

## INFLUENCE OF TEMPERATURE ON STRENGTH OF CEMENTED SURROGATE NITRATE SALT WASTE

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### ABSTRACT

The Rocky Flats Plant (RFP) generates large volumes of a low-level aqueous waste stream high in nitrate salts. The chemistry of this waste stream varies depending on the processes operating at a given time. The aqueous waste is concentrated by an evaporation process and then mixed with Portland cement to form a monolith suitable for transport and disposal. Planned process upgrades include a new horizontal thin film evaporator. The temperature of the concentrated brine at the discharge end of the new evaporator will be near the boiling point of the solution. Introduction of high temperature water to cement has been known to cause degradation of the monolithic waste form. However, the RFP salt waste contains high concentrations of compounds known to retard the hydration process, thus affecting the temperature at which the product could be deleteriously affected. This paper discusses the impact of introducing high temperature waste to cement.

The study evaluated three waste compositions: 1) highest probable nitrate composition, 2) highest probable chloride composition, and 3) current composition, derived from the chemical analysis of actual waste. Results demonstrated that the compressive strength of the final waste form increased with brine temperature, and waste forms from brine at the boiling point exhibited a near doubling of compressive strength when compared to waste forms from brine at room temperature.

### INTRODUCTION

Rocky Flats Plant (RFP) generates large volumes of a low-level mixed aqueous waste stream high in nitrate salts. This waste stream is derived from various sources, including production operations, laboratories, laundry processes, and incidental waters consisting of excess waters from runoff, solar evaporator ponds, and interceptor trenches. The chemistry of the nitrate salt waste stream varies depending on the processes operating at a given time. The waste is processed by neutralization, filtration, and precipitation. The brine is concentrated by evaporation to a solution consisting of approximately 35% solids. Currently, some of the brine is spray dried to make a dry salt. The salt and brine are then mixed with Portland type I/II cement to produce the final waste form, known as "saltcrete."

Rocky Flats is replacing the existing spray dryer and cementation equipment with a horizontal thin film evaporator and improved cementation equipment. Cement will be mixed with concentrated brine shortly after the brine is discharged from the evaporator. The brine will be near its boiling point when added to the cement.

Mixing waste with cement at elevated temperatures is a concern for three reasons. First, high temperatures may cause the cement to flash set and solidify in the mixing vessel. Second, the waste form may not meet waste acceptance criteria. Third, the waste may meet the waste acceptance criteria initially, but later be unacceptable due to degradation. Mixing cement with hot water (333 to 353 K) is known to cause flash setting (1) that can result in strength degradation (2).

The objective of this study was to identify, on a laboratory scale, the upper temperature at which surrogate brines can be mixed with cement to produce an acceptable waste form. An acceptable waste form meets the waste acceptance criteria for low-level mixed waste at the Nevada Test Site and Rocky Flats plant operational requirements. This study was designed to identify the mixing temperature at which significant strength degradation occurs for three extremes of waste composition: 1) highest nitrate, 2) highest chloride, and 3) current compo-

sition. Only the first two compositions were used in this study as the current waste had not yet been characterized. The first salt surrogate, highest nitrate, is very high in nitrates but low in chlorides. The second salt surrogate, highest chloride, is higher in chloride concentration but is still predominately nitrate based.

### EXPERIMENTAL PROCEDURE

Surrogate salts were prepared by weighing the different salt constituents on a top-loading balance. The specific chemical constituents for each surrogate are described in Table I.

TABLE I  
Composition of the Salt Surrogates

Chemical Constituent	Amount in the Surrogate (wt %)	
	Highest Nitrate	Highest Chloride
Sodium Nitrate	40.9	23.3
Potassium Nitrate	49.8	48.3
Sodium Chloride	0.9	7.1
Potassium Chloride	1.2	15.8
Sodium Sulfate	1.7	1.1
Potassium Sulfate	2.1	2.4
Sodium Phosphate	0.7	0.5
Potassium Phosphate	0.9	1.1
Sodium Fluoride	0.7	0.1
Potassium Fluoride	1.1	0.3
	100.0	100.0

A total of 0.3 kg of salt surrogate was added to  $3.36 \times 10^{-4}$  m<sup>3</sup> (336 ml) of distilled water in a beaker at room temperature. The contents of the beaker were then heated and agitated on a hot plate to form a brine. The temperature of the brine was measured with a thermometer until a predetermined

temperature was reached. That temperature was maintained for approximately five minutes before proceeding.

The four different brine temperatures investigated in this study were:

- T1 293 K (ambient temperature)
- T2 350 K
- T3 360 K
- T4 the boiling point of the brine solution, 375 K for highest nitrate, 376 K for highest chloride (at an elevation of 1828m)

A total of 0.564 kg of Portland type I/II cement was added to the brine. The ratio of cement to salt to water was .47:.25:.28, which represents a 25 percent waste loading, and a water to cement ratio of 0.6. The brine and cement were mixed according to ASTM C305-82 (3) except that the slurry was mixed at low speed to avoid splashing.

The slurry was poured into square 0.05 meter (two inch) stainless steel molds to produce triplicate samples for each of the four brine temperatures. The molds were immediately placed into a clear plastic enclosure that contained a water reservoir to provide a humid curing environment to prevent drying shrinkage, and the cracking associated with shrinkage. The humidity inside the chamber was monitored with a wet/dry bulb thermometer and ranged from 85 to 95 percent relative humidity.

After  $2.42 \times 10^6$  sec (28 days), the samples were weighed, measured, and destructively tested for compressive strength according to ASTM C109-90 (4). An Instron model 1137 with a 0.15 m (6 inch) bearing surface and a  $4.23 \times 10^{-5}$  m per sec (0.1-inch per minute) crosshead speed was used for compressive strength testing.

The compressive strengths of the chloride surrogates nearly exceeded the 4,540 kg (10,000 pound) load cell capacity of the Instron 1137. Therefore, the chloride samples were tested on a different Instron, model TTDL, that had a higher rated loaded cell of 9,080 kg (20,000 pounds). Since it was necessary to test these samples twice, the samples were stress-loaded more than once. The ambient temperature samples number 1 and 2 were loaded a total of three times and sample number 1, at the boiling point was loaded twice. The remaining highest chloride samples were loaded once to failure with the 9,080 kg (20,000 pound) load cell.

## RESULTS

The 28-day compressive strength values of the highest nitrate and highest chloride surrogates are presented in Fig. 1. The compressive strength of the highest nitrate surrogate increased with increasing brine temperature with the highest strength occurring at 360 K. From 360 to 375 K, the strength slightly decreased, but was still significantly greater than the 350 K and ambient temperature samples. The compressive strength values for the highest chloride surrogates were consistently higher at all temperatures than the nitrate surrogates. The compressive strength of the highest chloride samples increased with temperature and was highest at the boiling point of the brine (376 K).

## DISCUSSION

No significant loss of strength or waste form degradation occurred at the highest brine temperatures. Compressive strength generally increased with brine temperature, contrary to what was anticipated. Furthermore, there was no obvious

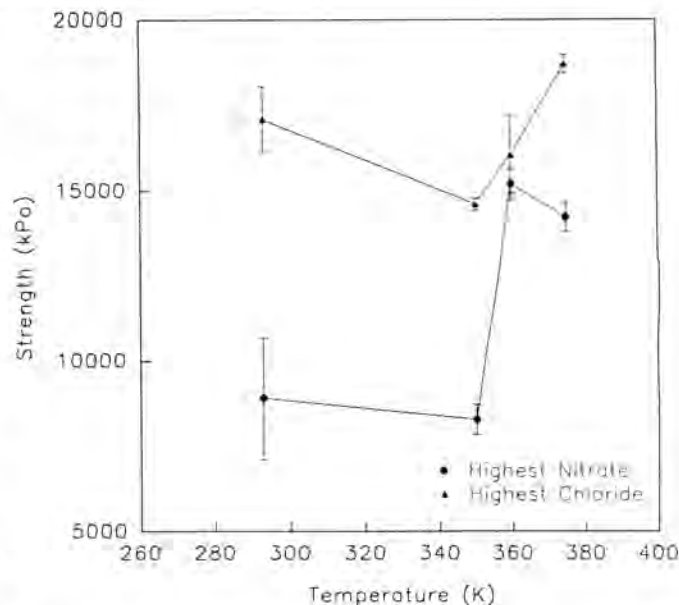


Fig. 1. Average compressive strengths of surrogate resulting from different brine temperatures. (95% confidence intervals shown; lines do not represent curve-fitted data.)

indication of flash setting or instantaneous hydration during mixing. As the surrogate samples were prepared, these observations were made:

1. Viscosity of the cement slurry increased with mixing temperature.
2. Bleed water was observed for the ambient temperature nitrate surrogate only.
3. Salt deliquescence increased with temperature.

The viscosity of the slurry increased with mixing temperature during the time that the material was mixed and poured into the molds. Possible explanations include early gel development and decreased dispersion as the salts became more soluble. Previous work at Rocky Flats has shown that these salts are strong dispersants (5).

Bleed water was observed for the ambient temperature nitrate surrogate only. Bleed water is water that forms as a layer or puddle on the top of the cement as a result of particle sedimentation. From Stokes' Law (6), the rate of sedimentation is directly proportional to viscosity; sedimentation decreases as the viscosity increases.

Salt deliquescence increased with brine temperature. Deliquescence occurs when salt becomes a liquid by absorbing moisture from the air. The samples reacted with moisture inside the clear plastic chamber and formed small puddles of high pH (12.5-13 measured with pH paper) salt solution under the samples. Although salt deliquescence was observed for all samples, observations were recorded for the chloride samples only. After curing in the stainless steel molds for one week, the samples were removed from the molds and placed back into the plastic chamber to complete the cure cycle. After  $2.6 \times 10^5$  sec (72 hours) of exposure (following removal from the mold) to the higher humidity level of the plastic chamber, the boiling point brine samples had larger salt solution puddles under the samples than the 360 K samples. Very little water accumulated on the 350 K samples, and the ambient temperature samples had no detectable water after  $2.6 \times 10^5$  sec (72

hours). Beads of liquid were finally observed on the ambient temperature samples after  $8.64 \times 10^5$  sec (10 days), and the beads eventually became large enough to run and form small puddles.

The temperature in the full-scale waste containers will be higher than observed in the laboratory-scale samples. This is because heat is dissipated at a slower rate from full-scale blocks than from laboratory-size samples and it is possible that residual heat from the input brine plus heat generated by the cement hydration reaction could result in unacceptably high temperatures in the full-scale blocks. Therefore, problems could occur in the full-scale system though none were observed in laboratory-scale tests. However, the salts strongly retard the hydration reaction of the cement constituents. Much of the heat introduced by the brine will dissipate before heat is generated by the cement hydration reaction.

### CONCLUSIONS

The objectives of the study were met, with one exception. Testing of a surrogate that reflects the current waste composition was not completed because the waste had not yet been characterized.

Laboratory-scale testing indicated that no significant loss of strength or waste form degradation occurred at high brine

temperatures. Compressive strength increased with temperature, contrary to expectations.

There is an apparent correlation between temperature, waste chemistry, and compressive strength.

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