CEWES-SC DOE/RF/00467--T3 July 26, 1994

Progress Report for the Period April 1 through
June 30, 1994

U. S. Army Engineer Waterways Experiment Station (WES) Support
to Department of Energy Rocky Flats Facility (DOE RF)
Saltcrete Processing

1. Background: This report summarizes work authorized under Interagency Agreement DE-AI34-93RF00467 to the WES for technical and scientific support to waste cementation and saltcrete processing operations. This report period included a site visit by the WES team and extensive interaction with DOE contract personnel involved in a study of the phase composition and microstructure of saltcrete using petrographic techniques.

2. Accomplishments:

a. During this report period, the WES team completed an important site visit to the Rocky Flats Facility (RF). This visit focused on extensive interaction with DOE contract personnel about microstructural and phase characterization of saltcrete. The WES assisted with this study for the purpose of identifying the mechanisms of unacceptable performance of saltcrete after it is cast in plywood halfcrates. A copy of the trip report prepared by the WES team is enclosed (encl 1).

b. Also following the site visit, the WES team prepared a document detailing procedures for sample preparation and analysis to enhance the usefulness of results of the forensic work underway at RF. A copy of this document is enclosed (encl 2).

c. After documenting the initial observations provided in encls 1 and 2, the WES team provided extensive assistance to RF personnel in interpreting data generated during the forensic studies. This included interpretation of data from X-ray diffraction, during which the WES confirmed the formation of the phase Darapskite in saltcrete. The WES interpreted that this phase is contributing substantially to the expansion of saltcrete observed at RF.

d. The WES prepared a proposal for additional short-term tasks to contribute significantly to gaining the most benefit from data gathered during forensic analyses of saltcrete, and waste-treatment studies, by EG&G. A copy of this proposal was forwarded to RF at the end of May, and it is included also as encl 3.

3. Plans for Next Quarter: RF has initiated another amendment to the existing Interagency Agreement, adding additional tasks, time of performance, and funding authority. The WES anticipates continuing technical input to interpretation and verification of the causes of unacceptable performance from saltcrete.

3 Encls

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DEPARTMENT OF THE ARMY
WATERWAYS EXPERIMENT STATION, CORPS OF ENGINEERS
3909 HALLS FERRY ROAD
VICKSBURG, MISSISSIPPI 39180-6199

REPLY TO ATTENTION OF

MAY 27 1994

Concrete Technology Division
Structures Laboratory

Ms. Mary Vargas
Rocky Flats Office
Department of Energy
P. O. Box 928
Golden, Colorado 80402-0928

Dear Ms. Vargas:

Enclosed is the Trip Report from the site visit by a research team from the U. S. Army Engineer Waterways Experiment Station (WES) to the Department of Energy (DOE) Rocky Flats Facility on April 19 and 20, 1994. It includes summaries of discussions with DOE contract personnel and interpretations and hypotheses formulated by the WES team in reference to the properties of saltcrete. Recommendations for immediate additional research needs also are provided.

This report completes all tasks undertaken by the WES at the request of DOE Rocky Flats under Interagency Agreement DE AI34 93RF00467 and subsequent tasking letters. The WES is currently engaged in interpretation of data from X-ray diffraction (XRD) analyses of saltcrete phases, based on XRD patterns provided by EG&G staff. A proposal for additional research related to saltcrete performance is in preparation, and will be forwarded to your office during June 1994.

The WES is pleased to continue our research and technical support on issues related to the performance of cement-based materials at the Rocky Flats Facility. If you have any questions, my point of contact for this effort is Dr. Lillian D. Wakeley (601/634-3215).

Sincerely,

Bryant Mather
Director, Structures Laboratory

Enclosure

Copies Furnished:

Tom Lukow, DOE/RFO
Jack Templeton, DOE/RFO

Encl 1

CEWES-SC-A 18 May 94

MEMORANDUM FOR RECORD

SUBJECT: Site Visit to U. S. Department of Energy Rocky Flats Office

Trip Summary

1. A research team from the U.S. Army Engineer Waterways Experiment Station (WES) visited the U.S. Department of Energy (DOE) Rocky Flats Facility (RF) on 19-20 Apr 94. This site visit was scheduled at the request of RF Operations and Waste Management, coordinated by Mr. Jack Templeton (Aguerre Engineers, representing DOE), and authorized under DE AI34 93RF00467.

2. The WES team visiting the site included Drs. Phil Malone and Toy Poole, and Mr. J. Pete Burkes. The purpose of the visit was to observe the data collection efforts underway by RF site staff of samples taken from saltcrete and to discuss possible mechanisms of expansion of saltcrete and failure of halfcrates.

3. Activities of 19 Apr included check-in procedures and a briefing by Mr. Templeton on the general nature of the saltcreting process and the current problems with wasteforms.

4. Activities of 20 Apr included a briefing by EG&G staff on current materials processing and problems. Also included were site visits to RF Building 779, which houses laboratory facilities for X-ray powder diffraction (XRD) and scanning electron microscopy (SEM); and Building 881, housing the light-microscopy (metallurgy) laboratory. Mr. Burkes and Dr. Malone spent some time with Mr. Dan Armentrout (EG&G), examining samples with SEM. The WES team recommended modifications to sample preparation and handling. (A written version of these recommendations was transmitted to RF in a letter to Ms. Mary Vargas, DOE, from Mr. Bryant Mather, WES, dated 29 Apr 94). No XRD analyses had been conducted at the time of the site visit, but analyses were expected soon.

5. Also on 20 Apr, Mr. Bill Caveny (Halliburton) presented a briefing on his examination of thin sections using light microscopy. He interpreted the thin sections as indicating that the portland cement is largely unhydrated. He presented the hypothesis that the abundant voids in thin-sectioned samples indicate gas generation, which could be causing expansion.

Notes on Briefings by Site Personnel

6. Waste salt is derived from all of the diverse wastewaters generated at RF. Disposal of this waste is essential to the continuing operation of RF. Wastewater is evaporated to a salt content of about 36 percent, neutralized, and stored in a 20,000-gal tank until it can be processed into saltcrete.

7. Saltcrete operations are batch processes and occur at intervals as needed to keep the inventory of concentrated wastewater at an acceptable level. At

these intervals, an appropriate amount of the wastewater concentrate is processed through a spray drier to generate a quantity of dry salt (dried at about 180 °C) sufficient to make the planned quantities of saltcrete. Very little dry salt is stored between batching operations because the salts are hygroscopic and agglomerate quickly.

8. Saltcrete is made in 1,200-lb batches, each comprised of about 35 percent salt, 30 percent water, and 35 percent portland cement. Salt loading levels were 50 percent early in the operations, but the frequency of failed halfcrates was unacceptable. Halfcrate failures still occur at 35 percent salt loading, but the frequency is much lower. One objective of the operation is to keep the waste loading as high as possible, to minimize the total volume of solid waste requiring special handling and disposal.

9. The high water content of saltcrete is dictated by the limitations of the mixer used in current operations. Initially, the water content was determined empirically. Process operators determined a water-solids ratio that would produce a mixable and self-levelling mixture (the presence of a vortex in the mixer is interpreted as indicating adequate mixability). Batches are mixed for 5 minutes and then emptied into polyethylene-lined plywood halfcrates. Each halfcrate holds 3 batches (3,600 lb). Batches are made in close succession and usually become comingled in each halfcrate as it is filled within a few inches of the top.

10. The wasteform becomes solid enough to be considered "set" after 5 to 11 or more days (this is a problem). "Setting" is defined qualitatively, by resistance to penetration of a steel rod inserted by hand. After the solids have been determined to have set, the polyethylene liner is folded over the top and a plywood lid is nailed on. Crates are then banded externally and transported to the storage tents where they are stacked four high. The load is supported by 2 by 4's that are integral to the crate construction. Neither the wasteform nor the plywood walls of the halfcrate support any load other than the internal load of the wasteform.

11. Wasteforms must comply with Nevada Test Site (NTS) limits on free liquid (none), radioactivity, and on certain chemical species. Containers must be tightly closed. There are no requirements on the physical properties or integrity of the wasteforms, consequently no physical properties are measured. Deteriorating wasteforms are only considered a problem if they breach the halfcrate and thus do not meet the requirement that containers be tightly closed.

12. During current operations, some number of halfcrates fail to meet NTS requirements for tight closure and cannot be shipped for disposal. Expansion of bulging is measured using a steel tape and straight edge. Levels of linear expansion on halfcrates considered to have failed vary from about 1 percent to about 5 percent. Failure occurs when boxes bulge and edge seams open. Bulging mostly occurs in the middle of the plywood panels. Expansion is not

as apparent near the top and bottom of the halfcrate where the panels are supported by the lid and floor. Sometimes bulging occurs on only one end of the crate.

13. The current petrographic study was initiated on the assumption that bulging is caused by chemical reactions within the saltcrete, forming phases that occupy more space than did the initial solid. As part of this study and to collect samples for petrographic analyses, several halfcrates had been opened and photographed and cores taken (top to bottom completely through the wasteform). Attempts were made to get some material from breached halfcrates and some from intact halfcrates. Extensive cracking was visible on the exposed surface of most saltcrete monoliths. Cracks of up to several millimetres wide were noted.

14. The mechanism of expansion proposed by EG&G in their Saltcrete Evaluation Report, and discussed by them during this visit, is formation of ettringite in the saltcrete by reaction between C_3A in the portland cement and sulfates in the salts.

Observations by the WES Team

15. When cementitious materials are used for purposes other than making a structural material, such as to create monoliths of stabilized waste, the resulting solid is not a concrete. The monoliths formed by mixing RF waste salts and concentrated wastestream liquids with portland cement are not concrete. The chemical composition and microstructure of solidified wastes have very little in common with portland-cement concretes, other than that both families of materials contain cement. The gross physical properties of solidified wastes have virtually nothing in common with a concrete having the same cement content.

16. Given the high waste loading and high liquid content of the RF wasteforms, the cementitious component of the wasteforms may not even form a continuous or strength-giving matrix. Therefore, assumptions or hypotheses about chemical reactions likely to occur in the wasteform or about causes of expansion or cracking of the wasteform monoliths should not be limited to processes understood for portland-cement concretes. Still, the nature of the processes that cause changes in wasteform volume or properties may have analogues in concrete technology.

17. One example is the occurrence of chemical reactions to create products that take up a larger volume than did the initial solids and thus generate stresses. This type of reaction is known to occur in some concretes and may occur but be controlled by different chemical species in RF wasteforms. For the saltcrete to develop expansive forces that would cause crate failures, there must be rigidity in the mass. If expansive species are formed before a rigid matrix is formed, then the expansion will occur in unconfined dimensions

and not cause a problem. Expansion-causing reactions become destructive to a monolith if they occur after some level of strength is achieved.

18. The chemical composition reported for the RF waste stream suggests that chemical reactions occurring in the wasteform may involve nitrate salts. Conceivably, crystallization of nitrate salts or mixed nitrate-sulfate salts in a relatively weak cement matrix could cause expansion. This could potentially happen following the temperature peak that occurs within a day or two of setting. Hot pore solution would be saturated with dissolved salts. Hydrating cement would withdraw free water from the system, which, along with a cooling trend, would greatly reduce the solubility of salts, favoring a strong crystallization process.

19. Chemical expansion causes cracking when the expansive forces exceed the tensile strain capacity of the solid. If the expansive forces are distributed uniformly through the monolith, the cracks will normally stay closed. However, if expansion is more substantial toward the middle of the wasteform, then relatively wide surface cracks could open. This could occur if gradients in temperature, chemistry, or mixture proportions existed from center to top surface. Moisture loss from the upper portion of the wasteform during early curing could create such a gradient.

20. The analytical methods currently being employed by EG&G (SEM, XRD, and light microscopy) are reasonable ways to determine whether expansion of the saltcrete is being caused by the formation of an expansive phase. Once crystalline phases have been identified, it should be possible to determine if any of the phases present are capable of causing the observed expansion.

21. Cycles of higher and lower solubility of salts, due to temperature cycling, could be a problem with saltcrete if the temperature range is large. If the tents are heated, freezing is a low probability event, especially considering the freezing point depression caused by the salts. But cold temperatures probably favor crystallization of nitrate salts. It is likely that nitrates are involved in the failure mechanism. The monoliths may expand from salt crystallization only after they have been removed to a colder storage area for some time.

22. The EG&G report describes temperature rises of 30 °C or more in saltcrete within a day or two of setting. By concrete standards, this is a relatively large temperature rise. The coefficient of thermal expansion of cement paste is about $2x10^{-5}$ in./in., or about 0.06 percent over this temperature range. This is not large enough to account for the expansions observed in the half-crates. Thermal stress could, however, contribute to cracks in the wasteform, but again the timing of events is critical.

23. Other physical factors also may contribute to propagation of cracks in the monoliths, once cracks have been initiated. The physical stress of being moved by forklift may propagate cracks in a low-strength wasteform.

Recommendations

24. A list of Tasks being proposed by the WES for near-term activities is enclosed (encl 1). These include:

a. Continued assistance in interpretation of data derived from petrographic studies at RF.

b. Assessment of the utility of various data sets in the Saltcrete Evaluation Report and statistical analysis of variables.

c. Calculation of plausible forces that might be generated by crystallization of the nitrate-sulfate double salt or other major phases identified by XRD.

d. Identification of performance envelopes defined by cement-stabilized wasteforms at other facilities.

25. The WES also recommends that the following activities be initiated under a new or amended interagency agreement to determine the mechanisms of halfcrate failure:

a. Investigate the mechanisms of any chemical reactions using small specimens.

b. Determine the performance envelope of salt loading, w/c, and salt composition.

c. Take cores of existing expansive saltcrete, insert stainless steel pins, and monitor for additional length change.

d. Do a statistical evaluation of data, including data on percentage of expansion, time when expansion was measured, any mixture proportion data, and salt composition data.

e. Develop a petrography manual, describing sample preparation techniques and giving photographic and other examples of data derived from known combinations of salts and cementitious materials.

f. Assist in developing test methods and establishing or modifying standard procedures for a QC/QA program to monitor saltcrete.

26. The WES principal investigator for this research is Dr. Lillian D. Wakeley. Please call 601/634-3215 if you have questions.

Encl

J. PETE BURKES
Petrography and Chemistry Group

TOY S. POOLE, PhD
Engineering Materials Group

for PHILIP G. MALONE, PhD
Leader, Petrography and Chemistry Group
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REPLY TO
ATTENTION OF

April 29, 1994

Concrete Technology Division
Structures Laboratory

Ms. Mary Vargas
Rocky Flats Office
Department of Energy
P. O. Box 928
Golden, Colorado 80402-0928

Dear Ms. Vargas:

At the request of Mr. Jack Templeton, a research team from the U. S. Army Engineer Waterways Experiment Station (WES) met with DOE and contractor staff at the Rocky Flats Office on April 19 and 20, 1994. Technical discussions during those meetings focused on expansion of blocks of cement-solidified wastes that have been prepared as a wasteform for disposal. The WES team has been asked to comment on the methods of investigation being applied by Halliburton NUS in trying to identify causes of unwanted expansion, and to assist in the interpretation of the data obtained during these investigations.

It is our understanding that the investigations being conducted by Halliburton include examination of cores taken from the wasteforms and determination of phases present in these wasteforms to identify phases produced during hydration or other chemical reactions that may be causing expansion and cracking of cement-based solids. Phase composition is being determined using X-ray diffractometry. The grain morphology and fabric of the samples are being determined using scanning electron microscopy and conventional optical microscopy.

The WES team uses these same analytical methods in research on questions of the performance of cement-based materials. We consider it reasonable and prudent to apply these techniques as the initial step in assessing the expansion problem. To assist in preparing samples and to help in obtaining the best results with the equipment available at Rock Flats Office, the WES team has prepared a list of recommendations for sample preparation (enclosure 1). We will be pleased to assist you further as X-ray diffraction patterns and additional photomicrographs are generated.

Encl 2

If you have questions about the enclosed recommendations or if we can be of any immediate help in the current laboratory activities, please call on us. My point of contact for this work is Dr. Lillian D. Wakeley (601-634-3215).

Sincerely,

Bryant Mather
Director, Structures Laboratory

Enclosure

Copies Furnished (w/enclosure):

Jack Templeton, RFO/DOE
Thomas E. Lukow, RFO/DOE

29 April 1994
CEWES-SC

Recommendations for Preparation of Saltcrete Samples for Investigations of Causes of Expansion and Cracking

1. Introduction -- The U. S. Army Engineer Waterways Experiment Station (WES) has had extensive experience with materials for and petrographic investigations of cement-based materials containing salts for various DOE facilities, and has gained experience in the preparation of samples for petrographic studies and examination using scanning electron microscopy and X-ray diffraction. These recommendations may be of some assistance in preparing samples of saltcrete for similar studies.

2. Preparation of Saltcrete Samples for Petrographic Examination -- Salt-cement materials are typically softer than most concrete or rock samples, and some components are water soluble. Preparation generally follows standard thin-section preparation practices with special handling as follows:

a. Samples are trimmed into slabs for mounting using an oil-based cutting fluid such as Hi-Sol 10 (Ashland Chemicals, Inc., Columbus, OH).

b. The cutting fluid is removed with acetone, and the trimmed slab is impregnated with epoxy.

c. After the epoxy has hardened, the slab is ground down starting with a grit size of approximately 35 μm. An intermediate grit approximately 15 μm is used as the slide specimen shows a smooth surface. The last stage of polishing is done with grit of 5 μm diameter.

d. The polished slab is mounted on a glass slide using epoxy. Any air bubbles between the slab and the glass are worked out so that bubbles are not trapped between the slab and the glass slide.

e. Mounted samples are typically cut and ground to a 20-μm thickness.

f. The final polish is done with 5-μm grinding compound, and a glass cover slip is glued over the top of the sample.

g. The slides are stored in a desiccator over silica gel or commercial desiccant and are ready for examination under a petrographic microscope.

3. Preparation of Saltcrete Samples for Examination by Scanning Electron Microscope (SEM) -- Samples containing salt are typically too moist to be treated as conventional concrete or rock samples. The following modifications of preparation procedures explain how these samples are typically handled:

a. Samples are trimmed to size by cracking the sample and chipping out fragments from the area of interest. Pieces are selected that have not been directly exposed to the atmosphere.

b. The chips are placed in a vacuum desiccator and dried overnight.

c. The dried samples are broken into halves to obtain fresh surfaces.

d. One half of each broken sample is placed in the sputter-coater. The fresh surface is coated with gold.

e. The surface of the second half of the sample is etched for 8 seconds in a 1 percent solution of maleic acid in methanol, washed in clean methanol, and dried. Care is taken to minimize the exposure of the sample to the atmosphere. The second sample is coated with gold.

f. The pairs of samples are placed on the stage in the SEM, and both samples are evaluated alongside each other.

g. The maleic acid etching will typically remove a portion of the calcium silicate hydrate gel allowing a better view of the hydrated cement paste. Generally, the interpretation of the images is done by comparing the etched and unetched surfaces.

4. <u>Preparation of Saltcrete Samples for Analysis by X-ray Diffraction</u> -- X-ray diffraction samples are typically prepared in the same manner as rock samples, but the samples are handled expeditiously to prevent excessive moisture collection and carbonation from the air.

a. Samples are obtained by breaking specimens and chipping out pieces that have not been directly exposed to the air.

b. Chipped samples are typically ground in a mullite mortar to pass a 45-μm sieve.

c. Ground samples are promptly packed into a powder holder and run on the X-ray diffractometer under dry nitrogen (if this is available).

d. A standard run made using copper K-alpha radiation would start at 2 degrees and run to 65 degrees 2-theta. A conventional X-ray tube would be run at an excitation voltage of 40 KV and an operating current of 50 mA although these settings will vary with the type of instrument used.

e. Pattern interpretation is done using automated powder data files.

5. These notes are intended as general guidance and are based on WES experience in investigating salt-concrete products. Saltcrete may present special problems that require adaptations of the basic procedures. Questions related to sample preparation should be directed to Dr. Philip Malone, CEWES-SC-EP (Phone 601-634-3960).

29 April 1994
CEWES-SC

Rocky Flats Project
17 May 1994

CEWES-SC
Wakeley

PROPOSED SHORT-TERM TASKS
WES SUPPORT TO ROCKY FLATS OPERATIONS AND WASTE MANAGEMENT

The following tests are proposed to be accomplished by the U. S. Army Engineer Waterways Experiment Station (WES) under the existing Interagency Agreement by 30 Sep 94, with additional funding authority of $55K.

TASK 1: Continued Technical Assistance.

Technical assistance in selection of sample preparation methods for X-ray diffraction (XRD) and scanning electron microscope (SEM) studies of saltcrete samples. Interpretation of data generated by XRD and SEM studies at Rocky Flats (RF). Recommendations about deriving the most useful results from ongoing petrographic analyses at RF.

TASK 2: Review of Saltcrete Evaluation Report (EG&G Technology Development).

Prepare a written review of the data analysis and interpretation of results of EG&G Saltcrete Evaluation report. WES written review will include: a summary of plausible hypotheses to explain the observed saltcrete problems; assessment of the utility of various data sets through statistical analyses and identification of confounding variables; recommendations about which data and conclusions are likely to provide the most insight into understanding saltcrete performance.

TASK 3: Assessment of Effects of Sodium Nitrate-Sulfate Double Salt.

Interpretation by the WES of initial XRD data provided by EG&G indicated the presence of a sodium nitrate-sulfate double salt (darapskite) as a major phase formed in saltcrete sometime after preparation of the wasteform halfcrates. The WES will evaluate the possibility that crystallization of this or other indicated salts can generate enough force to cause expansion of the saltcrete under confinement. This will include calculation of plausible forces generated by crystallization of the salt under the conditions of interest.

TASK 4: Performance Envelopes from Other Wasteforms.

Evaluate case studies of cement-stabilized wasteforms from other salt wastestreams, as reported in US and international literature. Identify performance envelopes defined by these wasteforms.

TASK 5: Reporting.

Results of these tasks will be provided to RF as letter reports.

Encl 3