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CEWES-SC
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Progress Report for the Period October 1 through December 31, 1993

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/processing operations.

2. Accomplishments:

a. The principal effort of this report period was a review of two documents provided by DOE RF. These were (1) Sampling and Analysis Plan for Saltcrete Process Inputs and (2) Waste Treatment Spray Dryer and Saltcrete Process. The WES review report for the latter of these two documents is enclosed.

b. During this period, the WES received a Request for Proposal from EG&G Rocky Flats, entitled "Saltcrete Petrology Study, CTMP Treatment Systems." Because the WES is a laboratory of the U.S. Army Corps of Engineers, the WES team could not respond to this RFP directed to private corporations. The WES team reviewed this RFP briefly and determined that it lacked technical merit in certain areas. As an example, it did not indicate how the data gathered by microscopic and compositional studies of saltcrete in half-crates would be interpreted or how the results would contribute to improvement in saltcrete processing.

c. Dr. Lillian Wakeley of the WES team discussed this document extensively by telephone with Mr. Reg Tyler, DOE RF, and Mr. John Schneider, DOE RF (contractor). Information provided to the WES during these conversations indicated that the RFP would be withdrawn for extensive revision, and no contract would be awarded for the work as described in the RFP. Mr. Tyler directed the WES to prepare a document describing the activities necessary to initiate a meaningful onsite forensic study of saltcrete products at Rocky Flats. This effort was initiated, including discussions between WES team members and several members of the scientific and technical laboratory staff in several laboratories at Rocky Flats, who provided informal information about their equipment and experience. The WES recommendations document will be completed by January 31, 1994.

d. Discussions also ensued among Mr. Richard Wallace, DOE RF; Mr. Schneider; and Dr. Wakeley, about modifications in report requirements for this project. As a result of these discussions, the IA was amended to delete funding reports already being provided by the WES in another form. The WES is awaiting additional information from Mr. Schneider who indicated he will provide a format for the required cost plan.

3. Plans for Next Quarter: Review of the second document will be completed during January, as will the recommendations for initiation of forensic studies

of saltcrete. Letter reports describing these activities will be provided to DOE RF when completed, prior to the end of the report period. Additional tasks will be proposed by the WES and a second site visit planned to discuss the ongoing activities.

DRAFT 4

January 24, 1994

Review of the Operational Process Instructions for the
"Waste Treatment Spray Dryer and Saltcrete Process"
A-001-LWTO, Rev 0

Executive Summary

1. A review of the batching instructions in the subject document indicates that mixture proportions for saltcrete are not optimal for the production of a consistent, quality wasteform. The water-cement ratio is high and variable, leading to inadequate and variable strength and precluding development of microstructural properties necessary for good durability. The salt loading also may be too high. Several practices should be investigated and defined better for system operators. These include mixing time, assessment of adequate mixing, and timing of clamp removal from the wasteform crates. Specifications for wasteforms and for portland cement used in the saltcrete process should be defined so that quality control procedures can be developed. A laboratory study should be executed to evaluate the effect of variation in mixture proportions and salt chemistry on the physical properties of the wasteform. In addition, microstructures of deteriorated and competent wasteforms should be compared to define an acceptable wasteform and identify contributing factors.

Introductory Comments

2. The document under review includes instructions for the start-up, operation, and shutdown of the spray dryer and saltcrete mixing system. The WES team could not judge the quality or adequacy of many of these instructions because we have not tried them ourselves. What we have tried to do is to use information in these instructions as indicators of possible problems in the concept and design of the saltcrete process.

Mixture Proportions

3. Paragraph 5.6.3 summarizes the formula for saltcrete. Batching instructions are in paragraph 6.2.4. According to this formula, constants in the mixture proportions are portland cement content (35.4 percent) and total batch weight (1,200 lb). Water and salt contents vary, depending on the specific gravity of the brine. Variations in water and salt contents are a source of significant variation in saltcrete properties, as described below.

4. Paragraph 5.6.3 allows for use of brines with specific gravities ranging from 1.15 to 1.33. As part of our review and to illustrate the effects of extremes in this variation on water content and salt loading, the mixture proportions of two hypothetical batches were calculated and compared. One mixture was calculated using a brine with the lowest specific gravity included in paragraph 5.6.3 (1.15) and the other calculated with the highest specific gravity (1.33). The specific gravity of the salt was assumed to be 2.11 (KNO_3), but this is a constant in the calculation and the comparisons would be similar with salts of other specific gravity. The calculated batch proportions are summarized in the following table.

Component	If Sp. Gr. Brine = 1.15	If Sp. Gr. Brine = 1.33
Mass of salt from brine	58.8 lb	177.2 lb
Mass of dry salt	340 lb	179.0 lb
Cement	425 lb	425 lb
Water	376.2 lb	418.8 lb
Cement-salt ratio	1.07	1.19
Water-cement ratio	0.89	0.99
Salt in wasteform	33 percent	30 percent

5. At these extremes, the water content of a batch could range from 376 lb to about 418 lb. Expressed as water to cement ratio (w/c), values range from 0.89 to 0.99. By normal grouting and concrete standards, these are very high values of w/c, and a change in w/c of 0.10 is large enough to account for significant changes in the properties of the product. Concretes and mortars, which typically contain large fractions of aggregate, commonly are made at a w/c of 0.4 to 0.6, although lower values can be achieved with use of chemical admixtures. Portland-cement pastes or grouts, which do not contain aggregate, typically are made at w/c's of 0.4 or less. The saltcrete formulation described in these instructions includes some salt that will not be dissolved and will behave somewhat like a fine aggregate. Therefore, the mixture is analogous to a mortar and somewhat higher w/c's may be required, but it is very unlikely that w/c's as high as 0.9 constitute good practice.

6. Water-cement ratio (w/c) is the single most important mixture-proportion property affecting physical properties of hardened material. A high w/c results in a low-density hydrated cement paste that, in turn, results in low strengths and a material which is generally more susceptible to chemical deterioration. A high w/c also results in considerable bleeding (settling of solid particles, leaving a layer of mixing water on the surface of the wasteform). Apparently some acceptable saltcrete is being produced at these high w/c's, but it is likely that these proportions are near the upper limit of acceptability so that variation in w/c (or other properties of the saltcrete materials) could result in unacceptable performance.

7. It is not apparent from the reviewed document how the w/c values for this mixture were determined or why they are so high. High w/c's are sometimes used to get adequate workability of the freshly mixed material when early stiffening problems occur. High salt concentrations or large amounts of calcium sulfate sometimes accelerate portland cement hydration, resulting in premature loss of workability. Rather than increase the w/c, a more technically sound approach would be to replace some of the portland cement with a slower reacting cementitious material, such as slag or fly ash. This would allow the w/c to be lowered to more reasonable levels and setting time

to be controlled. Use of retarding admixtures might also be reasonable, if one could be identified to be chemically compatible with the salts.

8. The above comments reflect general considerations about portland cement systems. It is not possible to predict in detail the properties of this saltcrete and its sensitivity to variations in proportions from knowledge of ingredients and proportions alone. These things need to be investigated in a laboratory study designed for this purpose. A wide range of cementitious materials and mixture proportions could be investigated relatively easily using small specimens and test methods already developed for investigating portland-cement concrete mixtures. Another benefit of such a study would be that the effects of minor variations in mixture proportions on wasteform properties could be determined. This would allow tolerance levels to be developed for the batching process, i.e., tolerable errors in batching. Larry Baagasen (formerly of EG&G Rocky Flats) conducted some laboratory experiments on effects of variations in waste loading and water content in 1989. Studies of this type are recommended.

9. The contents of some half-crates are known to have deteriorated during storage. This behavior is likely to be at least partially related to the high w/c condition and perhaps to other features of the mixture proportions. A laboratory investigation of the quality of the microstructure of some of these failed specimens compared to the microstructure of apparently sound specimens would be very informative. This kind of investigation would identify chemical phases present and how they are distributed. Formation of expansive phases can cause loss of physical integrity of the wasteform. As discussed later in the review, this can be particularly serious with some portland cements when high sulfate ion concentrations (>1,500 ppm) exist. The investigation would also reveal something about the physical structure of the hydrated paste and the interface between the hydrated paste and the insoluble salt.

10. Another cause of physical failure is the loss of bond between hydrated portland cement phases and any insoluble material, such as aggregate or salt crystals. Bond failures create microscopic defects in the microstructure that ultimately lead to macroscopic failure under load. When the microstructure is not very dense anyway, which typically occurs with high w/c's, this phenomenon may be particularly important. For mixtures with the highest salt loadings, the resulting product may actually be bits of hydrated cement with low strength and high porosity held together loosely by precipitated or undissolved crystalline salts.

Comparison with Another Saltcrete Formula

11. Comparison of the saltcrete mixture proportions with other mixtures that were developed for a similar purpose further supports the argument that the mixture proportions need to be changed for the quality of the product to improve. The Rocky Flats saltcrete formula differs from others that have been published (Langton, Dukes, and Simmons, 1984; Langton, 1985; and Barnes, Langton, and Roy, 1985) and used for disposal of waste salt at the Savannah River Plant (SRP) in that it contains a higher proportion of salt relative to portland cement and a higher w/c. The SRP saltcrete contained salt only as a dissolved component of the mixing water, and there was no salt present in the

solid state during mixing and early hydration. The total salt load of the SRP mixtures was 13 to 15 percent compared to about 30 percent for the Rocky Flats mixture. Cementitious materials comprised 50 to 60 percent of the SRP mixture, compared to 35 percent for the RF mixture. The w/c of the SRP mixtures ranged from 0.42 to 0.69, versus 0.9 or higher for RF.

12. The SRP mixtures were intended to comply with the following requirements (Langton, Dukes, and Simmons, 1984):

Property	Minimum Value
Compressive Strength	1 MPa
Permeability	10^{-10} cm/sec
Bulk Leach Rate	10^{-5} g/cm^2-day
Slurry Yield Stress	<300 dynes/cm^2
Slurry Set Time	>4 hours

Mixtures with w/c in the vicinity of 0.45 met these requirements without difficulty. The mixture with a w/c of 0.69 barely met the strength requirement and was not tested for the other requirements (Langton, 1985).

Mixing Saltcrete and Handling Specimens

13. Paragraph 6.2.4.43 directs that mixing last for 5 minutes. This is normally long enough for concrete mixtures to reach homogeneity, but since mixtures and mixing equipment vary so much, minimum necessary mixing time is normally verified by a mixer-performance test. The Corps of Engineers test method (CRD-C 55-92) comprises taking samples after various mixing times from three locations in the mixer and comparing the uniformity of their physical properties. If a similar procedure has not been done with the RF mixing equipment, it would be beneficial to determine if anisotropic mixing is contributing to batch variability and failure. Inconsistent mixing is likely to result in stratification in half-crates of materials with different water contents, densities, and salt loadings. A phenomenon such as this could explain why the contents of some half crates appear to be sufficiently solid on the upper surface (as measured by penetrometer resistance), but are semi-solid at best below this exposed layer. Again, laboratory analyses could identify the existence and cause of this property.

14. Paragraph 6.2.44 of the subject document directs that the mixture be visually inspected for proper cement "dissolution" and that extra brine should be added to achieve this condition if necessary. The term "dissolution" does not apply to portland cement in water-based fluids, given that cements are not soluble in this medium. In this instance, the term is probably intended to refer to the general dispersion and rheology of the mixture. Visual estimation of mixing and rheological properties may be adequate to guide a highly experienced worker, but this is probably an inadequate practice when exercised by less experienced people or unless all employees are trained to

judge cement dispersion to a constant requirement. Also, addition of brine will increase both the salt loading and the water-cement ratio, which are likely to be too high already, thus contributing to a poorer quality microstructure and instability of wasteforms.

15. Paragraph 6.5.1 directs that bracing clamps be removed after the saltcrete is cured, but there is no definition of when adequate curing has occurred. Once final time of setting has been reached, the saltcrete will bear light loads and may appear to be adequately cured. However, the load-bearing capacity of the wasteform at this early age is still quite low, possibly causing it to sag under its own weight when forms or support is removed. The length of time required for adequate curing needs to be determined from a laboratory testing program and a minimum time be determined and included in the manual.

Specifications

16. The subject document contains no specifications for the minimally acceptable properties of the saltcrete or the portland cement used to make it. This may be beyond the scope of the document and perhaps these exist elsewhere. Still, clear definition of the target properties could only help processing and product performance.

17. Specification requirements for workability and time of setting of fresh saltcrete and strength, permeability, and leachability of hardened saltcrete would be useful. These would allow objective mixture design studies to be used to optimize materials and proportions to develop a quality wasteform. These requirements would also serve as the basis for the development of a quality control program to insure that these requirements are consistently met. A quality control program would probably not include tests for all of these properties. A few easily measured properties could be identified that would correlate with performance. Workability, time of setting, strength, and density are easily performed tests and would be likely candidates for quality control tests.

18. There are also apparently no specifications for the portland cement used in the process. Although portland cement is a relatively narrowly defined product, there are several properties, which sometimes vary considerably, that could be important in the saltcrete process. Unless otherwise specified, Type I portland cement (ASTM C 150) is normally used. Type I cement is allowed to contain relatively high levels of tricalcium aluminate (C_3A). Although not common, some contain levels up to about 15 percent (5 percent or lower is considered low).

19. C_3A reacts strongly with sulfate ion to form the highly expansive phase ettringite, which can be the source of considerable destructive force even in large monoliths. Sulfate concentrations higher than 150 ppm in solutions in contact with portland cement can cause some deterioration with high-C_3A cements. Concentrations higher than 1,500 ppm will cause a strong reaction. Chlorides also react with C_3A in a similar way, but the reaction is less destructive. Given that sulfate and chloride concentrations in the waste salt are sometimes very high, specification of a low-C_3A cement would probably be

useful. Type V portland cement has a maximum limit on C_3A of 5 percent and would help control deterioration from this mechanism.

20. Replacement of some of the portland cement with other cementitious materials, such as class F fly ash or slag, also could improve the durability to chemical attack, as well as improve workability, setting time, and heat evolution properties of the mixture.

21. Other properties of the portland cement, such as fineness (particle size distribution) and strength-gain potential, can sometimes vary considerably either within or between portland-cement sources. Fineness will affect the workability of the fresh mixture and water required for adequate mixing. Strength gain potential will affect the length of curing required and the ultimate load-bearing potential of the wasteform. If your cement comes from a single source and is always the same type and is from the normal production of the plant (i.e., not a specialty product), variability in these properties is probably not significant. If cement comes from multiple sources, there is probably more variation in these properties, but if it is the same type, i.e., Type I, Type II, etc., then cement mills in a given geographical region tend to be similar and variability is probably not a serious problem. When no particular type of cement is specified, then you could be getting a mixture of types that could vary considerably in properties.

Recommendations

22. The following actions are recommended to improve the uniformity and quality of wasteforms:

a. Performance specifications should be developed for the properties of the completed wasteforms. Specifications should be defined for the portland cement.

b. A study should be initiated to identify the effects of variation in mixture proportions and material properties on the properties of the fresh saltcrete and completed wasteforms. This study should include examination of some cementitious materials other than portland cement.

c. A comparative analysis of failed and stable wasteforms should be undertaken which focuses on variations in mixture proportions and microstructural analysis.

d. A mixer efficiency study should be performed and mixing guidance modified, if found necessary.

e. Tighter guidance on addition of excess brine, on definitions of adequate mixing and curing, and on removal of form supports should be developed.

References

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