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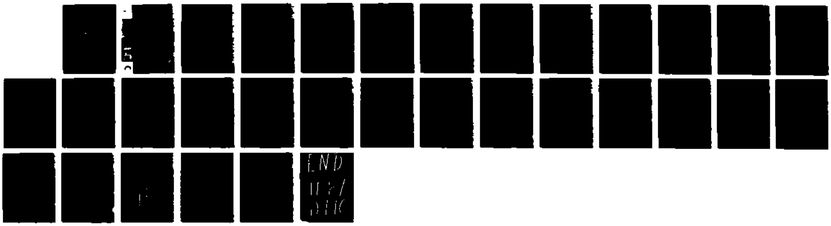

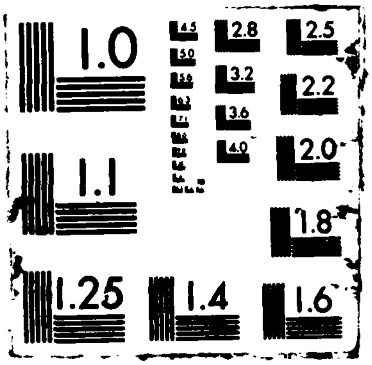
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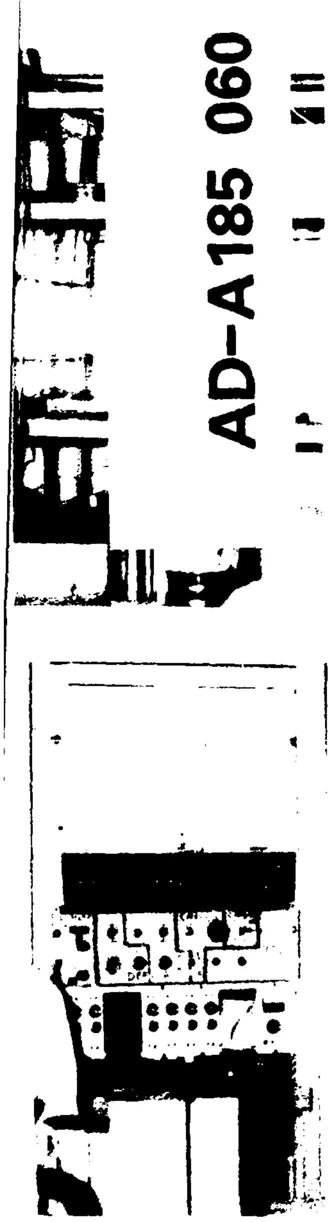

TECHNICAL REPORT SL-87-20

DEPENDENCE OF EXPANSION OF A SALT-SATURATED CONCRETE ON TEMPERATURE AND MIXING AND HANDLING PROCEDURES

by

Lillian D. Wakeley

Structures Laboratory

DEPARTMENT OF THE ARMY
Waterways Experiment Station, Corps of Engineers
PO Box 631, Vicksburg, Mississippi 39180-0631

July 1987

Final Report

Approved For Public Release, Distribution Unlimited

Prepared for Sandia National Laboratories
Albuquerque, New Mexico 87185

STRUCTURES
LABORATORY

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

AD-A185060

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188
Exp Date Jun 30, 1986

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report SL-87-20

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION: USAEWES Structures Laboratory

6b. OFFICE SYMBOL (If applicable): WESSC

7a. NAME OF MONITORING ORGANIZATION

6c. ADDRESS (City, State, and ZIP Code):
PO Box 631
Vicksburg, MS 39180-0631

7b. ADDRESS (City, State, and ZIP Code)

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Sandia National Laboratories

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS (City, State, and ZIP Code): Albuquerque, New Mexico 87185

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification): Dependence of Expansion of a Salt-Saturated Concrete on Temperature and Mixture and Handling Procedures

12. PERSONAL AUTHOR(S): Lillian D. Wakeley

13a. TYPE OF REPORT: Final report

13b. TIME COVERED FROM ________ TO ________

14. DATE OF REPORT (Year, Month, Day): July 1987

15. PAGE COUNT: 31

16. SUPPLEMENTARY NOTATION: Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161. This is CTIAC Report No. 82.

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Durability
Expansive admixtures
Expansive concrete
Retardation
Sodium chloride
Sodium citrate
Time of setting
Workability

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

In experiments with an expansive salt-saturated concrete (ESC), time of setting was controlled by amount of sodium citrate used. The rheological and physical properties required of ESC were determined by its intended use, in an underground repository for radioactive wastes in bedded rock salt. These properties, including a long working time and low air content, could not be achieved using conventional high-range water-reducing admixtures, such as melamine or naphthalene formaldehyde condensates. Within a fixed range of citrate percentages, expansivity of the concrete was proportional to the amount of citrate used.

The desired level of expansion resulted from delaying formation of ettringite until after formation of a rigid structure in the paste. Expansive potential was diminished by warmer temperatures of mixing curing, and by repeated episodes of mixing or disturbance during the extended period of workability (up to 4 hr). These variables should be considered in plans for field placement of this or any expansive concrete. (Continued)

4

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR
83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. ABSTRACT (Continued).

The potential for durability of this concrete in the environment for which it was formulated cannot be gauged by those properties commonly used as indicators of durability for conventional concrete in surface environments. Low permeability and minimal reaction to brine are interrelated factors which may better indicate durability than do traditionally cited properties such as compressive strength or resistance to cyclic phenomena.

PREFACE

The work described in this report is part of an ongoing research effort accomplished in the Concrete Technology Division (CTD), Structures Laboratory (SL), US Army Engineer Waterways Experiment Station (WES), under contract to Sandia National Laboratories (SNL), Albuquerque, New Mexico. Mr. John Stormont of SNL was technical monitor of the field operations, from which derived the laboratory studies reported herein. Most of the research was accomplished under SNL Document 32-8741, and reported under SNL Document 01-6321.

Mr. Donald M. Walley and Dr. Lillian D. Wakeley directed the laboratory studies in the CTD, with assistance from Messrs. Billy Neeley, Brian Green, and John Cook. The work was under the general supervision of Messrs. Kenneth L. Saucier, Chief, Concrete and Evaluation Group, CTD; Richard L. Stowe, Chief, Materials and Concrete Analysis Group, CTD; John M. Scanlon, Chief, CTD; James Ballard, Assistant Chief, SL; and Bryant Mather, Chief, SL. Dr. Wakeley was principal investigator, and prepared this report.

Funds for publication of this report were provided by the Concrete Technology Information Analysis Center (CTIAC); it is CTIAC Report No. 82.

COL Dwayne G. Lee, CE, is the Commander and Director of WES. Dr. Robert W. Whalin is Technical Director.

DEPENDENCE OF EXPANSION OF A SALT-SATURATED CONCRETE ON TEMPERATURE AND MIXING AND HANDLING PROCEDURES

PART I: VARIABLES CONTROLLING EXPANSION

Introduction

1. A salt-saturated concrete was formulated for experiments to develop technology for underground disposal and isolation of radioactive wastes in bedded rock salt. The field-performance requirements that guided development of this concrete included: (1) compatibility with the host rock salt, such that it would bond to the rock rather than dissolving it; (2) a slump of more than 203 mm (ASTM C 143) for at least 3 hr after mixing, to give adequate workability for complicated underground field placement after being mixed at the surface; (3) shrinkage compensation, such that the volume of concrete after it has set is never less than the original volume. This was desired to establish a tight seal at the interface within the first day after placement, and maintain that condition until inward creep of the host salt could effect permanent sealing.

2. Intended field use of this concrete required that it be placeable by either free-fall through a tremie into dry boreholes of 100 mm to 1 m in diameter, or pumping into horizontal holes of the larger size; and that it be self-levelling and cohesive, with no aggregate segregation. The hardened concrete had to be dense, with permeability of one microdarcy or less. To achieve these properties, the desired ratio of water to cementitious solids (w/cs) was 0.33. Concrete with these properties that is intentionally high in sodium chloride, for chemical compatibility, and having approximately 10 percent sulfate, for expansivity, is unknown in routine concrete practice.

Other background information

3. Components and proportions for this expansive salt-saturated concrete (ESC) appear in Table 1. Additional information about the components and reasons for their use are in Appendix A. Initial laboratory development of this concrete, and field placement at the Waste Isolation Pilot Plant (WIPP) in New Mexico during 1985 and 1986, are described by Wakeley and Walley (1986), Wakeley (1987), and Stormont (1986).

Attaining Required Concrete Properties

Retarding the time of setting

4. The need for a long working time and pumpable fresh concrete necessitated retarding the time of setting. The requirement of a dense, low-permeability product also prompted formulation of trial batches with high-range water-reducing admixtures, to lower the ratio of water to cementitious solids (w/cs). A low air content was essential, for permeability of less than 1 microdarcy, and for high density and strength (approaching 35 MPa (5,080 psi) at 28 days). Formulating for maximum expansion also made a low air content desirable, because measured expansion decreases with increased porosity (Wakeley and Buck 1986; Odler et al. 1972).

Using admixtures with salt

5. In salt-saturated mixtures tested during this study, use of either melamine or naphthalene formaldehyde condensates as high-range water-reducing and set-retarding admixtures caused the air contents of the concrete to exceed 15 percent by volume, when measured as described in ASTM C 231, Type B meter, even when the concrete also contained a defoaming agent. In this chemically and physically complex concrete, defoaming agents did not control the problem of incorporating unwanted air, even at several times the recommended dosage and regardless of which formaldehyde condensate was used (Wakeley and Walley 1986).

Extending working time

6. Common commercial set-retarding admixtures delay hydration of the calcium silicates and aluminates of ordinary portland cement, to lengthen their time of setting (Young 1972) and thus maintain workability of concrete for a longer time. In this mixture, cement hydration was delayed, whether or not organic retarders were added, by the presence of 2.5 percent (total mass) NaCl (Hansen 1952; Slagle et al. 1963; Moore et al. 1980); and by SO_3 content greater than the optimum 3 to 4 percent identified by Soroka and Abayneh (1986). Use of any of five set-retarding admixtures intended to delay hydration of calcium silicates did not add significantly to the working time, except in cases where the resulting air content was unacceptably high, or where time of setting was delayed by days to weeks. Instead, working time of

this concrete was lengthened by retarding hydration of the calcium sulfate components, using sodium citrate (hereafter called "citrate"), the retarding admixture used most commonly for gypsum cements. Using citrate proved to be the key to attaining the workability, low porosity, and expansive properties needed for this special concrete.

Experiments with Citrate Content and Mixing Temperature

Slump and air content with varied citrate content

7. To determine the effects of citrate on rheology and other properties, batches of concrete were prepared keeping mixture proportions constant and varying only citrate content. Citrate was added at 0.00, 0.25, 0.35, and 0.50 percent by mass of cementitious solids, with no other organic chemical water-reducing or set-retarding admixtures. The amount of defoaming agent was kept constant in these trials. Use of citrate without a defoaming agent caused the air content to rise above 7 percent, so the defoaming agent was used in all formulations.

8. Slump (ASTM C 143-78) and air content (ASTM C 231-82) were determined for laboratory-mixed batches of concrete with varied citrate contents, as indicators of potential workability and frothing. These data appear in Table 2. The salt-saturated concrete with 0.50 percent citrate maintained a slump of 10 in. for nearly 3 hr of either continuous or intermittent mixing, and the air content remained less than 2.0 percent.

Time of setting with varied temperature

9. Time of setting (ASTM C 403-85) was determined for concrete with 0.00 and 0.50 percent citrate, at two temperatures of mixing and storage, as shown in Table 3. Setting time was accelerated and slump was decreased in concrete with no citrate. Setting time also was accelerated at the warmer temperature; at a constant 0.50 percent citrate content, warmer concrete set faster.

10. Laboratory development of this mixture included using cold mixing water, a practice based on field experience with using cold water to increase working time of grouts. With this concrete, cold water increased effective

working time because hydration reactions occurred more slowly at lower temperature, as shown by the increased time of setting for concrete mixed and cured at 21°C rather than at 27°C (Table 3).

Relating expansion to citrate content and temperature

11. Specimens with all four levels of citrate were cast for measuring restrained linear expansion. Specimens were as described in ASTM C 878, except that they were coated with a liquid curing compound on the exposed face, and kept at 25°C (78°F) and near 50 percent RH for the first 24 hr. Following this, they were demolded and coated in beeswax twice, with foil between, to minimize gain or loss of moisture, and stored at laboratory ambient temperature (22°C). Duplicate sets of prisms of the mixtures with 0.00 and 0.50 percent citrate were mixed, cured, and stored at 27°C, to determine the impact on expansion of the temperature encountered in the field, where the concrete was to be placed.

12. Specimens with 0.50 percent citrate mixed with cold water and stored at the lower temperature reached 0.1 percent expansion by 7 days, 0.13 percent by 28 days, and 0.15 percent at 90 days age. Figure 1 compares data for expansion of prisms of concrete with four different citrate contents and constant temperature. Comparisons of expansion at the two mixing and storing temperatures, for 0.00 and 0.50 percent citrate, appear in Figure 2. The concrete with no citrate showed less than 0.02 percent expansion at 28 days, despite the presence of both plaster (Cal-Seal) and an expansive admixture containing $C_4A_3\bar{S}$ and gypsum (ChemComp III). The expansion of this mixture has been shown by XRD and SEM to result from ettringite formation (Wakeley 1987).

Effects of handling procedures on expansion

13. Field experience with this concrete had suggested that there were differences in its rheology or other early-age properties depending on the time elapsed between mixing and placing or casting of different batches. The expansion prisms cast in the field had been prepared after all other required placement was completed, more than 3 hr after initial mixing (as described by Stormont 1986). These showed less expansion than did those prepared in the

laboratory during preliminary testing of the mixture (Table 4). However, it seemed unlikely that the time delay, itself, could account for this difference: concrete from any single mixing event was all the same age relative to the time the solids were initially mixed with water, whether that concrete was in a hopper, in a borehole, or in prism or cylinder molds. In each case, there would have been the same time available for hydration reactions to occur, to form phases the formation of which is accompanied with an increase in volume and other hydrated components in the cement paste.

14. With temperature in the field a constant, the events of disturbance during the time between mixing and placement or casting were considered as a variable with potential effect on measured expansion. In the field, longer times between mixing and placing were accompanied by repeated events of dumping or pouring between containers and attendant remixing of the concrete, after intervals of rest of variable duration. Considering the importance of expansion following field placement, understanding the effects on expansion of field placement practices became an essential part of research on and development of this concrete.

Laboratory studies of episodes of disturbance

15. Following the first field placement of ESC (July 1985; Wakeley and Walley 1986, Stormont 1986), laboratory studies were designed to determine the effect on expansion of repeated episodes of rest and disturbance during the time between mixing and casting or placement. A batch of ESC (1.5 ft^3 or 0.042 $in.^3$) was prepared with cold water (42°F, 6°C) and 0.50 percent citrate, as it had been in the field, and held in the mixer for 4 hr. Expansion prisms were cast immediately after mixing, and at intervals of 30 min, and 1.0, 1.5, 2.0, 3.0, and 4.0 hr thereafter, for a total of 7 sets of expansion prisms. The mixer was at rest during this time, except for 1 min of mixing just prior to each casting. This schedule of repeated mixing and casting is summarized in Table 5. A second set of prisms was prepared at the same time intervals from a batch of ESC identical to the first except that the mixing-water temperature was 79°F (27°C). Slump and air content for the two batches are reported in Table 6.

16. Prisms were coated and cured as described previously. The duplicate sets were stored at the laboratory ambient temperature (23°C), and at the

field-simulation temperature (28°C), to isolate effects of repeated disturbance from those of temperature. All prisms were monitored for length change to 90 days. Figure 3 gives data from the lower temperature, and Figure 4 from the higher temperature. These figures compare the expansion at each age among prisms from each time delay, with the number of episodes of repeated disturbance increasing with time delay between initial mixing and casting. They show consistently less expansion with more disturbance, at both temperatures. This decrease in expansion is more pronounced at the lower temperature. Specimens stored at the lower temperature show more expansion for a given sequence of disturbance, relative to those stored at the field-simulation temperature (Figure 5).

Discussion

17. Time of setting of the mixtures with four different percentages of citrate shows that the citrate is an effective retarding admixture for this complex assemblage of sulfate and portland-cement phases with salt. The mixture had an initial time of setting of 3 hr 10 min with no citrate, and did not have a time of initial setting for more than 9 hr with 0.50 percent citrate. Workability at 4 hr, as indicated by both Tattersall apparatus and field use, was not attained with any of several other commercial retarding admixtures known to be effective with portland cement (Wakeley and Walley 1986). Use of citrate permitted extraordinary workability in conjunction with a low w/cs, even without addition of any other organic chemical retarding or water-reducing admixtures. The low fineness of the class H cement and use of fly ash probably also contributed synergistically to the favorable rheological properties of this concrete.

18. In the range of 0.00 to 0.50 percent citrate, linear expansion was directly related to percentage of citrate used in the concrete. This suggested that expansion might be directly proportional to extent of retardation. The concrete with 0.50 percent citrate showed more expansion with colder temperatures of mixing and curing. This also suggested a relationship between expansion and retardation. Thus it appears that the slower the formation of a rigid structure, the more concrete expands. This seems to contradict previous studies, in which it was shown that a critical level of hydration is required before expansion can begin: ettringite formed before this critical level

cannot exert outward pressure, because it forms either in voids or in a plastic matrix (Bentur and Ish-Shalom, 1974; Kalousek and Benton, 1970; Ogawa and Roy, 1982; Nakamura et al., 1968).

19. Expansion will be greater if the formation of ettringite is retarded more than the formation of a rigid structure in the paste, or if ettringite continues to form after the rigid structure is established. In this complex mixture, it is not possible to distinguish among the effects of all of the factors affecting hydration rates of portland-cement and sulfate phases. The citrate retards each of these, but the reactions and rates are different when the two are together than when they are monitored individually, and different again when salt and the other components are added. Colder temperature appears to increase expansion, possibly by further delaying formation of ettringite, but only in conjunction with the citrate retarder. In the absence of citrate, there was no difference in measured expansion of prisms at the two temperatures (Figure 2).

20. The critical parameter probably is the citrate itself, rather than the overall retardation of the concrete as indicated by time of setting. The citrate acts as a delayed hydration accelerator for the sulfate phases (Regourd, 1986), extending their reactivity after setting has taken place (Wakeley, 1986). In other studies at WES, in which higher percentages of citrate were added to grouts and concretes (up to 2.00 percent), setting time was lengthened to more than 24 hr, and expansion decreased, relative to comparable mixtures with 0.50 percent citrate (Wakeley and Boa, 1987). This suggests that it is possible to delay the time of setting too much, to the point that much of the expansive potential of the sulfate phases is effectively wasted, by early formation of ettringite in a non-rigid matrix.

21. The expansion, then, is not directly related to retardation. It apparently is maximized within a limited range of citrate content. This concrete with 0.50 percent citrate achieved a fortuitous balance between the amount of citrate required to control working time, and the amount that optimizes expansion.

22. Another variable with a measurable effect on expansion is disturbance or remixing of the concrete during the time between initial mixing and placement. This repeated breaking up of the early-formed microstructure might be expected to have an effect on other properties as well, such as compressive strength and pore-size distribution. These differences were suggested by

comparison of data from field-cast and laboratory-cast specimens, but have not been systematically explored.

23. Impact on expansion has been systematically explored. Each episode of remixing may bring more of the unreacted components in contact with water. This would effectively accelerate the rate of hydration of all components, and appears to expend the expansive potential in particular, before the concrete sets. The effect on measured expansion is the same as that of excessively retarding the overall mixture: the expansive potential is wasted by early formation of ettringite in a non-rigid matrix.

PART II: DURABILITY OF ESC

Introduction

24. Composite materials based on hydraulic cements are being asked to serve many functions in isolation and disposal of high-level radioactive wastes (radwastes).

25. For underground disposal of high-level radwaste, grout and concrete will line access shafts, and lock in shaft casings and liners. They will seal off fluid-bearing strata to keep groundwater from becoming a means of transporting potential contaminants. As borehole plugs and bulkheads, concrete will be a major components of the many-phased seal system, designed ideally to be a permanent series of barriers between radiologic hazards and life.

26. In its position as familiar construction material, concrete is perceived as being friendly, tractable, malleable to these many purposes. Those who concern themselves with radwaste disposal are asking concrete to be many things to all people, the main entry on a list of seal materials for which durable is the universal descriptor.

27. But durability is not a property of concrete, at least not in the ordinary, quantifiable sense in which compressive strength is a property. Durability has meaning only in terms of making some demand on concrete performance. The long list of current and intended uses for concrete in radwaste disposal accompanies an even more diverse list of environmental characteristics with potential impact on concrete properties and performance. A material cannot be classified as durable unless it is related to the appropriate limiting environmental conditions (Litvan and others, 1980). And there is also the demand of time.

28. For disposal of high-level radwastes, the total system must be effective for maybe 10^4 years, a period far longer than the entire documented history of portland-cement concretes. The concrete component of that underground, multiple-barrier system may need only to last a tenth of this or less, however, with longer term guarantees coming from the rock itself.

29. For disposal of high-level radwastes in a geologic repository in rock salt, the suite of potential hazards to concrete is quite different from those usually considered in normal concrete practice. Concrete filling a

shaft through halite (NaCl) beds 600 m beneath the earth's surface encounters no cycles of wetting and drying or freezing and thawing. There is no potential for physical abrasion, or acid rain. And there is a different set of rules about chlorides and sulfates. The following sections of this report are about the properties of ESC that determine its potential for durability.

Considering Durability in Formulating ESC

30. The short-term consideration prompting this use of NaCl as a component of ESC was avoiding dissolution of the host rock during placement. In the longer term, compatibility of sealing materials with the host environment is the critical reason for having the concrete initially saturated with salt. The working assumption for repository sealing is that chemical similarity between seal material and host rock will minimize adverse reactions between them. This is expected to simplify predictive modeling, and add confidence in long-term isolation (Stormont 1984). Thus, the durability sought for salt-saturated concrete in this environment might be thought of as chemical durability, because so many of the demands made of the concrete are chemical, and the usual physical threats to durability do not apply.

Concrete Properties for Durability

31. During 1985 and 1986, ESC was placed underground at the WIPP site for two series of tests of the performance of small-scale seals (up to 1 m diam) (Wakeley and Walley 1986). Characteristics of the environment in which it was placed, and in which it needs to be durable, affected curing and aging, and determined the physical and mechanical properties required of ESC. The WIPP repository temperature remains nearly constant at 28°C, accompanied by less than 50 percent RH. There is very little water, present in small brine pockets and fluid inclusions. Concrete placed in this environment must develop properties for durability with no additional water. Given that the real chemical processes of concrete are heavily dependent on temperature and relative humidity (Idorn 1984), this is, indeed, a unique environment in which to consider concrete durability.

32. Concrete placed underground in rock salt beds, as was ESC, is under continuous restraint as it ages, due to salt creep in response to stress

relief (Barr 1977; VanSambeek 1986). Specimens of ESC cast in the field and cured under restraint in simulated WIPP repository conditions continued both to develop strength and to show two-dimensional expansion, for ages of up to one year. These data are summarized in Table 7, and are reported extensively elsewhere (Comes and Pace, in prep).

Permeability

33. In addition to strength gain without shrinkage, the ESC mixture had very low permeability. Specimens to simulate small borehole plugs, for laboratory tests of permeability of the plug and plug-rock interface to saturated NaCl brine were cast in the field. The specimens were kept under restraining pressure in Hassler cells beginning at three days age. That pressure was increased systematically to simulate interface pressures measured in the field, caused by salt creep. Driving pressure was applied after 28 days, and increased to 2.75 MPa (400 psi).

34. There was no detectable flow through the specimens until about three months age. The time between application of driving pressure and detection of brine flow apparently was time required to saturate the specimens, and was consistent among specimens. Flow of about 0.02 microdarcy was detected for about two months, after which it ceased. This is the same magnitude of permeability measured for rock itself (Peterson 1986), which is considered impermeable in its field performance; and two orders of magnitude less permeable than high-quality construction concrete. Flow did not resume through ESC test specimens even when driving pressure was increased to 4.1 MPa (600 psi). Specimen descriptions and test specifications appear in Table 8.

Discussion

The prognosis for chemical durability

35. Concrete such as the ESC mixture, intentionally high in chloride and sulfate, is unknown in normal concrete practice. In the more usual environments in which concrete is placed, on or near the surface of the earth, the concrete would break down quickly. Chloride-containing components would be dissolved, altered, or replaced, resulting in loss of physical integrity of the concrete mass. Any structure made of ESC and exposed to non-brine water would experience extraordinary expansion, and the concrete would crack. Laboratory-cast specimens cured in the fog have cracked, even when stored in a

restrained condition. Either of these conditions would decrease concrete strength.

36. Although compressive strength is considered by many authors to be the essential property of concrete durability (MacKenzie and others 1986; Feldman and Ramachandran 1980), consideration of the conditions the concrete confronts in situ may be more important (Clarke 1986). Compressive strength of laboratory-tested specimens of ESC is impressive -- over to 50 MPa (7,250 psi) at one year, in simulated WIPP conditions. But this concrete may not need to be strong in order to be durable. In an underground repository in rock salt, ESC may be durable for other reasons.

37. ESC in situ at the WIPP is restrained, not by corrodible steel rods, but by the enclosing host rock. The rock, in turn, presses inward at a rate that exceeds the expansivity of the concrete monolith (VanSambeek 1986), effecting a very tight seal at the interface. The strength gained by the concrete is at least partly attributable to this restraint: it cures held tightly by rock, which prevents gain or loss of moisture.

38. Inward movement of rock coupled with concrete expansion appears to prevent the interface from becoming a preferred pathway for fluid flow, should any water approach the repository, and precludes dissolution of concrete components. Dissolution is unlikely anyway, considering how little water (brine) is available.

39. Evidence from permeability tests suggests that the ESC is unlikely to wash away, or dissolve to a notable extent even if it comes in contact with brine. Measured permeability is very low. If the concrete were in jeopardy of dissolution by invading brine solutions, flow measured in permeability tests should have increased with time. But interface specimens were essentially self-healing. Whether by inward creep of the enclosing rock salt under confining pressure, or by precipitation toward the downstream end of the specimen where pressure was reduced, or by a combination of these mechanisms, flow stopped after two months.

PART III: SUMMARY AND CONCLUSIONS

40. A salt-saturated concrete was formulated using commercially available components to achieve the following properties:

- a. Ratio of water to cementitious solids of 0.33 by mass;
- b. Air content of less than 2 percent in fresh concrete;
- c. Working time of 3 to 4 hr;
- d. Pumpable, self-levelling, non-segregating;
- e. Good bonding to rock salt; and
- f. Early and sustained net volume increase.

These properties were attained without addition of conventional organic chemical set-retarding or water-reducing admixtures, which cause air contents as high as 17 percent in salt-containing concrete. Mixture components were high in sulfate phases, giving expansion by formation of ettringite; monitored in other studies (Wakeley, 1986).

41. Delay in time of setting, and hence maintenance of workability for a longer time, increased with increasing percentage of sodium citrate. Measured linear expansion also increased with citrate content, in the range of 0.00 to 0.50 percent by weight of cementitious solids. Workability and expansion also were improved by using iced mixing water, at a constant level of citrate, although the colder temperature had no apparent effect on expansion of concrete formulated without citrate.

42. This combination of mixture proportioning and mixing methods improved both workability and expansion. The citrate content required for achieving needed workability is within the range for optimizing expansion. Expansion, rather than being related to overall retardation of the concrete, may depend on ettringite formation being delayed more than is the formation of a rigid structure in the paste, or on extending the time of reactivity of the sulfate phases.

43. Consistent with these observations of the impact on expansion of using the sodium-citrate retarder, multiple episodes of disturbance and remixing of the concrete during its 4-hr period of workability also decreased measurable expansion. Repeated agitation apparently increased exposure of unhydrated material to available water, thus accelerating hydration reactions that form ettringite before there was a rigid structure against which the ettringite could exert outward pressure to cause the concrete to expand.

Handling and placement procedures for this or any expansive concrete should minimize such disturbance if possible, if maximum expansion is desired.

44. Factors which indicate durability in routine concrete practice may not be related to durability of concrete placed deep underground in a repository for radwaste. A salt-saturated concrete, developed for ease of placement in rock salt and early-age expansion, has other characteristics which indicate likelihood of its long-term durability. Expansion, low permeability, and minimal reaction to brine are interrelated factors which may be more important for durability than is compressive strength or resistance to cyclic phenomena. The concept of chemical durability takes on new meaning in the unique environment of a deep geologic repository in rock salt.

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Table 1

Components and Proportions of Expansive Salt-Saturated Concrete

Component	% of total by mass	% of total solids by mass	Actual batch weight, lb[a]
Class H cement	9.03	9.66	1,822.5
Chem Comp III	6.02	6.45	1,215.0
Cal Seal	1.80	1.94	364.5
Class C fly ash	5.10	5.44	1,026.0
Fine aggregate[b]	34.11	36.50	6,823.6
Coarse aggregate[b]	34.58	37.00	6,903.6
Sodium chloride (NaCl)	2.50	2.65	499.5
Defoaming agent	0.21	0.24	42.9
Sodium citrate	0.11	0.12	0.16
Water	6.60	--	1,461.7

water/cementitious solids = 0.33

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a) Batch prepared and placed underground at the WIPP, July 1985 (Wakeley and Walley 1986). 1 lb = 453.6 g.

b) Aggregate total is 61.1% by volume of fresh concrete.

Table 2

Slump and Air Content of Concrete with Four Levels of Citrate

Citrate, %	Slump ASTM C143 mm	Time,[a] min	Air Content ASTM C231, %	Time, min
0.50	267	30	1.5	10
	254	120	1.5	120
0.35	241	30	2.6	30
	197	120	2.2	120
0.25	248	30	2.5	30
	191	120	2.3	120
0.00	114	15	2.4	15

---

a) Time elapsed since initial mixing of solids with liquid.

Table 3

Time of Setting (ASTM C 403-85) of Concrete with 0.0 and 0.5% Citrate at Two Temperatures

citrate, %	Average Time of Setting, hr:min initial	 final
A. Temperature after mixing 18°C, tested at 22°C.		
0.50	9:35	16:50
0.00	3:10	9:0
B. Temperature of mixing and testing 27°C.		
0.50	7:40	11:00
0.00	2:30	7:10

Table 4

Restrained Linear Expansion of Prisms from Field (SSSPT Series A) and Laboratory Casting, Cured at 27°C

Age, days	Field-cast prisms	Laboratory-cast prisms
2	0.010	0.027
4	0.030	0.064
7	0.042	0.073
14	0.033	0.080
21	0.036	0.090
27	0.036	0.102
56	No data	0.120

Table 5

Schedule for Casting Expansion Prisms of ESC Following Repeated Disturbances; Lower Temperature

Time delay, hr	Number of Times Mixed	Total Mixing Time, Min	Total Rest Time, Min	Mixing Temp, °F
0 (initial)	1	5	3	64
0.5	2	6	24	65
1.0	3	7	53	64
1.5	4	8	82	66
2.0	5	9	111	66
3.0	6	10	170	66
4.0	7	11	229	67

Table 6

Slump and Air Content of Batches of Salt-saturated Concrete Prepared at Two Temperatures

Time	Mixing Temperature, °F (°C)	Slump, mm	Air Content, %
Initial	64 (17.8)	267	1.7
	80 (26.7)	254	1.3
4 h	67 (19.4)	235	1.6
	82 (27.8)	127	1.8

Table 7

Compressive Strength (ASTM C 39-84) and Restrained Linear Expansion (ASTM C 878-80) of ESC

Age, days	Compressive strength[a]	Linear expansion, %[a]
2		0.029
5		0.044
7		0.084
14		0.113
21		0.110
28	32.9 MPa (4,780 psi)	0.111
56		0.127
90		0.124
180		0.118
270	50.4 MPa (7,320 psi)	0.120
374	51.0 MPa (7,400 psi)[b]	-

a) Average of two specimens.
b) Average of three specimens.

Table 8

Permeability of Field-Cast Simulated-Borehole Specimens Tested in Hassler-Type Cells

Specimen No.	Length (L), cm	Flow rate (Q), cm^3/s	Permeability, darcies[a]
B 140	27.0	$2.3x10^{-7}$	$2.1x10^{-8}$
B 141	20.3	$1.8x10^{-7}$	$1.3x10^{-8}$

---

[a] Assuming only concrete plug (5 cm diam) is permeable.

$$K = \frac{Q \mu L}{A \ \Delta P}$$

where Q = flow rate, cm^3/sec,

μ = viscosity of liquid, centipoises (1.9 for brine),

L = length of specimen, cm

A = end area of specimen, sq cm, (20.3 sq cm), and

ΔP = pressure difference across specimen, atmospheres.

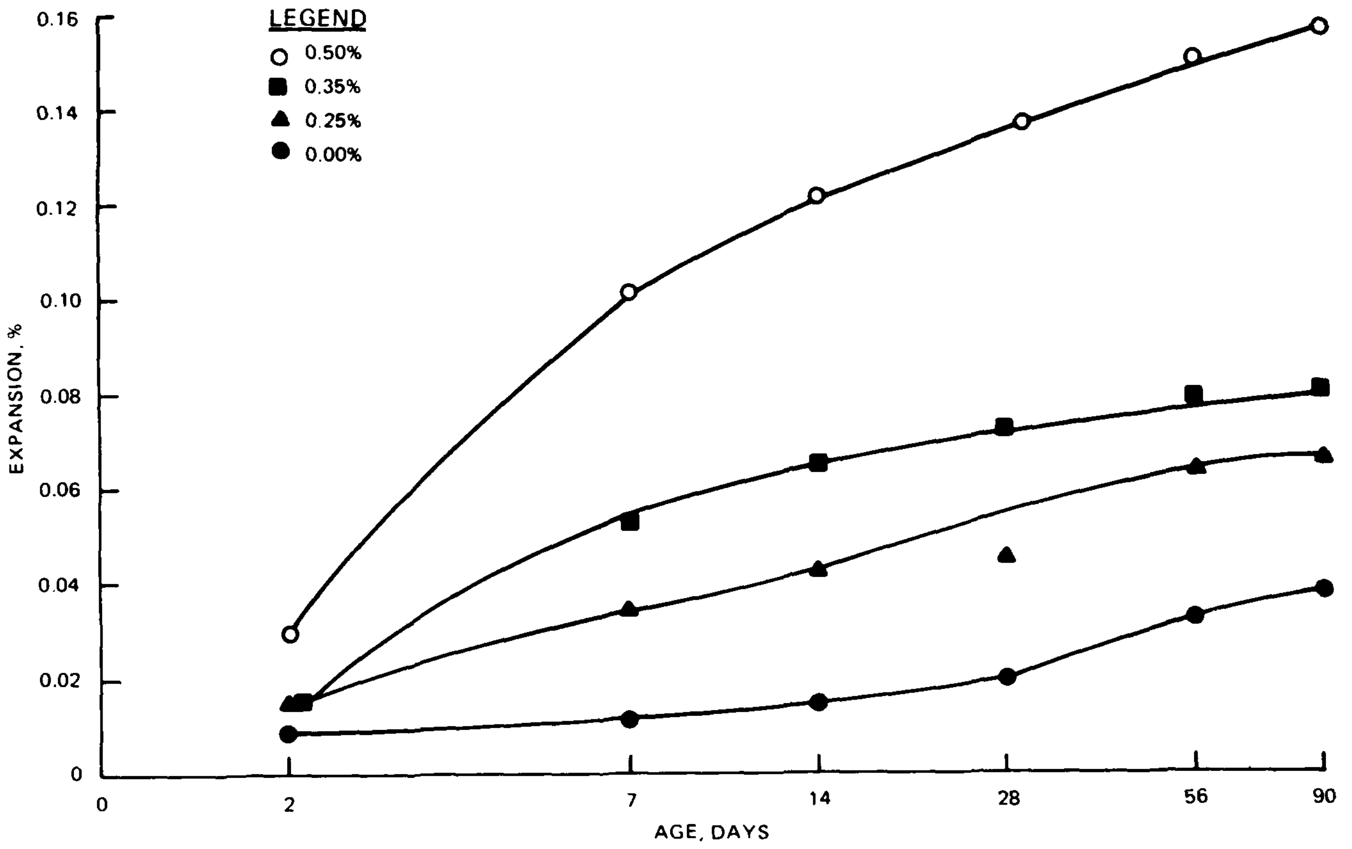

Figure 1. Expansion of restrained prisms of concrete with 4 different citrate contents, cured at 22°C.

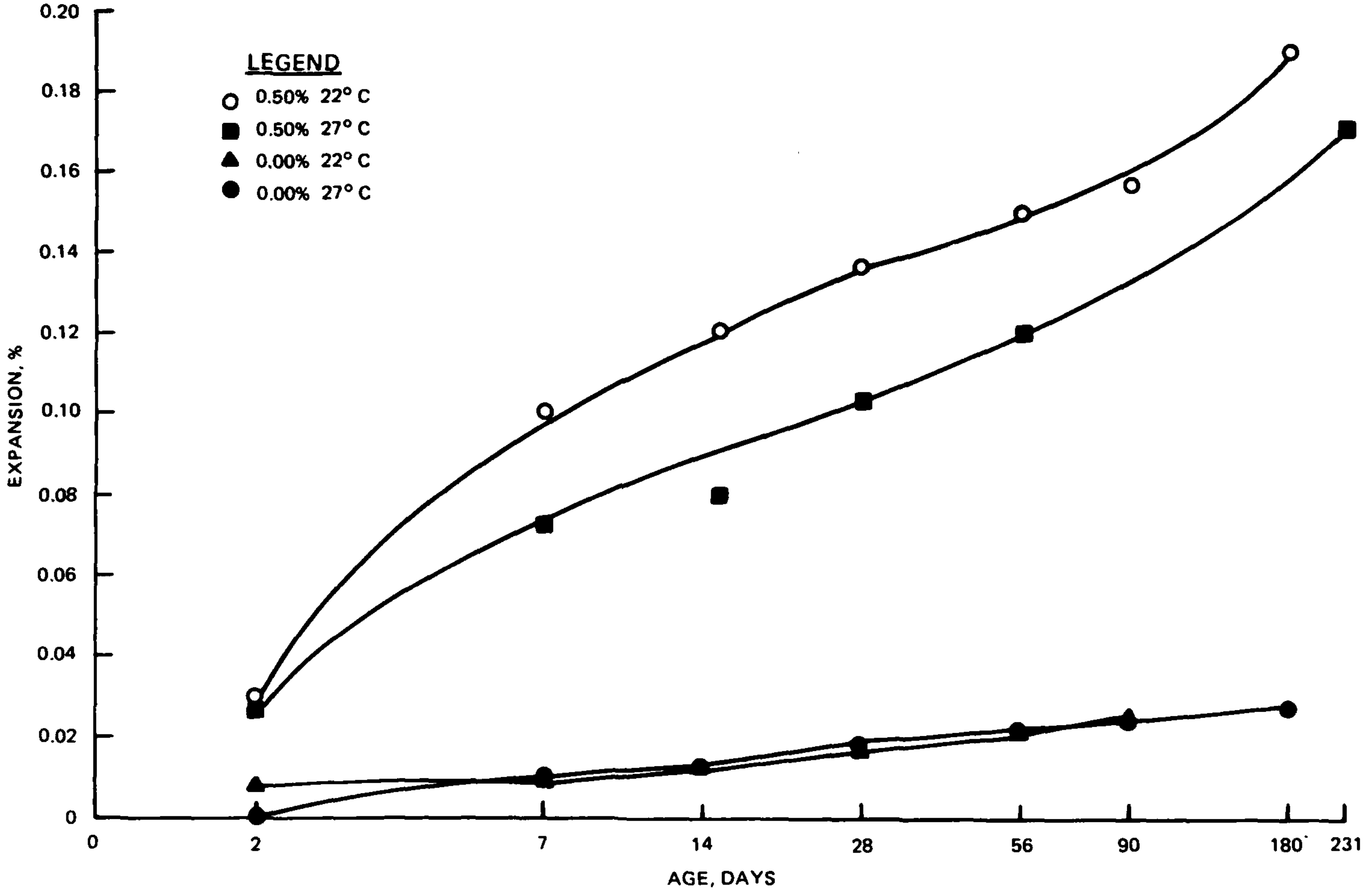

Figure 2. Expansion of restrained prisms of concrete with 0.00 and 0.50 percent citrate, cured at two temperatures.

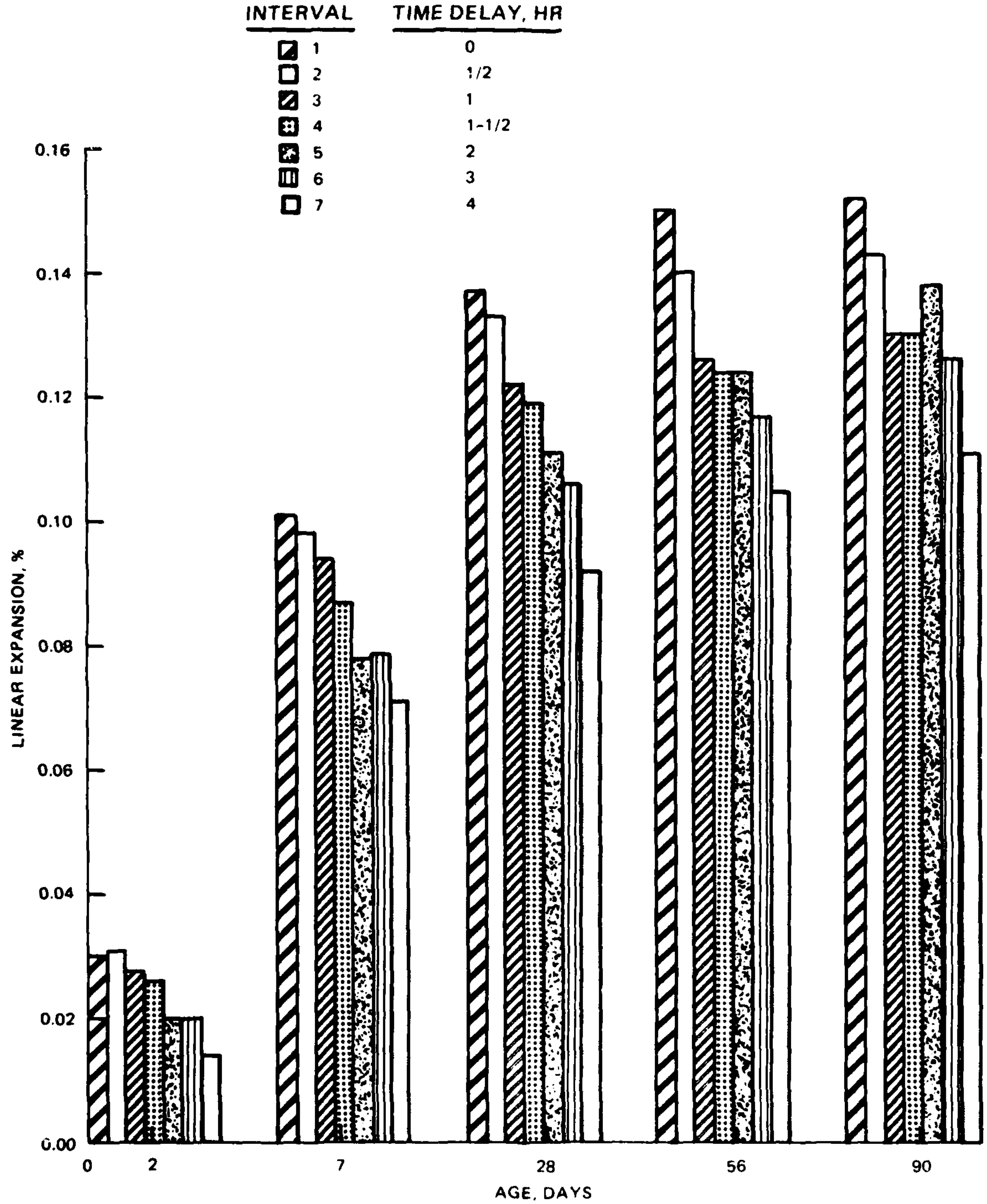

Figure 3. Expansion of prisms of salt-saturated concrete cast at seven intervals and cured at 22°C

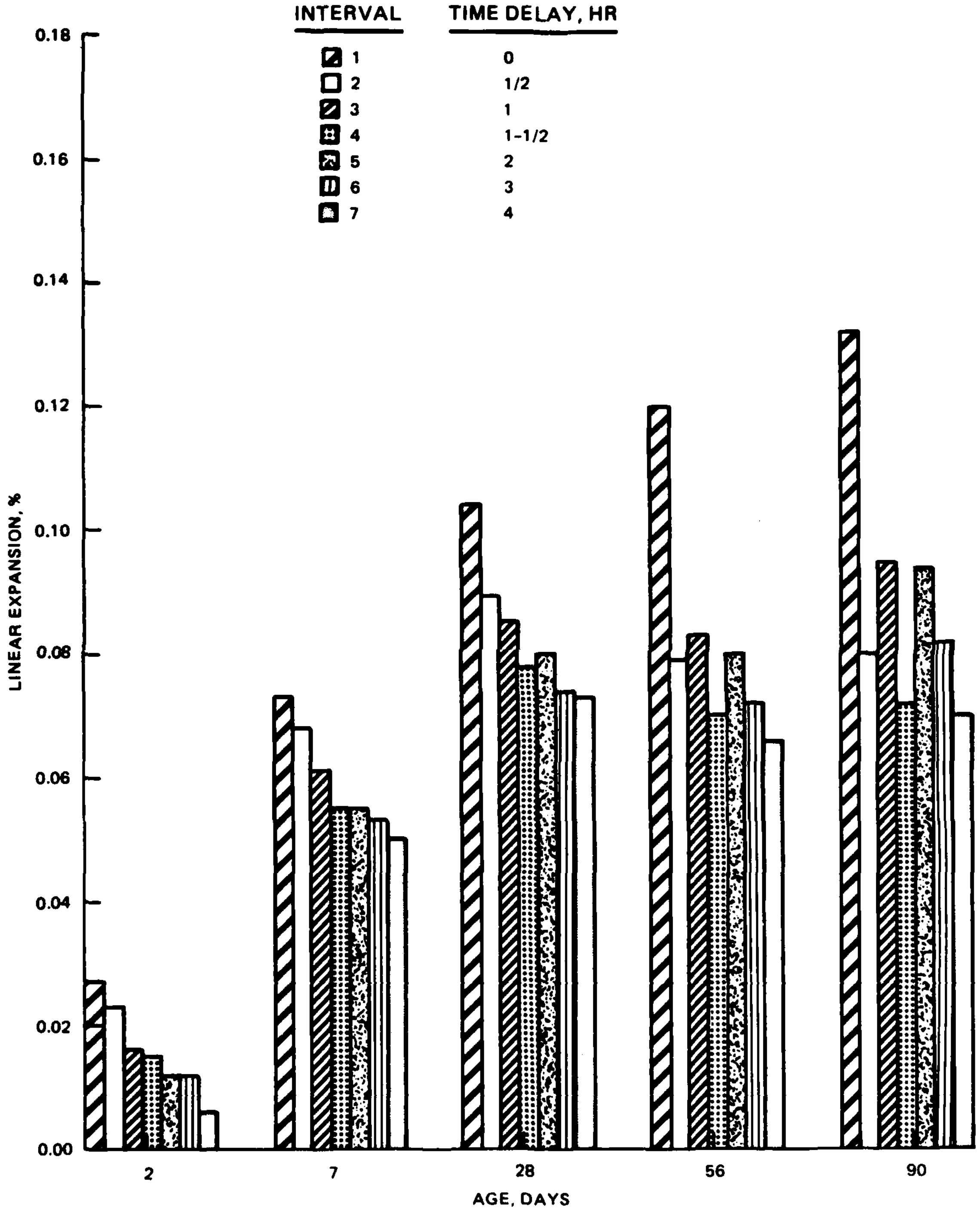

Figure 4. Expansion of prisms of salt-saturated concrete cast at seven intervals and cured at 27°C.

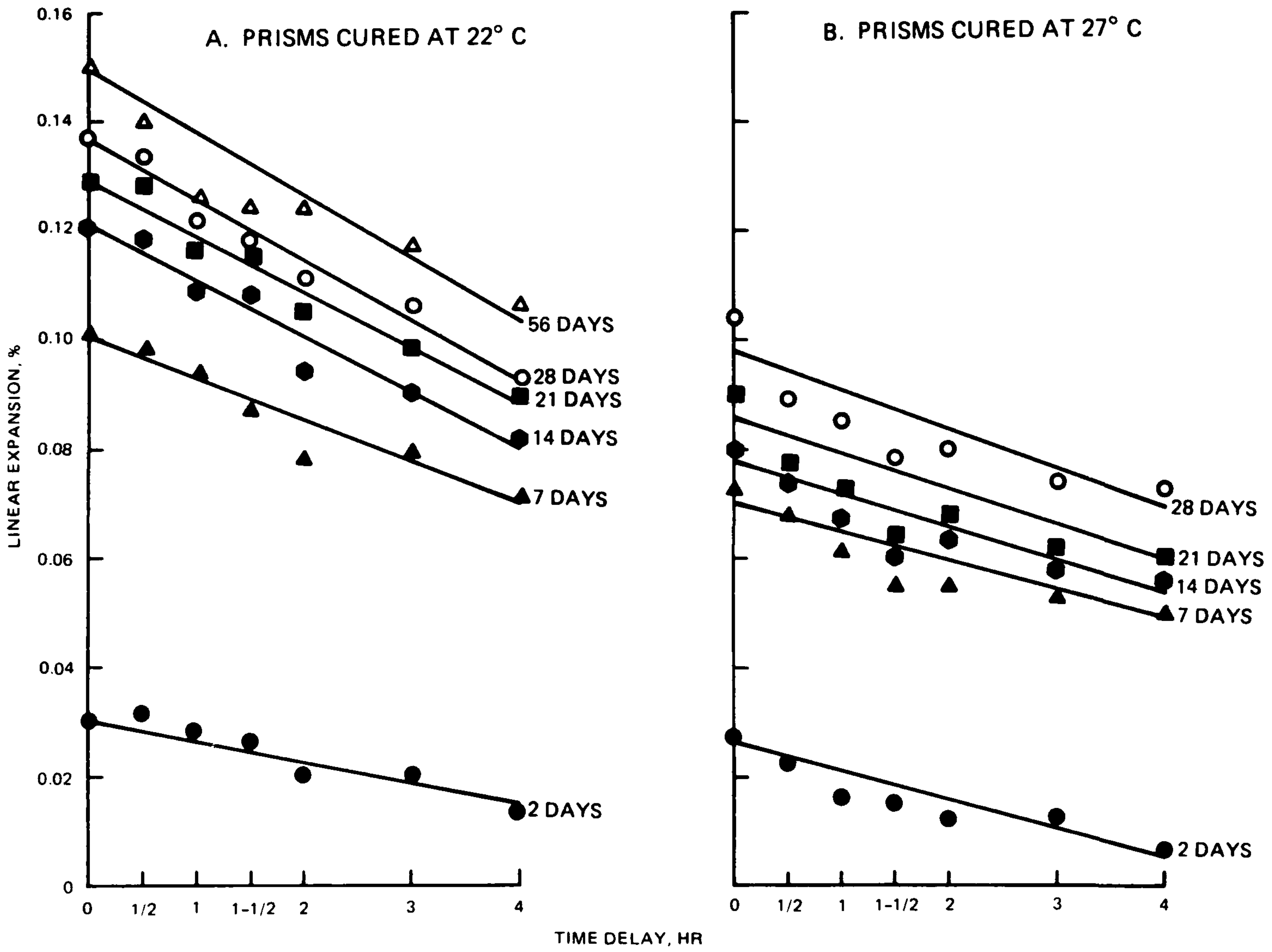

Figure 5. Linear expansion relative to time delay before casting.

APPENDIX A: COMPONENTS OF ESC AND REASONS FOR THEIR USE

1. Most components of ESC have been identified, through several years of development of grout and concrete for the WIPP site, as having characteristics considered beneficial to cement-based materials for use at a radioactive-waste repository in halite rock. Use of sodium citrate in these materials has the shortest history in this research program, beginning with ESC in June 1985. ESC components are:

a. Class H portland cement, an oil-well cement chosen for low surface area, low water demand, sulfate resistance, availability, and long history of successful commercial use.

b. Class C fly ash (ASTM C 618) with high calcium content, supplied by Southwest Public Service. It was chosen for its anticipated contribution to workability and chemical expansion, availability at a reasonable distance from the WIPP site, and uniform composition over time.

c. Cal Seal (a trade name for calcium sulfate hemihydrate) and ChemComp III (an expansive admixture marketed by Master Builders) both were intended to contribute to the expansivity of the concrete, and give favorable results when used with Class H cement and this high-lime fly ash.

d. Granular sodium chloride is added so that the mixture is saturated with sodium chloride, and can be placed in contact with halite (sodium chloride) rock without dissolving the rock at the interface. Secondarily, it contributes to the workability and expansiveness of the mixture.

e. De-Air #1 is a proprietary air-detraining agent of Halliburton Services, Inc. In conjunction with other admixtures used in ESC, this component allows mixing for up to 2 hr while keeping air content below 3%. Prolonged mixing without this agent has caused air contents as high as 17%.

f. The sand and gravel used as aggregates in ESC are commercially available near the WIPP site in southeastern New Mexico, and have had no noticeable deleterious effects on the concrete.

g. Sodium citrate acts as a water-reducing and retarding admixture in this concrete, and is used in lieu of other admixtures for these purposes because of its effects on sulfate phases, and compatibility with a high concentration of sodium chloride.

END

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