

April 29, 1996

Progress Report for the Period
April 15 through September 30, 1995U.S. Army Engineer Waterways Experiment Station (WES) Support
to Department of Energy Rocky Flats Facility (DOE RFO)
Saltcrete Processing

1. Summary: 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. During this report period, the remaining tasks described in the agreement were completed and the project was closed.

2. Accomplishments:

a. The WES concluded the tasks described in the Research Project Plan No. 95-2, a copy of which was provided in a previous progress report. This plan described the on-going work to be accomplished at WES through September 1995.

b. The previous progress report dated May 1, 1995 and the enclosed memorandum, entitled "Possible Reactions Producing Expansion in Rocky Flats Plant Saltcrete," had delineated the potential causes for expansion and had indicated that placing crushable liners in the containers was a logical solution for accommodating the expansion. The report concluded that some half-crates, using the current proportioning for saltcrete and the current packing and storage system (as reported in TD 94-DDT-001), would continue to fail. At the time the statement was made, a small-scale model study was underway to further evaluate the expansion problem. The results of this study (encl 1) are consistent with the hypothesis that expansion in materials like saltcrete can be caused by the recrystallization of soluble salts. The results of the now completed study suggest that soluble salts in high loading (39.4% by mass in this experiment) will, when stored in facilities where the temperature fluctuates, cause problems regardless of other changes in the proportioning of the saltcrete. The salt loading that will result in reducing the expansion to an acceptable level is not known.

c. In the interest of indicating an alternative solution to the problem of the disposal of soluble waste salts, a fact sheet, entitled "Use of Portland Cement-Asphalt Cement Composites in the Disposal of Toxic and Radioactive Wastes," was prepared by WES and furnished to RFO (encl 2). The suggested approach removes the problem of salt solution/recrystallization by enclosing the salt grains in a low-permeability polymer matrix. Particles of the salt-polymer complex are then mixed into a portland-cement based mortar. Centrifugation is used to move the denser mortar to the outside of the composite. The suggested approach is consistent with the on-going program at RFO for examining polymer-encapsulation of wastes.

d. The project was closed. All materials (copies of reports and photographs) received from RFO were collected and organized. All copies of data sheets and calculations were collected and assembled as files. Materials from this project will be kept as project files.

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SALT RELATED EXPANSION REACTIONS IN
PORTLAND-CEMENT-BASED WASTEFORMS

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ABSTRACT

A small-scale study was conducted to investigate the expansion of a simulated salt-cement wasteform made with a salt mixture containing sodium nitrate, sodium sulfate, and sodium chloride blended with water and Type I portland cement. The total salt loading was 39.4% by mass of simulated wasteform. Samples cured at 23 °C hardened within 90 hours and showed strength averaging 11.67 MPa after 23 days. Samples cured at 23 °C and 55 °C expanded when subjected to temperature cycling from 1 °C to 25 °C. The samples cured at 55 °C required only 4 cycles to disintegrate after showing 14% expansion. Samples cured at 23 °C required 8 cycles before disintegrating after showing 16% expansion. X-ray diffraction patterns from 1-, 4-, 6-, and 21-day-old samples showed the characteristic patterns of halite, sodium nitrate, darapskite, and unreacted portland cement. Samples older than 1 day also showed portlandite, sodium sulfate and calcium chloroaluminate hydrate which were not found

in the younger sample. The results are consistent with the hypothesis that expansion is due to recrystallization of confined soluble salts. Results suggest that wasteforms containing such high loadings of soluble salts may disintegrate if subjected to thermal cycling.

INTRODUCTION

Adding portland cement to an aqueous solution containing hazardous or radioactive salts is one of the most common methods of preparing these materials for disposal in landfills.^{1,2} The usual procedure involves adding salt solution to neat portland cement and allowing the water in the waste to react with and partially hydrate the portland cement, forming calcium silicate hydrate and related compounds. The goal of this treatment method is to produce a dust-free monolithic mass that has some useful strength. Characteristics of waste composites vary widely,^{1,2} and resulting strengths range from those of compacted soil to those of conventional concrete. The process can produce a dust-free solid with no free liquid. Monoliths have a smaller surface area for a given unit volume of hardened waste and should release less of the waste load to contacting water. The alkalinity of the cement also produces a solid medium that can neutralize the acidity of the waste or of solutions that may be present in the natural weathering environment.

The containment provided by the cement wasteform is largely due to the production of a dry, monolithic solid. Many of the desirable features of the wasteform can be lost if the hardened waste expands and fragments or fractures. Fracturing the cemented waste mass increases the surface area available for contact with surrounding water, increases the quantity of dust associated with the sample, and reduces the effective strength of the monolith. If the monolith is cast in a stay-in-place mold,

then expansion of the waste monolith can break the mold open, allowing the treated waste to escape in solution or as fragments or dust.

Expansion reactions in the solidified wasteforms are a particularly difficult problem because they are caused by reactions that necessarily take place after the initial setting of the cement-waste mixture. The expansion can often be related to some chemical reaction associated with the compounds in the waste and/or the cement. Expansion occurring after the waste containers have been inspected and sealed can result in the rejection of broken packages scheduled for shipment. This late expansion requires large-scale reprocessing of the expanded waste. Disposal of the broken packaging, such as pallets and crates, presents an additional problem.

Salt-cement wasteforms are often used with highly soluble salts containing low levels of radioactivity. Salts solidified using cement-based techniques typically include mixtures of sodium nitrates, chlorides, sulfates and phosphates, and calcium nitrates. Waste-loading levels vary widely with the types of salts being used, but for mixtures consisting of sodium nitrate and chloride, 10 to 12% salt by mass is common for a wasteform.

Deterioration of conventional concrete through the action of salt has been reported in the literature.³ The problems of incorporated salt in wasteforms and the fragmentation of concrete due to salt action are different in that the salt in deteriorated

concrete is typically introduced through capillary action, not as an original constituent of the concrete mixture. Further, wasteforms seldom achieve the strength and modulus of concretes, and never serve the same purposes.

The two problems become similar, however, when salt crystal growth in capillary spaces in the solid produces internal pressure that can expand and fracture the hardened products. Dlouhy¹ reports that cement-based wasteforms can contain up to 25 kg of NaCl per cubic metre of cemented waste. Concrete investigations show that as little as 14.3 kg of NaCl per cubic metre has been responsible for concrete failure.³ The salts in wasteforms seldom are present as separate, water-soluble, crystalline phases² even when loadings exceed 12% by mass of waste as sodium salts. The presence and growth of separate, easily recrystallized crystalline phases may be an important factor in the fracturing and fragmentation of salt-cement wasteforms. The durability of these wasteforms can be maintained by using initial loading levels that prevent separate crystalline phases from forming^{2,5} and by preventing the migration of any additional soluble salts into the hardened wasteforms from the surroundings.

To investigate the problem of salt recrystallization and wasteform deterioration, a series of tests was undertaken using a simple simulated wasteform made by combining Type I portland cement and a mixture of sodium nitrate, sodium sulfate, and sodium chloride salts. Loadings were sufficient to produce

abundant soluble crystalline phases in the hardened wasteform. The experimental samples were subjected to conditions that promote solution and recrystallization of soluble salts without additional water. The control samples were maintained in a constant condition. The differences in expansion observed in the samples allowed the effects of recrystallization to be evaluated.

METHODS AND MATERIALS

The proportions for the test mixture are given in Table 1. The chemical composition of the portland cement is presented in Table 2. Samples were prepared by blending the components in a 1-liter high-shear laboratory mixer until the liquid was uniform. Specimens consisted of eight 25-mm-diam cylinders cast in plastic pipe and ten 17- by 70-mm cylinders cast in 28-ml polyethylene vials. Four of the latter specimens were cured at a constant 55 °C; all other samples were cured at 23 °C on a laboratory bench. The molds were left open to the air, and the vials were sealed with plastic snap caps.

The samples cured at 55 °C had hardened after 17 hours. The samples at ambient temperatures were all hardened within 90 hours. It was noted that a clear brine was produced by specimens open to the air, collecting on the upper surface and emanating from seams in the molds.

Strength Gain

Specimens were prepared for tests of unconfined compressive strength by cutting four 2.5-cm by 2.5-cm cylinders from each 10-cm-long, 2.5-cm-diameter cylinder using a band saw. The specimens were cured in plastic molds until the day they were prepared and tested. Compressive strengths were measured on a Tinius-Olsen Super L Testing Machine. The samples were not capped or ground prior to testing. Results are presented in Table 3.

Thermal Cycling

Specimens cured in sealed cylindrical vials at 55 °C were demolded after 3.5 days and were allowed to equilibrate to room temperature. Three samples were marked and measured at reference points on the circumference of the cylinder using a vernier caliper. Specimens cured at 23 °C were demolded after 7 days and marked and measured. Three experimental samples of each set were placed in a refrigerator at 1 °C for 24 hours. The specimens were then removed from the refrigerator and allowed to equilibrate to 23 °C and measured again. Samples initially cured at 55 °C were not sealed to prevent desiccation. The samples initially cured at 23 °C were kept in plastic bags to prevent desiccation. The test cycling was continued for six days. The measurements are presented in Tables 4 and 5.

X-ray Diffraction (XRD) Analysis

Samples of hardened salt-cement matrix wasteform materials were analyzed by X-ray powder diffraction to determine the crystalline components present. Samples selected from the 28-ml sealed vials were used for analysis. Material was obtained from crushed samples and was ground to pass a 200- μm sieve. The powder was packed to produce flat, randomly oriented powder pellets. All samples were analyzed on a Philips PW 1800 X-ray Diffractometer using nickel-filtered copper radiation. Identification of phases was assisted by an automated search/identification system and confirmed with patterns obtained from the literature. The results are summarized in Table 6, and sample diffractograms are presented in Figures 1 and 2.

RESULTS

The samples of salt-cement prepared in this project gained strength throughout the 23 days (Table 3) of sample storage. The 4-day and 6-day strengths (1.29 MPa and 3.19 MPa averages) were low, but the average strength of specimens after 23 days was 11.67 MPa (1692 psi). The strength gain observed is plausibly sufficient to provide confinement that will produce expansion if crystal growth or recrystallization occurs.

The length changes noted for samples cured at 55 °C and cycled from 1 °C to 23 °C showed a uniform increase (Table 4), with a maximum expansion of 14%. While cylinder length was the

measured dimension, all of the cylinders that expanded were also deformed by bulging (Figure 3). Samples maintained at a constant temperature of 23 °C showed an increase in length that was approximately one-twentieth, that of the cycled specimen. The cycled specimens fell apart after 4 days of testing.

The length changes noted for samples cured at 23 °C and cycled for 1 °C to 23 °C also showed a relatively uniform increase in length (Table 5) with a maximum expansion of 16%. These cylinders also showed circumference expansion or bulging. The specimens maintained at a constant temperature showed no consistent change in length that could be interpreted as expansion. The samples that were subjected to temperature cycling disintegrated after six cycles.

The X-ray diffraction results (Table 6) indicate that the original chemical composition of the salt solution changed rapidly when the wasteform was prepared. The sodium nitrate and sodium sulfate combined to form a sodium nitrate-sulfate double salt, similar to the mineral darapskite. Even the 1-day-old samples showed crystalline sodium nitrate-sulfate salt. The appearance of calcium hydroxide in the 4-, 6-, and 21-day-old samples and not in the 1-day sample indicates the hydration of the portland cement was delayed. Also, calcium chloroaluminate is evident in the samples that were older than 1 day.

DISCUSSION

Expansion of hardened samples of cement-salt mixtures prepared for this study appears to be related directly to the recrystallization of highly soluble salts in the rigid mass. Sodium nitrate-sulfate salt is a low-density phase (density = 2.20 g/cm³) compared to the materials from which it forms.⁴ The formation of the double salt will cause a 3.6% volume increase over the volume of the reactants.

The XRD data indicate that the development of a darapskite-like phase from sodium nitrate and sodium sulfate occurred within 1 day while the mixture was still fluid or before the mixture gained measurable strength. The volume change attributed to the formation of the sodium nitrate-sulfate double salt would not contribute to the change in volume measured after the specimens hardened. Further, the presence of consistent expansion in samples involved in heating and cooling cycles and the lack of consistent expansion in samples maintained at a constant temperature suggest that cyclic changes in salt solubilities are the mechanism driving expansion in this salt-cement mixture.

The XRD data indicate that the hardened mixture consistently contains three highly soluble components: sodium chloride, sodium nitrate, and sodium nitrate-sulfate hydrate. The dissolution and reprecipitation of soluble salts such as sodium chloride and sodium sulfate have been well-documented as a mechanism for fracturing stone and concrete.^{3,6,7}

The hardened salt-cement mixture is particularly interesting as an example of expansion because of the uniform way in which the length of the test cylinders changed when the specimens were cycled through temperature changes. This uniformity suggests that only a specific amount of material could be transferred from small crystals to large crystals in a single cycle.

Ping and Beaudoin⁶ point out that only two conditions are necessary for crystallization to exert a force in a solid: (1) confined crystal growth, and (2) a difference in the solubility product ratios of initial and final conditions. All of the soluble salts in this system show an increase in solubility with increasing temperatures. This type of crystal growth can be visualized as having the solubility increase as the temperature rises. Existing crystals are brought into solution with the smaller crystals dissolving preferentially due to their high surface energy.^{8,9} As the temperature begins to drop, the solution is supersaturated and material is added to the larger crystals that did not dissolve completely and can act as nucleation sites. This mechanism grows the larger crystals at the expense of the smaller crystals. The total volume of material in the sample does not change but is transferred from smaller crystals in the hardened mixture to the growing surface of larger crystals leaving porosity where the small crystals had originally formed. Crystals typically do not grow uniformly. Faces containing surface defects grow faster, and surface defects tend to be self-perpetuating.⁸ Mechanical effects tend to maintain and promote dislocations and sustain non-uniform growth.

The samples that were cured at 55 °C expanded as the samples cured at 23 °C had, but the rate of expansion was faster. The samples reached 14% expansion after 4 cycles and disintegrated. The samples cured at 23 °C showed a maximum 12% expansion and disintegrated after 7 cycles. The more rapid expansion of the samples cured at the higher temperature is consistent with the hypothesis that recrystallization is causing the expansion. The sample solidified at the higher temperature should contain more small, imperfect crystals that would recrystallize to form larger crystals more readily, in fewer temperature cycles.

CONCLUSIONS

The results of this study of a model salt-cement wasteform indicate:

- a) The hardened salt-cement material gains strength more slowly than conventional grouts or mortar mixtures, but can reach an unconfined compressive strength of over 11 MPa at 23-days age.
- b) Expansion of samples was observed during temperature cycling (1 °C to 23 °C), with expansions approaching 14 to 16% prior to sample disintegration.
- c) Samples cured at 55 °C expanded to disintegration in fewer cycles than those cured at 23 °C.

d) The results from the XRD study show no major changes in the soluble salt components from 1- to 4-day-old and older samples although cement hydration products appeared in the samples older than 1 day.

e) The results are consistent with the hypothesis that expansion is the result of recrystallization, with large crystals growing at the expense of the smaller crystals during cycles of solution and reprecipitation produced by raising and lowering the temperature.

f) Salt-cement wasteforms should be formulated with care if the monolithic character of the waste is a feature in guaranteeing the containment of the waste salt.

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Table 1. Proportions for the salt-cement mixture.

Material	Mass (g)
NaNO ₃ reagent grade	360
NaCl reagent grade	55
Na ₂ SO ₄ reagent grade	170
Water (from tap)	400
Portland Cement Stock No. 920297	500
Total	1485

Table 2. Chemical composition and fineness of Type I portland cement used in this study (Stock No. 920297).

SiO ₂ , %	19.6	Na ₂ O, %	0.26
Al ₂ O ₃ , %	5.7	K ₂ O, %	1.23
Fe ₂ O ₃ , %	2.0	C ₃ A, %	13
CaO, %	63.7	C ₃ S, %	55
MgO, %	2.7	C ₂ S, %	14
SO ₃ , %	3.5	C ₄ AF, %	6
Loss on Ignition, %	0.8	Blaine Fineness, m ² /kg	366

Table 3. Unconfined compressive strength data for hardened salt-cement mixture cured at 23 °C.

Age (days)	Specimen* (position)	Strength, MPa (psi)	Mean Strength, MPa (psi)
4	not noted	1.23 (178)	
	not noted	1.25 (181)	
	not noted	1.39 (202)	1.29 (187)
6	1	2.71 (393)	
	2	3.03 (439)	
	3	2.76 (400)	
	4	4.24 (615)	3.19 (462)
8	1	5.27 (765)	
	2	4.12 (597)	
	3	5.03 (729)	
	4	6.32 (917)	5.18 (752)
12	1	6.54 (948)	
	2	7.02 (1018)	
	3	6.89 (1000)	
	4	8.74 (1268)	7.30 (1059)
23	1	11.16 (1618)	
	2	9.60 (1392)	
	3	11.50 (1668)	
	4	14.40 (2089)	11.67 (1692)

* 1=cut from top of specimen, 4=cut from bottom of specimen.

Table 4. Changes in length observed in specimens cured at 55 °C with and without exposure to temperature cycles.

Age from mixing (days)	No. of Cycles	Not Temperature Cycled length change, %	Temperature Cycled length change, %
3.5	1	0.17*	2.80†
4.5	2	0.08*	6.53†
5.5	3	0.75**	9.85*
6.5	4	0.85**	13.9*

* Average of two specimens.
 ** Single specimen.
 † Average of three specimens.

Table 5. Changes in lengths observed in specimens cured at 23 °C with and without exposure to temperature cycles.

Age from mixing (days)	No. of Cycles	Not Temperature Cycled length change, %	Temperature Cycled length change, %
7	1	0.00	0.90
8	2	0.03	3.30
9	3	0.03	7.20
10	4	0.00	7.60*
10.2	5	--	7.00*
11	5	0.07	12.40*
11.2	--	--	11.70**
12	6	0.00	16.00

* Measured with sample cold.
 ** Measured with sample warm.

Table 6. Results of X-ray diffraction analysis of salt-cement materials.

Phase	1-day-old sample	4-day-old sample	6-day-old sample	21-day-old sample
Halite (NaCl)	+	+	+	-
Nitratite (soda niter) NaNO ₃	+	+	+	+
Sodium sulfate-10-hydrate Na ₂ SO ₄ • 10H ₂ O	-	tr	tr	+
Darapskite Na ₃ (SO ₄) (NO ₃) • H ₂ O	+	+	+	+
Unhydrated PC	+	+	+	+
Portlandite, Ca(OH) ₂	-	+	+	+
Friedel's salt [Ca ₂ Al(OH) ₆][Cl • 2H ₂ O]	-	+	+	+

+ = present
 - = absent
 tr = present in only trace amounts

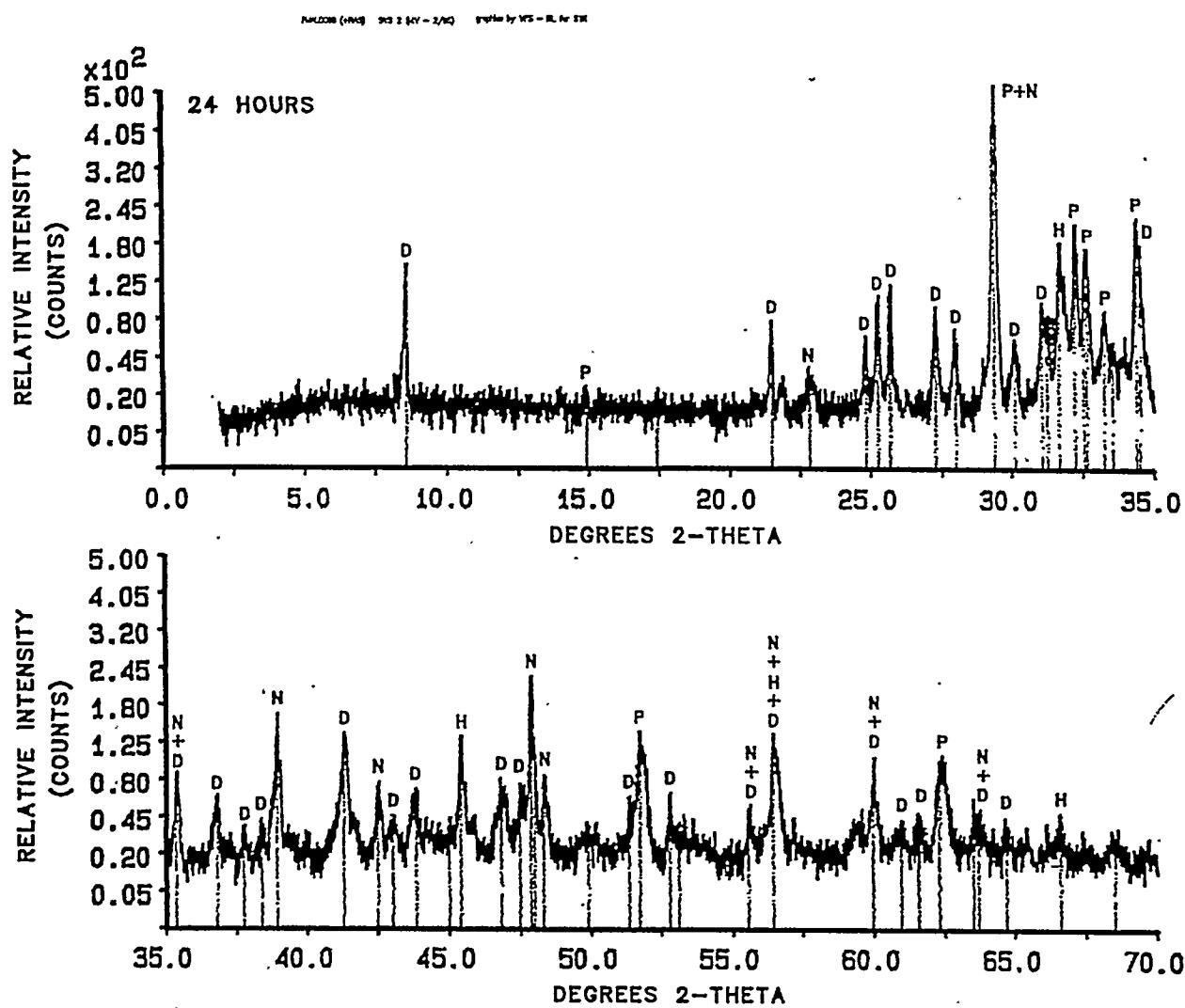


Figure 1. X-ray diffractogram of salt-cement mixture after curing at 23 °C for 1 day. Pattern shows no evidence of cement hydration. H=sodium chloride, D=sodium nitrate-sulfate hydrate, N=sodium nitrate, P=unhydrated portland cement.

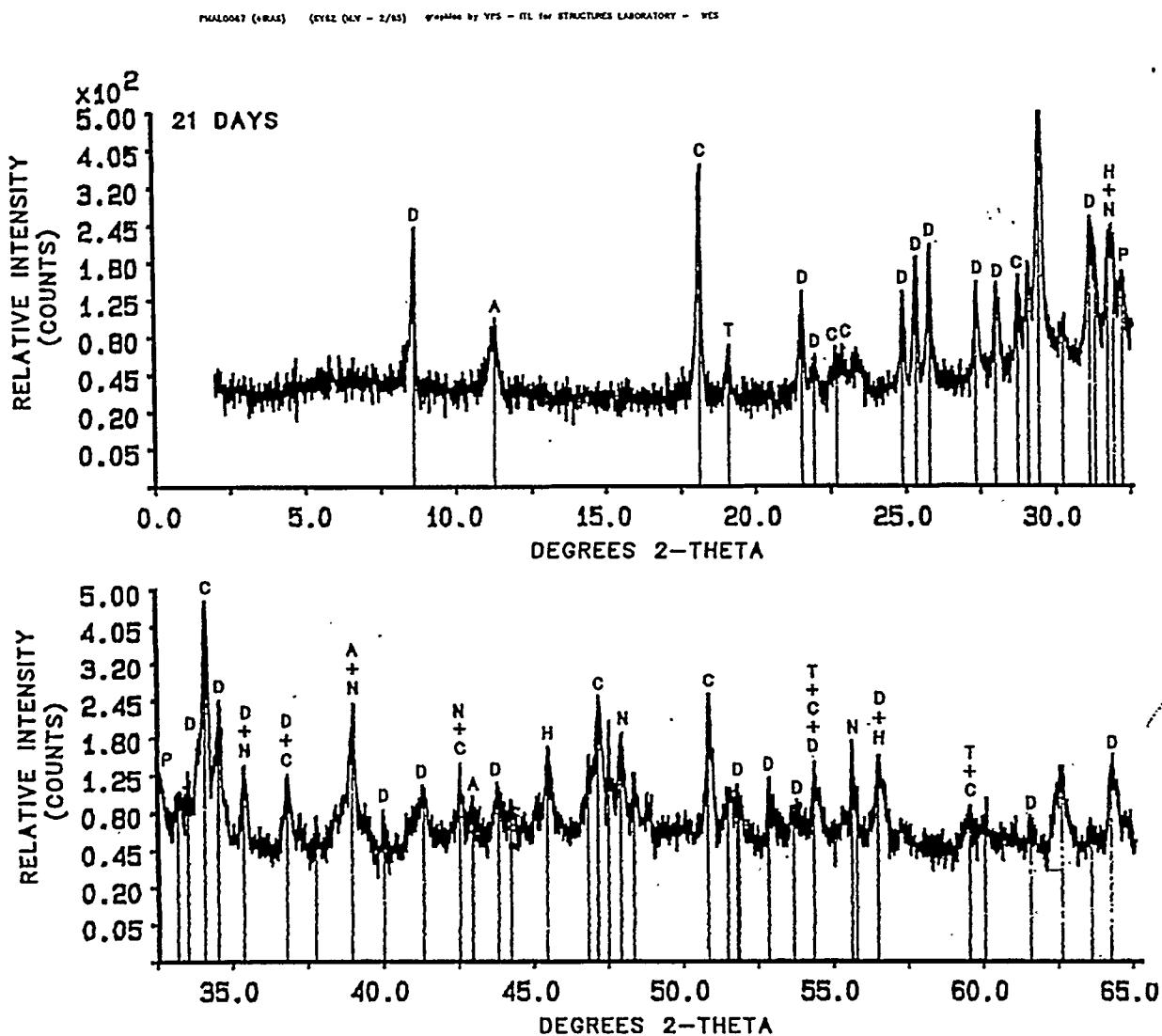


Figure 2. X-ray diffraction pattern prepared from a sample of salt-cement mixture cured for 21 days at 23 °C. Note the presence of crystalline calcium hydroxide. A=calcium chloroaluminate, H=sodium chloride, T=sodium sulfate hydrate, D=sodium nitrate-sulfate hydrate, N=sodium nitrate, P=unhydrated portland cement, C=calcium hydroxide.

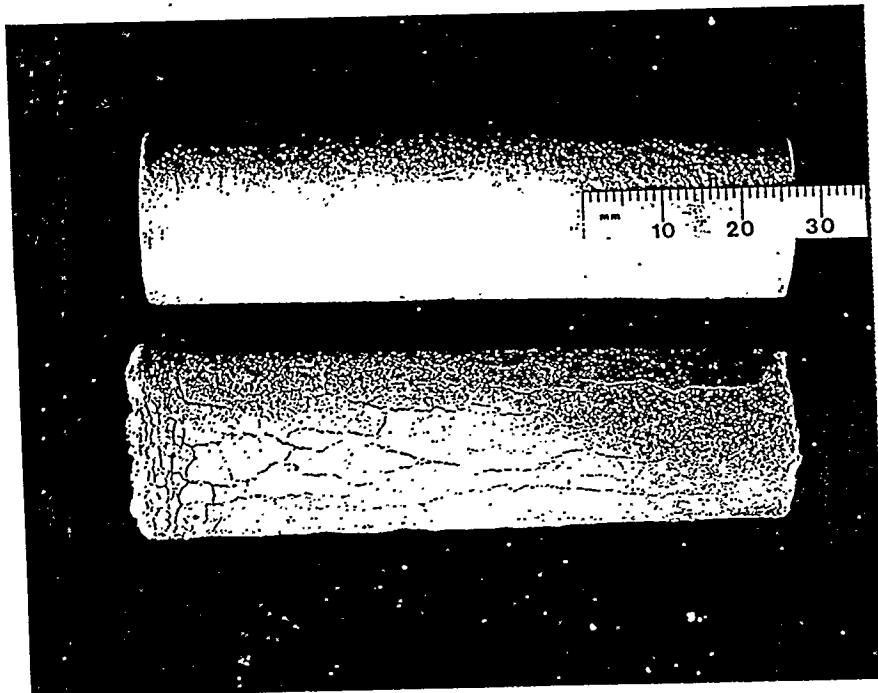


Figure 3. Photo of experimental and control test specimen. The experimental sample has expanded after 5 cycles of alternating 1 °C and 23 °C equilibration in a sealed condition where moisture was maintained. Note the experimental sample bulged as well as expanded lengthwise.

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