type I/II and type V (see Figures 3.2.1.2-3 and 3.2.1.2-6) cement the waste slurry was virtually the same as type I/II alone mixed with full-scale equipment (see Figure 2.3.3-1). Neither of the class F formulations were near the limitations of the full-scale mixing equipment. The average dial readings at 300 rpm for class F mixed 50/50 with type I/II and type V were 79.5 and 73.5 respectively.

The two formulations that were based on the HNUS 207C Pond exhibited higher than normal (for the full-scale mixer) readings. The low water content version was too viscous to measure in the viscometer. The low water content version was slightly higher than the normal readings, 89.5 compared to 79.5 for the normal full-scale process. See Figure 3.2.1.2-7.

Two plasticizers showed improvement over the normal viscosity. PSP-L, a liquid additive made by Protex Industries, reduced the dial reading at 300 rpm only slightly, but reduced the 1 rpm to 10 rpm readings more significantly. The second plasticizer to improve the viscosity was Desco, made by Drilling Specialties, Inc. The average dial reading at 300 rpm for type I/II with Desco was 67.

The other five superplasticizers that were evaluated, D-19, D65, Tannathin, SAPP, and Spersene, did not improve the viscosity.

Table 3.2.1.2-1:

Viscometer Readings at 300 rpm. The Data Used to Build This Table is in Appendix D.

	Dial Reading at 300 rpm
Mixer limit, full-scale	210
Normal full-scale	82
Type I/II	78.5
Type V	83
50% type I/II, 50% class C	75
50% type V, 50% class C	79
50% type I/II, 50% class F	79.5
50% type V, 50% class F	73.5
Latex	152
V/C/Lime, high water content	89.5
V/C/Lime, low water content	>300
V/F/Attapulgate	>300
Type I/II with PSP-L	75
Type I/II with Desco	67

Figure 3.2.1.2-1: Type VII Cement Viscosity Data.

Figure 3.2.1.2-2: 50% Type VII Cement, 50% Class C Flyash Viscosity Data.

Figure 3.2.1.2-3: 50% Type VII Cement, 50% Class F Flyash Viscosity Data.

Figure 3.2.1.2-4: Type V Cement Viscosity Data.

Figure 3.2.1.2-5: 50% Type V Cement, 50% Class C Flyash Viscometer Data.

Figure 3.2.1.2-6: 50% Type V Cement, 50% Class F Flyash viscometer data.

Figure 3.2.1.2-7: Type V Cement, Class C Flyash, Lime Viscosity Data.

Figure 3.2.1.2-8: Type I/II Cement, Latex Viscosity Data.

Figure 3.2.1.2-9: Type V Cement, Class F Flyash, Attapulgite Clay Viscosity Data.

3.2.2 Surrogate Salts

3.2.2.1 Experimental Procedure

A surrogate of the actual process chemistry was required so that changes in chemistry could be evaluated for their effect on cement properties under controlled laboratory conditions. Initially, one sample was identified as representing the average chemistry of the twelve samples of salt submitted for characterization. This chemistry was used to formulate the surrogate salt and was derived from Lockheed Analytical Laboratory (LAL) results of salt sample D884-10191. Variations of the original surrogate chemistry will be developed in order to evaluate their effect on the saltcrete process and product.

The major constituents present in the sample were used to formulate the surrogate salt. These constituents were obtained from the Lockheed Inorganics Report and were converted from the reported concentration units of milligrams (mg) per kilogram (kg) to the number of moles present. This information is presented in Table 3.2.2.1-1.

The surrogate cation constituents were obtained from the Target Analyte (TAL) Metals Report completed by LAL. The reported analyte concentration units of mg per kg were converted to the number of moles present. When the conversion was completed, only four of the analytes were present in significant concentrations. The four cations are sodium, potassium, calcium, and magnesium.

The surrogate anion constituents were obtained by directly reading the concentration of the anion off of the Lockheed Inorganics Report. The reported concentration units of mg per kg were then converted to the number of moles present.

The formulation of the various salt compounds was derived through an iterative process that attempted to use all of the moles of anion and cation while balancing the stoichiometry of the compounds. The number of moles of cation were not expected to exactly equal the number of moles of anion, as presented above. Because the anion analysis method required a leaching procedure, preference for accuracy was given to the cation method and some of the anion moles were rounded to balance the constituents. The results of the process are presented in Table 3.2.2.1-2. All surrogate saltcrete dry blend formulation studies used a surrogate based on the constituents shown in Table 3.2.2.1-2 and the number of moles available for those constituents.

Viscosity testing indicated that salt crystal size affected the operation of the EG&G Chandler Viscometer. Large crystals present in the reagent grade containers degraded instrument response. Therefore, several size reduction techniques were used to prepare the surrogate for analysis. Size reduction methods included ball milling, salt dissolution (consisting of heating the salts in excess water until they went into solution, then boiling off the remaining water so that the salts re-crystallized into finer particles that could be easily crushed), and finally, pulverization. All of the salts were sieved through a 100 mesh screen allowing a particle size of 150 microns or less to pass. Table 3.2.2.1-3 presents the results of the size reduction methods.

TABLE 3.2.2.1-1

Cation and Anion Distribution of Major Constituents for Salt Sample D884-10191.

<u>Cations</u>	<u>Moles</u>	<u>Anions</u>	<u>Moles</u>
Sodium	6.6	Chloride	3.66
Potassium	3.4	Nitrate	3.5
Calcium	0.5	Sulfate	0.94
Magnesium	0.15	Fluoride	0.53

TABLE 3.2.2.1-2

Surrogate Salt Chemistry Based on the Lockheed Analysis of Sample D884-10191

<u>Compound</u>	<u>Moles</u>	<u>Moles-Cation</u>	<u>Moles-Anion</u>
Magnesium Chloride	0.15	0.15	0.3
Sodium Sulfate	0.5	1.0	0.5
Potassuim Sulfate	0.5	1.0	0.5
Sodium Nitrate	2.5	2.5	2.5
Potassium Nitrate	1.0	1.0	1.0
Sodium Chloride	2.5	2.5	2.5
Potassium Chloride	1.0	1.0	1.0
Sodium Fluoride	0.4	0.4	0.4
Potassium Fluoride	0.2	0.2	0.2
Calcium Carbonate	0.5	0.5	0.5

TABLE 3.2.2.1-3:
Assessment of the Different Size Reduction Methods

<u>Methods</u>	<u>Comments</u>
Ball Milling	Very time consuming
Salt Dissolution	Unsuccessful; additional treatment required
Pulverization	Labor intensive and time consuming

3.2.2.2 Results

Ball milling and pulverization successfully reduced the crystal size of the various salts so that the viscometer response was no longer affected by large salt crystals. Surrogate salt waste based on the LAL analysis was prepared by mixing the salt with water and then adding Portland type I/II cement in proportions that resulted in a salt to cement to water ratio of 0.32 to 0.38 to 0.30. The results that were obtained are shown in Figure 3.2.2.2-1. Two surrogate samples were prepared using a Hobart mixer and characterized with the viscometer in Building 881. A third surrogate sample was prepared using the Osterizer and viscometer in Building 374. The surrogate results can be compared to the results that were obtained for the actual D884-10191 salt sample that was prepared using identical ratios of salt to cement to water. The actual salts were mixed with the Osterizer and viscosity testing was conducted using the Building 374 EG&G viscometer. Independent of the mixing method that was used, the surrogate consistently underestimated the viscosity obtained for the actual D884-10191 salt by 30 to 40%.

Characterization of the rheological properties of surrogate saltcrete with various dry blend formulations was discontinued because of the large discrepancy in viscosity between the surrogate and the actual salt. The surrogate salt is being reviewed to determine if modifications to the chemistry or physical form of the salt will improve the correlation between tests conducted with surrogate salts and tests conducted with actual salts.

Figure 3.2.2.2-1: Viscosity Data

Hobart Mixer: ◆ ●

Blender: ◆ ◻

Actual salt waste rheological characterization data is presented for comparison.

3.2.3 Conclusions

Viscosity testing indicated that the type of cement or fly ash, in the concentrations tested, did not affect the flow properties of the paste and therefore the ability of the existing equipment to mix six of the ten formulations tested. Five of the seven superplasticizers (or thinners) were tested with no success in reducing the amount of water in the paste and were eliminated from further consideration. The two that had a beneficial effect, Desco and PSP-L, delayed the time of set (see Section 2.6). These additives are considered unsuitable for reducing the water content of the saltcrete on the basis of the time to set data.

Cold surrogate waste was tested in Building 881 to simulate the actual waste but had differing properties to the actual waste. As a result, characterization of the rheological properties of surrogate saltcrete with various dry blend formulations was discontinued.

The waste loading and the water content in the lab-scale samples were approximately the same as that of the currently-produced, saltcrete product. These samples contained 28 wt% water, 32 wt% salt, and 38 wt% cement to match the composition of the full-scale paste used for the process evaluation. This differs slightly from the intended composition in the Liquid Waste Treatment Operations SOP of 28 wt% water, 35 wt% salt, and 37 wt% cement.

The viscosities of type I/II cement were virtually the same as type V cement. This was expected because for other applications the water requirements and flow properties of the two types of cement are the same. The particle size distribution of the cement has more effect on viscosity than the type of cement. Since there was no significant difference between the rheology of the two types of cement tested, they can be interchanged with no adverse effect on the mixing. The comparison of the two cements was made to see if a chemical reaction with the waste affected the rheology of one type of cement in a unique way and because type V cement is commonly used to resist degradation due to sulfate attack.

The two classes of fly ash tested on lab-scale in this study did not significantly affect the rheology. Class C and class F fly ash were each blended 1:1 on a weight basis with Type I/II and Type V cement and then mixed with the Building 374 brine and spray-dried salt. Since there was no significant difference between the use of fly ash and cement, the fly ash can be substituted with no loss of effectiveness of the mixer. Fly ash is used in waste treatments to reduce mobility of the hazardous constituents, bind water, and reduce the cost of the treatment. Both classes of fly ash were used during the durability testing (see Section 3.3).

Seven superplasticizers were tested to see if viscosities would be reduced. If the viscosity of the paste could be reduced when the water content is the same as the full-scale process, then the amount of water could be reduced to give the same viscosity. Reduction of the water content is beneficial to waste form stability and immobilization of the waste. The superplasticizers were added to lab-scale samples of saltcrete at a concentration of 1.5 wt% of cement + fly ash, except for PSP-L which is a liquid. The PSP-L concentration, 20.4 ml/(kg cement + fly ash), was doubled from the manufacturer's recommendation after the normal concentration was found to be ineffective. Two superplasticizers, Desco and PSP-L, had the desired effect. Desco is a product of Drilling Specialties, Inc. that contains sulfomethylated tannin. PSP-L is a product of Protex Industries that contains modified naphthalene sulfonate. Since both increased the time to set, they were not considered suitable for use in the saltcrete process.

Dow Modifier A, a latex additive, was added to lab-scale samples of type I/II cement in the concentration recommended by the manufacturer. It had such an adverse effect on the viscosity that it is beyond the limitations of the full-scale mixer. This additive was tested because it thought that it might improve the durability of product. It was eliminated from further testing because of the adverse effect on viscosity.

Attapulgate clay, an additive used at Hanford in the cementation treatment nitrate salts waste (7), was tested to see how it might improve the viscosity. It was eliminated from further testing because it had the opposite effect, an increase in viscosity.

Two versions of the HNUS 207C Pond formulation were tested to see if the knowledge gained from that project could be applied to the newly generated saltcrete. One formulation was the HNUS version as it was recommended for the 207C Pond. The second formulation was modified to contain the same amount of water as the currently generated saltcrete. The high water content version was tested to provide a more direct comparison to the other formulas and it was thought the mixer limitations would prohibit use of the low water content formulation. The limitations of the mixer were exceeded by the original version of the formula. The high water content version was more viscous than the currently generated saltcrete although it did not exceed the limitations of the mixer. Both versions of the 207C Pond formulation were eliminated from further testing because they exhibited higher viscosities than the current formulation.

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3.3 ACCELERATED AGING TESTS

The objective of the work described in this section was to evaluate various formulations for durability. Duplicate lab-scale samples were subjected to hot, cold, humid and dry conditions. The waste loading was approximately the same as the newly generated saltcrete to make a comparison to the full-scale process. The list of formulations and additives is in Table 3.3-1. Surrogate salts were used to find cause and effect of waste components. The purpose of the accelerated aging was to evaluate the relative durability of various formulations

3.3.1 Actual Salts

Duplicate lab-scale samples of each formulation were evaluated to eliminate those that would not tolerate freeze/thaw cycling. The formulations and additives evaluated are listed in Table 3.3.1-1. The samples were poured into 1" diameter X 2" high cylindrical molds and cured at 55°C for 2 days. After curing, the samples were weighed and the dimensions measured and recorded.

TABLE 3.3.1-1

FORMULATIONS FOR FREEZE/THAW AND WET/DRY TESTING

Cement Type		Admixture	
I	100%		
I	50%	C fly ash	50%
I	50%	F fly ash	50%
I/II	100%		
I/II	50%	C fly ash	50%
V	100%		
V	50%	C fly ash	50%
V	50%	F fly ash	50%

3.3.1.1 Investigation of Wet/Dry Cycling of Saltcrete

3.3.1.1.1 Experimental Procedure

The dry blend formulations were randomly selected and mixed with salt and brine in a Hobart mixer. Duplicate samples were poured into 1" diameter X 2" high plastic molds that were sealed with a plastic lid. The samples were cured for 2.5 days at 55°C then removed from the molds. Before-and-after weights and dimensions were measured and are presented in Figure 3.3.1.1.1-1. The wet/dry cycling was as follows:

- The samples were placed in a wet/dry chamber at 40°C (104°F) and 95% relative humidity for 48 hours.
- The relative humidity was then reduced to 20% and the temperature raised to 55°C for 48 hours.
- The wet and dry cycles were each repeated one more time, so that each sample was subjected to high humidity and low humidity twice after curing.

3.3.1.1.2 Results of Wet/Dry Cycling

All of the samples lost weight after the wet/dry cycling test. The samples lost an average of 28% of the original weight. Type V cement with class C fly ash lost the lowest percentage of weight, 27%. The results are presented in Table 3.3.1.1.2-1 and Figures 3.3.1.1.2-1, -2, and -3.

In contrast to the weight loss measurements, the samples did not show significant changes in dimension after the wet/dry testing. The type I cement samples were the only ones that increased in volume. The increase was slight, 0.35%. All of the other samples decreased in volume.

None of the samples showed significant cracking or other signs of degradation. The samples of type V cement had a few hairline cracks, probably due to shrinkage.

3.3.1.2 Investigation of Freeze/Thaw Cycling of Saltcrete

3.3.1.2.1 Experimental Procedure

Samples for freeze/thaw cycling were prepared according to the procedure used for wet/dry cycling. The freeze/thaw cycling was conducted as follows:

- The samples were placed in a freezer at -20°C for 2 days.
- The samples were moved to the oven where the temperature was 55°C for 2 days.
- The above two steps were repeated so that each sample was frozen twice and heated twice after curing.

Table 3.3.1.1.2-1: Actual Salt Wet/Dry Data

Formulation	Sample Number	Average Diameter Change, %	Average Height Change, %	Average Weight Change, %	Initial Volume, cc	Final Volume, cc	% Volume Change
100% Type I	1	0.15	-0.25	-27.68	19.71	19.72	0.06
	2	0.42	-0.20		19.56	19.69	0.64
50% Type I 50% Fly Ash C	3	-0.54	-0.28	-27.89	19.36	19.10	-1.35
	4	-0.42	-0.42		19.77	19.52	-1.25
50% Type I 50% Fly Ash F	5	-0.45	-0.35	-27.86	20.22	19.97	-1.25
	6	-1.40	-0.47		19.96	19.31	-3.25
100% Type V	7	-0.83	-0.45	-27.58	19.92	19.50	-2.11
	8	0.54	-0.47		19.69	19.81	0.59
50% Type V 50% Fly Ash C	9	-0.61	-0.10	-26.58	19.62	19.37	-1.31
	10	-0.04	-0.40		19.53	19.44	-0.47
50% Type V 50% Fly Ash F	11	-0.46	-0.37	-27.20	20.02	19.76	-1.27
	12	-0.68	-0.50		20.17	19.80	-1.84
100% Type I/II	13	0.42	-0.44	-31.55	18.00	17.77	-1.27
	14	0.46	-0.27		19.55	19.31	-1.19
50% Type I/II 50% Fly Ash C	15	0.57	-0.18	-31.26	19.53	19.28	-1.31
	16	0.31	-0.27		19.33	19.16	-0.89

Figure 3.3.1.1.2-1: Actual Salt Sample Diameter Change After Wet/Dry Cycling

Figure 3.3.1.1.2 -2: Actual Salt Sample Length Change After Wet/Dry Cycling

Figure 3.3.1.1.2-3: Actual Salt Sample Volume Change After Wet/Dry Cycling

3.3.1.2.2 Freeze/Thaw Cycling Results

All of the samples lost weight after the freeze/thaw cycling test. The samples lost an average of 22% of the original weight. Type V cement with class C fly ash lost the lowest percentage, 22%. The results are presented in Table 3.3.1.2.2-1 and in Figures 3.3.1.2.2-1, -2, -3.

The type I cement and the type I cement with class C fly ash had the greatest change in dimensions after the freeze/thaw testing. The overall average diameter increase was 0.29% while the overall length increase was 0.22%. The type I cement and the type I cement with class C fly ash increased in volume by 17% and 17.18% respectively. The diameters increased by 5.45% and 5.81%, respectively. The lengths increased by 5.22% and 4.66%, respectively. The type V cement samples increased slightly in volume, diameter, and length (1.06%, 0.44%, and 0.17%, respectively). The other samples decreased in volume.

Photographs taken of the samples after freeze/thaw testing show the swelling of the type I cement, and the type I cement with class C fly ash. Photograph 3.3.1.2.2-1 is a comparison of the type I cement samples. Sample 4C and 1C are noticeably taller than the other type I cement samples. Photograph 3.3.1.2.2-2 is a comparison of type V and type I cement samples after freeze/thaw testing and after wet/dry testing. The samples that are noticeably taller (1C and 1D) are the type I cement samples after freeze/thaw testing.

Only the type I cement with class C fly ash showed significant cracking or other signs of degradation (see Photograph 3.3.1.2.2-1). The type I cement with class C fly ash samples were on the verge of crumbling. Other samples did have small fractures and exhibit signs of degradation. Type V cement and type V cement with class F fly ash (see Photograph 3.3.1.2.2-3) had hairline fractures. The swelling and cracking was evident for some of the samples after the first freeze/thaw cycle. The dimensions were measured at the end of the test to minimize damage and outside influence to the samples.

The relative harshness of the wet/dry testing and the freeze/thaw testing is illustrated in Photograph 3.3.1.2.2-4. It shows type I cement with class C fly ash samples after wet/dry testing (samples 4A and 4B) and the freeze/thaw testing (samples 4C and 4D). Only samples subjected to freeze/thaw testing showed significant swelling. Photograph 3.3.1.2.2-5 shows another difference between freeze/thaw and wet/dry testing: salt migration is more evident on the wet/dry samples (samples A and B) than on the freeze/thaw testing (samples C and D).

The freeze/thaw testing indicated that four of the formulations were prone to swelling, while the wet/dry test did not show any serious degradation. Since swelling is an occasional problem in the full-scale process, the freeze/thaw test proved to be a good one. Swelling was noticeable after the first 48-hour freeze cycle indicating that one freeze cycle could be a production-line quality check. (Since the temperature of the samples quickly reaches the temperature of the refrigerator, it may be possible to use a shorter test.)

Two formulations exhibited significant swelling while two others swelled slightly. The two formulations that exhibited significant swelling were type I cement and type I cement with 50% class C fly ash. Samples of both formulations swelled 5% in diameter, 5% in length, and 17% in volume. A 5% increase in length is

significant if it is applied to the length of a full-size waste container. The halfcrates used to store saltcrete are 84 inches long. A 5% increase corresponds to 4.2 inches, which is enough to cause damage to the container. Based on the freeze/thaw test, type I cement and class C fly ash are not good choices for treating saltcrete. The two formulations that swelled slightly were type I/II cement, and type I/II cement with 50% class C fly ash. Type I/II cement swelled 1.7% in length and 5.1% in volume. Type I/II cement with class C fly ash swelled 2.5% in length and 7.9% in volume. Type I/II cement is used to solidify saltcrete at RFP.

Type I/II cement and type I/II with 50% class C fly ash swelled approximately 5% in length after freeze/thaw cycling. See Photograph 3.3.1.2.2-6 and -7.

Class F fly ash was beneficial in all samples subjected to freeze/thaw cycling. Class F fly ash reduced swelling when mixed with type I, I/II, and type V cement. This was in contrast to class C fly ash.

Samples made with type V cement exhibited less swelling than samples of the other two cements. Comparison of each cement with no fly ash shows type V cement swelled the least. Comparison of each cement mixed with class C fly ash shows the type V cement swelled the least. Comparison of the type V cement and type I cement mixed with class F fly ash shows that the type V cement swelled less (type I/II cement mixed with class F fly ash was not tested).

The swelling of the saltcrete is likely due to a chemical reaction between sulfates and nitrates in the waste and tricalcium aluminate and calcium oxide in the cement. This reaction is aggravated by large temperature changes but is not influenced by changes in humidity. Cements with high tricalcium aluminate concentrations exhibited more swelling in the freeze/thaw test.

In summary, freeze/thaw testing showed that:

- Type I cement and class C fly ash caused swelling of 5% in length, (more than was observed for the halfcrates in storage).
- Type I/II cement, the type currently used in saltcrete production, swelled 2% in length (about the average of the swelling crates).
- Type V cement and class F fly ash reduced or eliminated swelling.

Table 3.3.1.2.2-1: Actual Salt Freeze/Thaw Data

Formulation	Sample Number	Average Diameter Change, %	Average Height Change, %	Average Weight Change, %	Initial Volume, cc	Final Volume, cc	% Volume Change
100% Type I	1	5.40	5.38	-21.63	19.81	23.20	17.08
	2	5.50	5.05		19.74	23.08	16.91
50% Type I 50% Fly Ash C	3	5.51	4.35	-22.67	19.59	22.75	16.15
	4	6.12	4.97		19.59	23.16	18.20
50% Type I 50% Fly Ash F	5	-0.95	-0.85	-23.74	20.04	19.50	-2.72
	6	-0.61	-0.67		19.96	19.59	-1.98
100% Type V	7	0.77	0.30	-21.87	19.64	20.00	1.83
	8	0.11	0.05		19.90	19.96	0.28
50% Type V 50% Fly Ash C	9	-0.69	-0.55	-21.62	19.65	19.27	-1.91
	10	-0.65	-0.52		19.71	19.36	-1.81
50% Type V 50% Fly Ash F	11	-0.88	-0.59	-23.17	19.93	19.47	-2.32
	12	-0.76	-0.72		19.92	19.48	-2.23
100% Type I/II	13	1.49	1.55	-21.05	19.49	20.39	4.61
	14	1.91	1.77		19.68	20.80	5.70
50% Type I/II 50% Fly Ash C	15	2.53	2.43	-21.40	19.46	20.95	7.69
	16	2.85	2.13		19.32	20.88	8.02

Figure 3.3.1.2.2-1: Actual Salt Sample Diameter Change After Freeze/Thaw Cycling

Figure 3.3.1.2.2-2: Actual Salt Sample Length Change After Freeze/Thaw Cycling

Figure 3.3.1.2.2-3: Actual Salt Sample Volume Change After Freeze/Thaw Cycling

Photograph 3.1.2.1. Sample comparison of zeolite cement and actual salt waste after 4 freeze thaw cycles.

Figure 1. Comparison of Type V current samples mixed with additives and actual salt waste (for 4 freeze/thaw cycles)

Dry Blend
50% Type I
50% Elvash C
4 Cycles Wet Dry

50% Type I
50% Elvash C
4 Cycles Freeze Thaw

Photograph 3.3.1.2.2-4 Comparison of Type I cement mortar with Elvash C and a 50% Type I wet dry and 4 cycles of freeze thaw testing

Photograph 3.3.1 2-2-5 Comparison of wet dry samples (A & B) to freeze thaw samples (C & D).

Dry Blend

100% Type I/II Cement
(After Wet Dry Cycling)

100% Type I/II Cement
(After Freeze Cycle)

Photograph 3.3.1 2.2-6: Type I/II cement after wet dry cycling and after the freeze cycle using actual waste

Dry Blend: 50% Type I/II Cement
50% Type C Flyash
(After Wet/Dry Cycling)

50% Type I/II Cement
50% Type C Flyash
(After Freeze Cycle)

Photograph 3.3.1.2.2-7: Type I/II cement after wet/dry cycling and after the freeze cycle using actual waste.

3.3.2 Surrogate Salt Durability Testing

3.3.2.1 Wet/Dry Cycling

3.3.2.1.1 Experimental Procedure

The surrogate salt chemistry used for these experiments was the average chemistry as described in Section 3.2.2.1. A total surrogate mass of 450 gms was blended to provide sufficient samples for the wet/dry, and freeze/thaw cycling tests.

Surrogate brine was prepared by adding approximately one liter of distilled water to 450 grams of salt. The mix was heated to the brine boiling point while stirring. Additional distilled water was added as the temperature increased in order to facilitate dissolution. When the brine began to boil, all of the crystalline salts appeared to be in solution although the powder salts appeared to be suspended in solution. Based on the solubility of the different salts, it is reasonable to assume that the material not completely solubilized was the calcium carbonate, which has an extremely low solubility. The solubilities of the salts (ref Merck and CRC) in cold and hot water are presented in Table 3.3.2.1.1-1.

The brine was allowed to continue boiling until enough water had been driven off to bring the water volume to slightly less than 374 ml. At this point, heating was discontinued and the brine was allowed to cool to room temperature while stirring to prevent large crystal growth. When the brine reached room temperature, it was placed in a Hobart mixer and the container was rinsed with enough distilled water to bring the volume to 374 ml.

Six identical brine solutions were prepared as described above to test the six different proposed dry blend formulations (described in Section 3.2.3). All of the component percentages were based on weight percent.

A total of 506 grams of cement or cement/admixture was incorporated into the brine solution. The mixture was gently stirred by hand for 30 seconds with a rubber spatula to facilitate wetting of the cement. The slurry was then mixed in a Hobart mixer in accordance with ASTM C305-82 (ref) at low speed due to the viscosity of the slurry.

The mixture was poured into 1 x 2-inch cylindrical polyethylene molds, tapped ten times to eliminate air bubbles, and capped. The molds were then placed in a laboratory oven and cured for 86 hours at 55°C followed by additional curing at 75°C for 73 hours. A total of four samples were poured for each of the six formulations, providing duplicate samples for the wet/dry and freeze/thaw cycling tests.

At the end of the curing cycle, the samples were allowed to cool and then removed from the molds. Before and after weights and dimensions were measured and are presented in Figure 3.3.2.1.1-1.

TABLE 3.3.2.1.1-1:

Solubility of Reagent Salts

Compound	Solubility-Cold Water	Solubility-Hot Water
Magnesium chloride	167gm/100ml*	367gm/100ml
Sodium sulfate	4.76gm/100ml	42.7gm/100ml
Potassium sulfate	1gm/8.3ml	1gm/4ml
Sodium nitrate	1gm/1.1ml	1gm/0.6ml
Potassium nitrate	1gm/2.8ml	1gm/0.5ml
Sodium chloride	1gm/2.8ml	1gm/2.6ml
Potassium chloride	1gm/2.8ml	1gm/1.8ml
Sodium fluoride (CRC)	4.22gm/100ml	
Potassium fluoride (CRC)	349.3gm/100ml	Very soluble
Calcium Carbonate (CRC)	0.0014gm/100ml	0.0018gm/100ml

(Reference solubility data from the Merck Index unless noted as from the Handbook of Chemistry and Physics (CRC). Solubility reference given for potassium fluoride dihydrate and magnesium chloride hexahydrate as they were the chemicals used for the surrogate brine).

The duplicate samples of the six dry blend formulations were placed in a laboratory Blue "M" Environmental Chamber. The cycling test began with a "wet" cycle that had a temperature of 40°C and a relative humidity of 95%. These conditions were maintained for 48 hours. The "dry" cycle was then initiated by increasing the temperature to 55°C and reducing the relative humidity to $\leq 20\%$. The wet and dry cycles were each repeated one more time.

At the completion of the wet/dry cycling test, the samples were allowed to cool before weighing. The dimensions and mass were then measured and recorded.

3.3.2.1.2 Results of Wet/Dry Cycling Tests

The majority of the samples expanded in diameter, height, and volume during the test cycle. However, expansion was not large for any of the samples. These results are summarized in Table 3.3.2.1.2-1. The largest volume increase occurred for sample 7, the 100% type V cement. This sample increased in volume nearly 4%. The smallest amount of expansion occurred for sample 12 (50% type V cement with 50% class F fly ash), approximately 0.5%. Figure 3.3.2.1.2-1 demonstrates the magnitude of the diameter changes that occurred for the individual samples. Figure 3.3.2.1.2-2 shows the magnitude of the height changes and Figure 3.3.2.1.2-3 shows the magnitude of the volume changes that occurred for the surrogate samples. Overall, the most expansive formulation was 100% type V cement and the least expansive formulation was 50% type V with 50% class F fly ash. Expansion of the surrogate samples was significantly less than the expansion observed in the samples prepared with actual salt waste.

Table 3.3.2.1.2-1: Surrogate Wet/Dry Data

Formulation	Sample Number	Average Diameter Change, %	Average Height Change, %	Average Weight Change, %	Initial Volume, cc	Final Volume, cc	% Volume Change
100% Type I	1	0.93	0.35	-5.18	22.548	22.835	1.27
	2	0.66	-0.07		22.399	22.529	0.58
50% Type I 50% Fly Ash C	3	-0.05	-0.17	-12.57	22.668	22.612	-0.25
	4	0.38	0.25		22.175	22.316	0.64
50% Type 50% Fly Ash F	5	1.80	0.15	-10.16	22.498	22.936	1.95
	6	0.61	-0.15		22.427	22.531	0.46
100% Type V	7	3.09	0.76	-3.82	16.082	16.701	3.85
	8	1.27	-0.07		22.619	22.887	1.18
50% Type V 50% Fly Ash C	9	1.35	0.20	-6.79	22.458	22.804	1.54
	10	1.49	0.15		22.516	22.885	1.64
50% Type V 50% Fly Ash F	11	-0.11	-0.08	-9.42	22.487	22.445	-0.19
	12	0.38	0.07		22.544	22.647	0.46

All of the dry blend formulations lost weight. Table 3.3.2.1.2-2 illustrates the differences in the magnitude of weight loss for the different formulations. The samples that contained 100% cement lost the least amount of mass whereas the samples containing fly ash C lost the most mass.

The overall percent average of the mass lost is 8%, which is less than half of the average percent mass loss that occurred during the wet/dry cycling test of actual saltcrete containing the dry blend formulations.

Photographs 3.3.2.1.2-1, through -5 show the samples of the various dry blend formulations that were evaluated from the wet/dry cycle test. Photograph 3.3.2.1.2-1 shows samples 1,2 (100% type I Portland cement), 3,4 (50% type I with 50% fly ash C), and 5,6 (50% type I with 50% fly ash F), from left to right. Photograph 3.3.2.1.2-2 shows samples 7,8 (100% type V cement), 9,10 (50% type V with 50% fly ash C), and 11,12 (50% type V with 50% fly ash F). Sample number 7 (100% type V cement) failed upon removal from the polyethylene mold.

Photograph 3.3.2.1.2-3 compares samples 1 and 2 (100% type I) with samples 7 and 8 (100% type V cement). Of the set, samples 7 and 8 had slightly more salt on the sample exterior. Also, the type V samples had a "greenish" appearance, indicating that they had not completely hydrated.

Photograph 3.3.2.1.2-4 compares samples 3 and 4 (50% type I and 50% fly ash C) to samples 9 and 10 (50% type V and 50% fly ash C) where it can be seen that samples 9 and 10 had slightly more salt on the exterior. Photograph 3.3.2.1.2-5 compares samples 5 and 6 (50% type I and 50% fly ash F) to samples 11 and 12 (50% type V and 50% fly ash F). This set of samples appeared to have an equivalent amount of salt on the exterior of the samples.

TABLE 3.3.2.1.2-2:

Percent Mass Lost for the Wet/Dry Samples Ranked from Greatest to Least Amount of Loss

<u>Ranking</u>	<u>Sample No.</u>	<u>Formulation</u>	<u>Mass Lost (%)</u>
1	3	50%I/50%FA-C	13.6
2	4	50%I/50%FA-C	11.5
3	6	50%I/50%FA-F	11.1
4	12	50%V/50%FA-F	10.6
5	5	50%I/50%FA-F	9.2
6	11	50%V50%FA-F	8.3
7	9	50%V/50%FA-C	7.6
8	2	100% type I	6.4
9	10	50%V/50%FA-C	5.9
10	7	100% V	4.4
11	1	100% I	4.0
12	8	100%V	3.2

Figure 3.3.2.1.2-1: Average Percent Diameter Change for Surrogate Saltcrete After Wet/Dry Cycling

Figure 3.3.2.1.2-2: Average Percent Height Change for Surrogate Saltcrete After Wet/Dry Cycling

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Figure 3.3.2.1.2-3: Percent Volume Change for Surrogate Saltcrete After Wet/Dry Cycling

DRY 100% Type I
BLEND:

50% Type I
50% Flyash C

50% Type I
50% Flyash F

PHOTOGRAPH 3.3.2.1.2-1: 1" X 2" Samples after 4 wet/dry cycles.

DRY 100% Type V
BLEND:

50 % Type V
50% Flyash C

50 % Type V
50 % Flyash F

PHOTOGRAPH 3.3.2.1.2-2: 1" X 2" samples after 4 wet/dry cycles.

DRY 100% Type 1
BLEND

PHOTOGRAPH 102123 Comparison of sample #s 1, 2 with 3, 4 after 4 wet dr. cycles

Type
F145F

Type
F145F

Micrograph of sample #3 with 4 wet dry cycles

DRY 100% Type I
BLEND:

50% Type I
50% Flyash C

50% Type I
50% Flyash F

PHOTOGRAPH 3.3.2.2.2-1: 1" X 2" samples after 4 freeze/thaw cycles.

3.3.2.2 Freeze/Thaw Cycling of Surrogate Salt Samples

3.3.2.2.1 Experimental Procedure

Duplicate samples of surrogate saltcrete containing the six different formulations were prepared at the same time as the wet/dry samples. Therefore, the experimental procedure for sample preparation is identical to that of section 3.3.2.1.1.

The set of surrogate formulation samples was placed in a freezer at -12°C for 48 hours. When this cycle was completed the samples were immediately placed in a Blue M laboratory oven at 55°C for 48 hours. The samples were then subjected to one more freeze/thaw cycle for a total of four cycles, two thaw cycles and two freeze cycles.

Once the freeze/thaw cycles were completed, the samples were weighed and the dimensions recorded.

3.3.2.2.2 Results of Freeze/Thaw Cycling Tests

All of the samples expanded in diameter, height, and volume as a result of the freeze/thaw test. The largest volume increase was noted for sample number 18 (50% type I with 50% fly ash F) and was 9%, more than twice the largest volume increase that occurred during the wet/dry cycling. The smallest volume expansion occurred in sample number 20 (100 type V cement) at 2.5%. This can be compared to the smallest amount of volume expansion that occurred during the wet/dry cycling test (0.46%) which occurred for samples 6 (50% type I with 50% fly ash F) and sample number 12 (50% type V with 50% fly ash F).

Diameter expansion for all of the samples is shown in Figure 3.3.2.2.2-1. Figure 3.3.2.2.2-2 shows the height increase and Figure 3.3.2.2.2-3 shows the volume increase for all the samples subjected to the freeze/thaw cycling test. These results are summarized in Table 3.3.2.2.2-1. When the dimensional changes were averaged for each sample, the most expansive formulation was 50% type V cement with 50% fly ash C (8.2%). In contrast, the most expansive formulations for actual saltcrete were 100% type I cement and 50% type I with 50% type C fly ash, both of which demonstrated volume increases of approximately 17%. Testing conducted with surrogate salts underestimated the magnitude of expansion by approximately 47%.

All of the dry blend formulations lost weight. Table 3.3.2.2.2-2 illustrates the differences in the magnitude of weight loss for the different formulations. The samples that contained 100% cement type V lost the least mass whereas the samples containing fly ash C lost the most mass.

Overall, the average of the mass that was lost is 15.6%, approximately twice that which was lost during the wet/dry cycle test.

Photographs 3.3.2.2.2-1 through -5 illustrate the visual appearance of the samples at the completion of the freeze/thaw cycle test.

Photograph 3.3.2.2.2-3 compares samples 13 and 14 (100% type I) with samples 19 and 20 (100% type V cement). It can be seen that samples 19 and 20 appear to have significantly more transport of salt occurring through the cement based matrix to produce the hairlike crystal growth.

Photograph 3.3.2.2.2-4 compares samples 15 and 16 (50% type I and 50% fly ash C) to samples 21 and 22 (50% type V and 50% fly ash C). The incorporation of fly ash C into the cement matrix appears to produce a microstructure that is prone to cracking. Photograph 3.3.2.2.2-5 compares samples 17 and 18 (50% type I and 50% fly ash F) to samples 23 and 24 (50% type V and 50% fly ash F). Although cracking is present in the samples containing class F fly ash, the extent and depth of the cracks is less than that observed in the samples that contained class C fly ash.

Table 3.3.2.2-1: Surrogate Freeze/Thaw Data

Formulation	Sample Number	Average Diameter Change, %	Average Height Change, %	Average Weight Change, %	Initial Volume, cc	Final Volume, cc	% Volume Change
100% Type I	13	0.02	0.03	-14.29	22.523	23.292	3.41
	14	0.03	0.03		22.417	23.501	4.83
50% Type I 50% Fly Ash C	15	0.03	0.05	-19.64	22.231	23.664	6.44
	16	0.04	0.05		22.495	24.205	7.60
50% Type I 50% Fly Ash F	17	0.02	0.03	-16.39	22.407	23.304	4.00
	18	0.06	0.04		22.535	24.571	9.03
100% Type V	19	0.02	0.11	-10.59	21.290	22.988	7.97
	20	0.01	0.02		22.515	23.084	2.53
50% Type V 50% Fly Ash C	21	0.04	0.06	-18.71	22.530	24.379	8.20
	22	0.04	0.06		22.478	24.320	8.19
50% Type V 50% Fly Ash F	23	0.02	0.02	-14.29	22.439	23.255	3.64
	24	0.02	0.02		22.516	23.310	3.53

TABLE 3.3.2.2.2-2:

Percent Mass Loss from the formulation following the freeze/thaw test. The ranking is from the most amount of mass lost to the least amount.

Ranking	Sample No.	Formulation	Mass Lost (%)
1	15	50%I/50%FA-C	19.6
2	16	50%I/50%FA-C	19.6
3	22	50%V/50%FA-C	19.2
4	21	50%V/50%FA-C	18.2
5	18	50%I/50%FA-F	16.8
6	17	50%I/50%FA-F	16.0
7	14	100% type I	14.7
8	23	50%V/50%FA-F	14.5
9	24	50%V/50%FA-F	14.1
10	1	100% type I	13.9
11	19	100% type V	11.3
12	20	100% type V	9.8

Figure 3.3.2.2.2-2: Average Percent Height Change for Surrogate Saltcrete After Freeze/Thaw Cycling

Figure 3.3.2.2.2-3: Percent Volume Change for Surrogate Saltcrete After Freeze/Thaw Cycling

DRY 100% Type V
BLEND:

50% Type V
50% Flyash C

50% Type V
50% Flyash F

PHOTOGRAPH 3.3.2.2-2: 1" X 2" samples after 4 freeze/thaw cycles.

DRY
BLEND:

100% Type I

100% Type V

PHOTOGRAPH 3.3.2.2-3: Comparison of sample #'s 13, 14 with 19, 20 after 4 freeze/thaw cycles.

DRY 50% Type I
BLEND: 50% Flyash C

50% Type V
50% Flyash C

PHOTOGRAPH 3.3.2.2-4: Comparison of sample #'s 15, 16 with 21, 22 after 4 freeze/thaw cycles.

DRY 50% Type I
BLEND: 50% Flyash F

50% Type V
50% Flyash F

PHOTOGRAPH 3.3.2.2.2-5: Comparison of sample #'s 17, 18 with 23, 24 after 4 freeze/thaw cycles.

3.3.3 Discussion/Conclusions

The criterion used to evaluate the relative stability of the various formulations was expansion. Increases in diameter, height, and volume were recorded for each sample tested and assigned a ranking of 1 through 8 for actual saltcrete samples and 1 through 6 for surrogate saltcrete samples. A ranking of 1 was given to the sample with the smallest diameter, height, and volume increase whereas a ranking of 8 (or 6 for the surrogates) was assigned to the samples with the greatest diameter, height, and volume increase. The rankings for both durability tests are summarized in Table 3.3.3-1.

Also included in Table 3.3.3-1 is a ranking based on a visual determination of the amount of time the different formulations required to set (the "Time to Set" column). A ranking of 1 equates to the shortest time required to set whereas a ranking of 6 means that the formulation took the longest time to set. This is discussed in more detail in Section 3.4.

The formulation that exhibited the least amount of swelling was the 50% type V cement and 50% class F fly ash blend. The formulation that exhibited the greatest amount of swelling was type I cement with class C fly ash for the actual salts and type I with class F fly ash for the surrogate salts.

Type V cement and class F fly ash generally reduced the amount of swelling, while type I cement and class C fly ash generally increased the amount of swelling. Samples prepared with type I/II cement swelled less than samples prepared with type I cement but more than samples prepared with type V cement. The type I, type I/II, and type V cements used in this study had tricalcium aluminate concentrations of 12%, 6%, and 5%, respectively. The calcium oxide concentration in the class C fly ash was approximately 29% while the calcium oxide concentration in the class F fly ash was approximately 20%. These results indicate that the observed waste form swelling is probably due to a chemical reaction between sulfates and nitrates in the waste and tricalcium aluminate and calcium oxide in the cement and fly ash.

The freeze/thaw cycle test is significantly more challenging to the cement microstructure than the wet/dry cycle test. Therefore, future durability testing can be simplified by eliminating the wet/dry cycle test.

**TABLE 3.3.3-1:
DRY BLEND RANKINGS**

Ranking of the different dry blend formulations based on results obtained following durability testing of actual and surrogate saltcrete. A ranking of 1 indicates the least amount of swelling. Dia=diameter; Ht=height; Vol=volume; C=fly ash type C; F=fly ash type F. Roman numerals indicate cement type.

Formulation	Actual Saltcrete						Actual Saltcrete Time To Set	Surrogate Saltcrete					
	Freeze/Thaw			Wet/Dry				Freeze/Thaw			Wet/Dry		
	DIA	HT	VOL	DIA	HT	VOL		DIA	HT	VOL	DIA	HT	VOL
Type I/II	5	5	5	3	5	1		NOT AVAILABLE					
Type I/II-C	6	6	6	6	7	3		NOT AVAILABLE					
Type V	4	4	4	4	4	4	4	6	1	4	6	6	6
Type V-F	1	2	1	1	2	1	6	1	1	1	1	1	1
Type V-C	2	3	3	2	3	3	2	5	4	5	3	4	4
Type I-F	3	1	2	3	1	2	5	3	6	6	2	5	5
Type I-C	8	7	8	8	7	8	1	2	3	3	4	2	2
Type I	7	8	7	7	8	7	3	2	3	2	5	3	3

3.4 TIME OF SET

As previously mentioned, the set time of the saltcrete halfcrates is an important parameter for production operations. Saltcrete half crates are staged in the Building 374 waste treatment facility until the paste hardens, at which point the half crates are closed and transferred to interim storage. Due to space limitations, production operations cannot begin on the next saltcrete run until the half crates produced by the previous run have been transferred out of Building 374. Since Liquid Waste Treatment Operations (LWTO) tries to operate at two week intervals, saltcrete formulations that take longer than approximately 5 days to harden could delay operations. Thus, an important success criteria for new formulations is time to set.

Probably the least subjective method for measuring set time is to monitor the temperature of the cement as it cures. The time to the peak of the exotherm can be interpreted as the time to set.

The problem with using temperature profiles to identify time to set in a strongly retarded cement is the fact that heat dissipates so rapidly in the small samples that no temperature rise associated with the hydration exotherm is observed. In an attempt to retain sufficient heat such that the temperature profile can be recorded, three insulated curing chambers were built. A paste consisting of actual salt waste and 100% type I/II cement was prepared using the same component ratios used for all other tests. The paste was poured into three 4 x 12 x 2.5 inch molds and each mold was placed in an insulated curing chamber. Thermocouples connected to an Omega data logger were placed in each mold and the temperature profile was logged over a period of 15 days.

Results are graphed in Figure 3.4-1. The hydration peak was clearly observed approximately 14 days after the samples were poured, which is delayed several days from what was observed in the full-scale production runs. The delay is probably due to differences in heat retention between the half crates and the small laboratory samples. Increased heat retention will accelerate the hydration reaction. In spite of the delay, the insulated curing chamber can provide a means of accurately evaluating and comparing the reaction time of various formulations. Unfortunately, each of the three insulated curing chambers can accommodate only one sample and, since the samples take approximately 2 weeks to hydrate, it was not possible to gather time to set information on all of the dry blend formulations tested using this method.

A qualitative assessment of time to set was made for actual salt waste encapsulated in the various dry blend formulations. A pocket penetrometer was used to test for hardness. The formulations set in the following order from fastest to slowest:

1. 50% type I, 50% class C fly ash
2. 50% type V, 50% class C fly ash
3. 100% type I
4. 100% type V

5. 50% type I, 50% class F

6. 50% type V, 50% class F

Qualitative time to set information was not recorded for the type I/II formulations.

Samples prepared with Desco, the thinner that provided the best viscosity results, never hydrated. For this reason, plus the fact that only marginal improvements were noted with the thinners, Desco and other thinners were excluded from further evaluation.

4.0 CONCLUSIONS

The performance of the saltcrete process was evaluated and compared to the applicable waste acceptance criteria. The process is capable of producing acceptable waste forms. The major issues precluding certification are inadequate process controls and a lack of legally defensible waste characterization.

Process Control

Documentation and control of the process parameters are necessary for certification of the saltcrete. Process parameters that impact the operations or product quality, such as waste loading or water to cement ratio, must be maintained within established control boundaries in order to certify saltcrete. The key process parameters identified in this study are:

1. Waste loading;
2. Water to content;
3. Tricalcium aluminate concentration in cement; and
4. Calcium oxide concentration in fly ash (if recommended for production operations).

Waste load and water content ratio currently controlled by measuring the specific gravity of the brine using a hydrometer and by measuring the component weights using load cells on the mix tank. In addition to the current documentation, the weight of the empty crates, the weight of the crates just after filling, the cumulative zero readout, adjustment of the weighing systems, and a data acquisition system to provide a confirmation of transcribed data are recommended. This will help establish process control and improve documentation. Currently, all of the data is manually transcribed.

Calibration of the process control instrumentation is also necessary for certification. Hydrometers, the saltcrete weighing system, and the floor scale should be calibrated regularly to provide defensible data and process control. In the case of the saltcrete weighing system, control of the process was lost and is the suspected cause of a number of swelling crates due to inaccurate waste loading. The hydrometers and the floor scale are currently calibrated, but the saltcrete weighing system remains uncalibrated.

Documentation of the waste treatment process can be improved by keeping an analysis of the cement (known as the mill run sheet) on file and by collecting a sample of the cement for bench scale testing. More stringent specifications also need to be added to ensure consistent behavior of the cement. Changes to the vendor's contract have been made to incorporate these recommendations.

Waste Characterization

A sampling and analysis plan has been prepared to characterize the saltcrete and determine if the newly generated saltcrete meets the LDR treatment limits. The chemical analysis will be of sufficient quality to certify that the waste form meets the NTS acceptance criteria.

Informal analytical characterization of the untreated waste (spray dried salt) indicates that it nearly meets the leachability standards for land disposal. Performance of the toxicity characteristic leaching procedure (TCLP) on cemented waste produced since June 1990 shows that the treated waste meets leachability standards.

The only certification issue related to the waste form itself is the long term integrity of the saltcrete containers. A portion of these containers do not meet DOT standards for "strong, tight" containers. The containers were damaged by swelling of the saltcrete which, in turn, broke the seal made by the caulking in the nailed seams of the crates. A statistical analysis of the inventory revealed that:

- There was a 1 1/2 year period when the portion of swelling boxes was approximately 2%,
- This period coincided with the time when the target waste loading was 30 wt%,
- Higher waste loading increases the likelihood of bulging,
- Increasing water content increases the likelihood of bulging, and
- Increased bulging coincides with higher waste loadings and with the replacement of the load cells that weigh the saltcrete components.

It is worth noting that much of the saltcrete was produced based on the premise that the solidified waste would have to be reprocessed; Liquid Waste Treatment Operations, took the most expeditious approach to solidifying the waste by increasing the waste load. Even so, most of the saltcrete produced meets all waste form acceptance criteria.

Formulation Studies

Limited bench-scale testing prior to production runs could be an effective means of trouble shooting. A production laboratory equipped with an infrared (IR) spectrophotometer, a viscometer, an oven, a freezer, and some basic laboratory equipment can perform the tests described in this report and also analyze for major anions present. The equipment is in Building 374, with the exception of the IR spectro photometer, is operational.

Formulation studies indicate that different types of cement and fly ash influence the durability of the final waste form. Freeze/thaw testing showed that:

- Type I cement with class C fly ash caused swelling of 5% in length (more than was observed for the halfcrates in storage),
- Type I/II cement, the type used in saltcrete production, swelled 2% in length (about the average of the swelling crates), and
- Type V cement and class F fly ash reduced or eliminated swelling.

The swelling of the saltcrete is likely due to a chemical reaction between sulfates and nitrates in the waste and tricalcium aluminate and calcium oxide in the cement. This swelling is aggravated by large temperature changes but is not influenced by changes in humidity. Cements with high tricalcium aluminate concentrations exhibited more swelling in the freeze/thaw test. Type I, type I/II, and type V had tricalcium aluminate concentrations of 12 wt%, 6 wt%, and 5 wt% respectively.

The class F fly ash reduced swelling while the class C fly ash aggravated the swelling problem. This is probably due to the high concentration of calcium oxide in the class C fly ash. The calcium oxide concentration in the class C fly ash was approximately 29 wt% while the calcium oxide concentration in the class F fly ash was approximately 20 wt%.

Qualitative time to set testing indicated that type V cement with class F fly ash increased the time of set. Testing is under way to quantify the time of set for type I/II cement, type I/II cement with 50% class F fly ash, type V cement, and type V cement with 50% class F fly ash. When the time to set data is available, the relative merits of the formulas can be compared. It is apparent that there may be a trade-off between tendency to swell and time to set.

Viscosity testing showed that the type of cement or fly ash, in the concentrations tested, did not affect the flow properties of the paste and, therefore, would not interfere with the ability of the existing equipment to mix any of the formulations. A number of superplasticizers (or thinners) were tested with no success in reducing the amount of water in the paste and can be eliminated from further consideration.

Recommended Waste Loading

The best formulation will be selected after the time of set data is evaluated and then factorial studies will be performed as required to establish the operating envelope. Many of the control parameters, such as waste loading and water to content, may be determined from a statistical evaluation of historical data. These evaluations are scheduled for completion in fiscal year 1993. In the mean time, the target waste loading should be reduced to 30 wt% rather than the current 35 wt%, waste loading because the lower waste loading consistently produced a certifiable product in the past. Once the operating range is established, the target waste loading may be readjusted.

5.0 REFERENCES

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2. "Saltcrete Waste Characterization Report 244C", Halliburton NUS Environmental Corporation, October 1992.
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5. Manual of Drilling Fluids Technology, NL Baroid/NL Industries, Inc., 1979.
6. Ramachandran, V. S., Concrete Admixtures Handbook, Noyes Publications, Park Ridge, NJ, 1984.
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APPENDIX A
CERTIFICATION WORKSHEET

ANALYTICAL LABORATORIES BALANCE CALIBRATION WORKSHEET

RF NUMBER: 75319 | BLDG: 374 | SECT: 57 | RM: | BOX:

DATE: 11/12/92 | RNG: 0-5000 lb. | TOL: +/- 7 lb.

STANDARDS

RF NUMBER	VALUES	EXPIRES
74727	500 lb WTS.	08/95

CALIBRATION DATA

OV	SV	ERROR	AFT ADJ	AFT ADJ ERROR
1499	1500	-1		
2999	3000	-1		
4500	4500	0		
3000	3000	0		
1500	1500	0		

COMMENTS:

[illegible]

CONTROL NO (8)	TYPE (4)	BLDG. (4)	SEC (2)	ROOM (4)	BOX (4)	LAB (4)	DESCRIPTION (40)										
075319	1164	374	57	3809	FLR	707M	SCALES IND										
MFG. MODEL NO. (10)		SERIAL/DRAWING NO. (12)		T	D	TOLERANCE (16)				RANGE (14)			REFERENCE (14)				
FAT 22-6105						7 LB\$				0 TO 5000 LB\$			110K				
INIT. (4)	AC. RECD. (2)	ACT CODE (2)	CAL. HRS. (4)	CAL. FR (2)	CAL. COMP. (6)	CAL. DUE (6)	INSP. HRS. (4)	INS. FR (2)	INSP. COMP. (6)	INSP. DUE (6)	PROCEDURE (4)	TRANSACTION DATE (8)					
KRC	C	1A	6.0	12	10-90	10-91					NCWP	10-30-90					
MASTER 1		EXP. DATE	MASTER 2		EXP. DATE	MASTER 3		EXP. DATE	MASTER 4		EXP. DATE	MASTER 5		EXP. DATE	MASTER 6		E D.
PO74727			PO74727		06/92												
HISTORY 1			HISTORY 2			HISTORY 3			HISTORY 4			HISTORY 5			HISTORY 6		

CONTROL NO (1)	TYPE (4)	BLOG (4)	SEC (2)	ROOM (4)	BOX (4)	LAB (4)	DESCRIPTION (40)	5
319	1164	374	57	38	09	707N	SCALES IND	

MFG. MODEL NO. (10)	SERIAL/DRAWING NO. (12)	T	D	TOLERANCE (18)	RANGE (14)	REFERENCE (14)
22-6105				7 LB	0 - 5000 LB. 0 TO 5K LB.	11012

INIT. (4)	AO. RECO. (2)	AOY CODE (8)	CAL. HRS. (4)	CAL. FR (2)	CAL. COMP. (8)	CAL. DUE (8)	INSP. HRS. (4)	INS. FR (2)	INSP. COMP. (8)	INSP. DUE (8)	PROCEDURE (4)	TRANSACTION DATE (8)
JRW	C	1A	2.0	12	01/90 12/88	01/91 12/89				11/80	NCWP	01/11/90

MASTER 1	EXP. DATE	MASTER 2	EXP. DATE	MASTER 3	EXP. DATE	MASTER 4	EXP. DATE	MASTER 5	EXP. DATE	MASTER 6	EXP. DATE
074727	0692										

HISTORY 1	HISTORY 2	HISTORY 3	HISTORY 4	HISTORY 5	HISTORY 6
JRW 121588 074727 8905	JRW 120187 74727	DAV 110187 74727	DAV 110185 74727	0912 110185 74727	
2.0 A 12	-1 A	-80LB 3	-2LB A	A	

LINE	DATA (70)
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MAXIMUM ERROR: -4 LB			CAP. EQUIP. #:
O.V.	S.V.	ERROR	
1499	1500	-1	
2997	3000	-3	
4996	4500	-4	
2998	3000	-2	
1500	1500	0	

NO IMEX
JRW

TFB

[illegible]

Resistant to Corrosion Steel

Q.F. No.	Sign	Sec.	Rm	Box	Mag. Cd.	Mag. Index	Service Date	Cost	Remarks	Spec.	Notes
5-12-71	5-13	10-17	10-20	21-23	24-27	28-46	17-19	10-12	10-10	10-10	10-10
1164 075319 374 57										1018 12	

Description	Range	In Place	Min. Succiv.	Carl. St.	Prev. Hours To Coll.
13-42 (30)	43-52 (10)	53	54-56	57	

Date 3-18-	Maximum Error 17-24 (8)	Action Cd. 25-27 (3)	Man Numbers 28-33 (6)	Man Hours 34-39 (6)	Man Hours 40-43 (4)	Repair Cd. 44-46 (3)	Repairs Mns. 47-50 (4)	Masters Used 51-57 (7)	Masters Used 58-64 (7)	Masters Used 65-71 (7)	Area 72
87	-1	1A	512032 512372	2				74727			

History 1	History 2	History 3	History 4	History 5	History 6

Units 13-20 (8)	Units 21-28 (8)	Units 29-36 (8)	Units 37-44 (8)	P. I. D. or C. L. No. 45-59 (13)	Cal. Proc. 60-66 (5)	Mfg. Serial No. 66-74 (10)	C
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OV	SV	ERRA
999	1000	-1
2499	2500	-1
3499	3500	-1
2499	2500	-1
999	1000	-1

12-16-87

JEZ

OAV 12-18-87

NI IMEX

1/6/88

APPENDIX B
LABORATORY PROCEDURES

APPENDIX B

PROCESS SIMULATION

NOTE: All mixing with Oster blender is to be done at the lowest speed

1. Pour brine from tank 826-C into a bucket, and carry it to the lab (room 3805).
2. Scoop salt from the spray-dryer into a one-gallon paint can, and carry it to the lab.
3. Scoop Type V/I cement into a plastic bag from a drum in Building 374, and carry it to the lab.

MIXING METHOD

4. Stir the brine bucket.
5. Fill a 100 ml graduated cylinder with brine.
6. Determine the specific gravity with a hydrometer.
7. Determine the pH of the brine with a pH meter
8. Measure the room temperature.
9. Measure the temperature of the brine.
10. Return the 100 ml of brine to the bucket.
11. Stir the brine bucket.
12. Tare the blender vessel.
13. Weigh 485 g of brine into the blender.
14. Tare a 500 ml (or larger) beaker.
15. Weigh 227 g salt into the beaker.

MIXING THE SALT

16. Add the salt to the blender.
17. Turn the blender on for 10 seconds at the lowest speed. All mixing is to be done with the blender at the lowest speed.
18. Scrape the walls of the blender with a rubber spatula, and stir until no dry salt is floating on the fluid.
19. Turn the blender on for 5 sec.
20. Scrape the walls of the blender with a rubber spatula, and stir as before.
21. Turn the blender on for 5 sec.

MIXING THE CEMENT

22. Tare a 500 ml (or larger) beaker.
23. Weigh 439 g of cement into the beaker.
24. Pour approx 1/3 of the cement into the blender.
25. Turn the blender on for 5 sec. All mixing is to be done with the blender at the lowest speed.
26. Repeat the previous two steps twice, using all of the cement.
27. Scrape the walls of the blender with a rubber spatula, and stir until no dry cement is floating on top of the fluid.
28. Turn the blender on for 10 sec.
29. Scrape the walls of the blender with a rubber spatula, and stir as before.
30. Turn the blender on for 10 sec.

31. Wait 10 sec.
32. Turn the blender on for 20 sec.

VISCOSITY MEASUREMENTS

33. Fill viscometer cup to the scribed line.
34. Place the viscometer cup in position for viscosity measurements.
35. Wait 3 minutes.
36. Record the dial reading at all 12 viscometer speeds beginning at 600 rpm and ending at 1 rpm.
Wait until the cylinder reaches full speed, then wait 5 seconds to take the dial reading.

DETAILED PROCEDURE USING RECONSTITUTED BRINE

This procedure is for building a cold surrogate brine then adding surrogate salt for cold studies in Building 881. Air entrainment was found to be a problem when reconstituted brine made from 10-1-91 salt was mixed with the dry salt. The 10-1-91 salt sample was used because a chemical analysis has been performed on this sample.

1. Tare a 1,000 ml beaker and add 344 g distilled water.
2. Mix the water and 141 g spray-dried salt on a magnetic stirrer.
3. Heat the salt and water to 60°C while stirring.
4. Cool brine in a room-temperature pan of water until the brine temperature reaches 25°C.
5. Add enough distilled water to make up for water lost due to evaporation.
6. Mix 227 g salt into the reconstituted brine using the magnetic stirrer.
7. Add the cement as in the above steps 22-32.
8. Measure the viscosity as in the above steps 33-36.

FORMULATION EVALUATION

DETAILED PROCEDURE

NOTE: All mixing with Oster blender is to be done at the lowest speed

1. Pour brine from tank 826-C into a bucket, and carry it to the lab (room 3805).
2. Scoop salt from the spray-dryer into a one-gallon paint can, and carry it to the lab.
3. Scoop Type I/II cement into a plastic bag from a drum in Building 374, and carry it to the lab.

MIXING METHOD

4. Stir the brine bucket.
5. Fill a 100 ml graduated cylinder with brine.
6. Determine the specific gravity with a hydrometer.
7. Determine the pH of the brine with a pH meter.
8. Measure the room temperature.
9. Measure the temperature of the brine.
10. Return the 100 ml of brine to the bucket.
11. Stir the brine bucket.
12. Tare the blender vessel.
13. Weigh 485 g of brine into the blender.

14. Tare a 500 ml (or larger) beaker.
15. Weigh 227 g salt into the beaker.

MIXING THE SALT

16. Add the salt to the blender.
17. Turn the blender on for 10 seconds at the lowest speed. All mixing is to be done with the blender at the lowest speed.
18. Scrape the walls of the blender with a rubber spatula, and stir until no dry salt is floating on the fluid.
19. Turn the blender on for 5 sec.
20. Scrape the walls of the blender with a rubber spatula, and stir as before.
21. Turn the blender on for 5 sec.

MIXING THE CEMENT

22. Tare a 500 ml (or larger) beaker.
- 23A. If a plasticizer is used:
 - Weigh it on a weighing boat.
 - Add the plasticizer to the brine/salt slurry.
 - Turn on the blender for 10 seconds.
- 23B. Weigh 439 g total of cement and dry additives (if additives are in the formulation). If dry additives are part of the formulation, blend the dry ingredients with a spatula for 30 seconds.
24. Pour approx 1/3 of the dry cement into the blender.
25. Turn the blender on for 5 sec. All mixing is to be done with the blender at the lowest speed.
26. Repeat the previous two steps twice, using all of the cement.
27. Scrape the walls of the blender with a rubber spatula, and stir until no dry cement is floating on top of the fluid.
28. Turn the blender on for 10 sec.
29. Scrape the walls of the blender with a rubber spatula, and stir as before.
30. Turn the blender on for 10 sec.
31. Wait 10 sec.
32. Turn the blender on for 20 sec.

VISCOSITY MEASUREMENTS

33. Fill viscometer cup to the scribed line.
34. Place the viscometer cup in position for viscosity measurements.
35. Wait 3 minutes.
36. Record the dial reading at all 12 viscometer speeds beginning at 600 rpm and ending at 1 rpm. Wait until the cylinder reaches full speed, then wait 5 seconds to take the dial reading.

APPENDIX C
VISCOMETER DATA

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Appendix C, Table 1: Process evaluation viscometer data.

SAMPLE	WATER SOURCE	TYPE CEMENT, ADDITIVE	VISCOMETER DIAL READING											
			1 rpm	2 rpm	3 rpm	6 rpm	10 rpm	20 rpm	30 rpm	60 rpm	100 rpm	200 rpm	300 rpm	600 rpm
SAMPLES FROM FULL-SCALE PRODUCTION														
HO 3885, 3rd, "Nearly too thick"	Brine tank	VI	24	34	43	54	67	80	72	84	98	131	182	230
HO 4008, 2nd, "Too thick"	Brine tank	VI	41	52	62	85	88	97	101	129	141	186	250	
HO 4088, 2nd, "Nearly too thick"	Brine tank	VI	26	32	39	47	48	55	62	81	102	151	210	
HO 4086, 3rd, "Normal"	Brine tank	VI	19	20	20	20	22	25	27	34	43	65	85	127
HO 4087, 1st, "Normal"	Brine tank	VI	19	19	20	20	21	24	27	32	41	63	81	128
NORMAL VISCOMETER READINGS, SAMPLES FROM FULL-SCALE PRODUCTION														
"Normal" Viscometer Readings, Average 4086, 3rd & 4087 1st			19.0	19.5	20.0	20.0	21.5	24.5	27.0	33.0	42.0	64.0	83.0	131.0
"Normal" + 2 Std. Deviations			20.1	20.6	21.1	21.1	22.7	26.0	28.5	34.0	44.0	67.0	87.7	130.0
"Normal" - 2 Std. Deviations			17.9	18.4	18.9	18.9	20.3	23.1	25.5	31.3	39.5	60.4	78.3	124.3
LAB-SCALE SAMPLES FOR SIMULATION														
Salt & Brine from 2-11-93	Brine tank	VI	27	27	27	27	28	30	32	38	46	66	82	132
Salt & Brine from 2-11-93	Brine tank	VI	27	28	27	28	28	31	33	39	47	67	86	137
Salt & Brine from 2-11-93	Brine tank	VI	27	27	27	27	28	30	31	37	45	64	82	131
AVERAGE OF ABOVE 3			27.0	27.3	27.0	27.3	28.0	30.3	32.0	38.0	46.0	66.3	83.0	132.3
LAB-SCALE RECONSTITUTED BRINE, BASELINE FOR SURROGATE SIMULATION														
Salt from 10-1-91	Distilled	VI	26	70	89	106	100	115	118	127	137	164	186	281
Salt from 10-1-91	Distilled	VI	34	47	54	66	58	61	63	70	79	98	113	198
Salt from 10-1-91	Distilled	VI	26	35	36	36	37	40	43	48	58	74	91	130
Salt from 10-1-91	Distilled	VI	29	35	35	35	36	38	40	46	54	73	90	135

Appendix C, Table 2: Treatability study viscometer data.

SAMPLE	WATER SOURCE	TYPE CEMENT, ADDITIVE	VISCOMETER DIAL READING											
			1 rpm	2 rpm	3 rpm	6 rpm	10 rpm	20 rpm	30 rpm	60 rpm	100 rpm	200 rpm	300 rpm	600 rpm
TREATABILITY STUDIES, EVALUATION OF SURROGATE SALTS														
Surrogate, mixed by ASTM std.	Distilled	I	13	16	20	22	22	24	26	30	35	50	63	103
Surrogate, mixed by ASTM std.	Distilled	I	13	16	22	25	25	26	30	35	40	55	66	101
Surrogate, simulation procedure	Distilled	I	12	18	25	26	26	28	29	33	37	52	57	80
TREATABILITY STUDIES, LAB-SCALE EVALUATION OF CEMENTS & FLY ASHES														
Salt & Brine from 2-11-83	Brine tank	100% VI	23	24	23	23	24	26	28	34	42	60	79	129
Salt & Brine from 2-11-83	Brine tank	100% VI	24	24	24	24	25	27	29	35	42	61	78	126
Salt & Brine from 2-11-83	Brine tank	50/50 VI, C	24	24	24	24	25	26	28	34	42	60	78	124
Salt & Brine from 2-11-83	Brine tank	50/50 VI, C	23	23	23	23	24	26	27	33	46	57	72	117
Salt & Brine from 2-11-83	Brine tank	50/50 VI, F	27	28	28	27	28	30	31	38	45	64	80	130
Salt & Brine from 2-11-83	Brine tank	50/50 VI, F	27	28	28	26	26	29	31	38	44	62	78	123
Salt & Brine from 2-11-83	Brine tank	100% V	25	26	26	26	27	29	31	38	47	66	88	141
Salt & Brine from 2-11-83	Brine tank	100% V	19	19	19	20	21	24	25	32	40	60	76	127
Salt & Brine from 2-11-83	Brine tank	50/50 V, C	24	24	24	24	24	27	29	36	44	64	81	127
Salt & Brine from 2-11-83	Brine tank	50/50 V, C	21	21	20	21	22	24	26	32	40	59	77	126
Salt & Brine from 2-11-83	Brine tank	50/50 V, F	19	19	19	19	20	22	27	30	38	56	72	114
Salt & Brine from 2-11-83	Brine tank	50/50 V, F	20	20	20	20	21	23	25	32	38	57	75	121
Salt & Brine from 2-11-83	Brine tank	WCA line	34	41	42	40	38	41	43	60	67	79	88	151
Salt & Brine from 2-11-83	Brine tank	WCA line	28	29	29	29	30	32	33	39	46	64	80	126
Salt & Brine from 2-11-83	Brine tank	Latex	31	36	35	36	36	40	44	55	68	101	130	214
Salt & Brine from 2-11-83	Brine tank	Latex	43	62	53	53	54	60	65	80	97	130	173	280
Salt & Brine from 2-11-83	Brine tank	WFI/Attaguilla	135	161	210	267	271	246	245	259	262	300	300	300
Salt & Brine from 2-11-83	Brine tank	WFI/Attaguilla	300	300	300	300	300	300	300	300	300	300	300	300
TREATABILITY STUDIES, EVALUATION OF SUPERPLASTICIZERS														
Salt & Brine from 5-11-83	Brine tank	VI, Sparsene	26	27	27	27	27	29	34	41	51	74	96	149
Salt & Brine from 5-11-83	Brine tank	VI, Sparsene	26	26	26	26	26	29	32	40	50	72	92	152
Salt & Brine from 5-11-83	Brine tank	VI, Dowell D-19	27	27	28	28	28	31	33	40	50	72	90	144
Salt & Brine from 5-11-83	Brine tank	VI, Dowell D-20	27	28	28	28	28	31	38	40	50	72	91	146
Salt & Brine from 5-11-83	Brine tank	VI, Deaco	6	6	6	6	7	9	10	17	25	44	62	111
Salt & Brine from 5-11-83	Brine tank	VI, Deaco	5	5	5	5	6	8	11	27	25	46	65	114
Salt & Brine from 5-11-83	Brine tank	VI, Tannathin	24	25	24	24	25	28	30	37	48	67	84	136
Salt & Brine from 5-11-83	Brine tank	VI, Tannathin	28	29	28	28	29	31	33	41	50	71	88	143
Salt & Brine from 5-11-83	Brine tank	VI, SAPP	25	25	24	24	25	28	29	33	41	61	79	130
Salt & Brine from 5-11-83	Brine tank	VI, SAPP	26	26	26	25	26	25	27	29	35	64	84	137
Salt & Brine from 5-11-83	Brine tank	VI, PSP-L	20	20	20	20	21	24	26	32	40	59	75	122
Salt & Brine from 5-11-83	Brine tank	VI, PSP-L	26	26	25	26	26	28	30	36	44	62	80	125
Salt & Brine from 5-11-83	Brine tank	VI, Dowell D-65	27	28	27	27	27	30	32	40	48	70	88	142
Salt & Brine from 5-11-83	Brine tank	VI, Dowell D-65	30	31	31	30	31	34	36	44	53	78	97	155

**DATE
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11 / 22 / 93

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