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Selection and Durability of Seal Materials for a Bedded Salt Repository: Preliminary Studies

Technical Report

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ABSTRACT

This report details preliminary results of both experimental and theoretical studies of cementitious seal materials for use in a proposed nuclear waste repository in bedded salt. Effects of changes in bulk composition and environment upon phase stability and physical/mechanical properties have been evaluated for more than 25 formulations. Bonding and interfacial characteristics of the region between host rock and seal material or concrete aggregate and cementitious matrix for selected formulations have been studied. Compatibilities of clays and zeolites in brines typical of the SE New Mexico region have been investigated, and their stabilities reviewed.

Results of these studies have led to the conclusion that cementitious materials can be formulated which are compatible with the major rock types in a bedded salt repository environment. Strengths are more than adequate, permeabilities are consistently very low, and elastic moduli generally increase only very slightly with time. Seal formulation guidelines and recommendations for present and future work are presented.

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EXECUTIVE SUMMARY

The preliminary results of studies relating to the durability/longevity of seal materials for a variety of environments expected in a bedded salt repository are detailed. Cementitious seal materials ranging in complexity from simple cement-sand mortars through complex non-conventional calcium chloride-containing cementitious materials, to concretes containing several aggregate types have been considered. This range of cementitious materials provides possible options for seals in strata of different rock types. Such materials may be considered for use as components of shaft and tunnel bulkheads, structural concrete and borehole plugs.

The sedimentary and evaporite rock types encountered in such a salt repository have been grouped as follows: salt strata consisting of nearly pure sodium chloride; various thicknesses of carbonate, sulfate and clay strata members; and finally, silicate rock materials (both well consolidated and poorly consolidated). Each of these strata presents significantly different conditions, giving rise to the requirement that seal materials should be optimized to take advantage of the local host rock chemistry and physical characteristics.

The salt-containing mixtures, both expansive and nonexpansive, have been designed for compatibility with salt-dominated horizons. Moderate to high chloride and/or sulfate activities were characteristic of these mixtures. The permeabilities were consistently very low, and the mechanical properties more than adequate.

Probable limits to stabilities of some of the constituent phases have been set by theoretical and experimental thermodynamic considerations. Results of some diffusion studies suggest a means for determining rates of change under certain circumstances.

For less saline environments a number of mixtures were designed for intrinsic stability and for the potential to generate silicate-cement bonding. Reduction in free lime content (a relatively soluble component), to produce more stable cementitious materials, was achieved by reaction with silica and other pozzolans. As a consequence, and also through use of super water reducers, porosity and permeability were significantly reduced.

Observations on the compatibilities of these formulations in various environments were made by studying contacts with rock materials from a bedded

salt region (either as concrete composites or as rock-cement pair samples).

Clays and possibly zeolites and their composites are also likely to constitute components of shaft, tunnel and borehole seals. Therefore, both theoretical and experimental studies addressed their behavior in brine solutions. Consolidation of salt, though not generally considered as a primary seal, may constitute the logical bulk backfill mechanism for repository rooms.

Results of the experimental program have demonstrated that cementitious materials suitable for all rock types in a salt environment can be formulated. Specific mixtures can be designed with specific properties to take advantage of the chemistry of the host rocks.

Conclusions and recommendations are presented, which give direction for future research.

1 INTRODUCTION

1.1 OBJECTIVE

The acceptance of bedded salt as a viable nuclear waste repository will in part be dependent upon demonstration of the ability to effectively isolate those man-made penetrations, i.e. shafts, boreholes, and tunnels common to the repository site.

Candidate seal materials which show greatest potential from the standpoint of properties, performance and cost effectiveness are cement-based or earth-based; however, prior to utilization of such, a thorough understanding of their behavior in the host environment for extended periods of time is necessary.

Therefore, it has been our objective to formulate and evaluate potential seal materials specific to these environments. The evaluation of the durability and longevity of these materials will play a key role in determining the feasibility of such sites.

1.2 MATERIALS SELECTION, PLACEMENT AND LONGEVITY

From the outset, the objective has been to design seal materials which would be durable and long-lived and at the same time fairly easily emplaceable as well as inexpensive. Various feasibility studies were completed and a number of concepts, although meritorious, were discarded as either too expensive or presenting insurmountable engineering problems. Materials derived from portland cement and its mixtures have been the subject of primary attention, since they are major structural materials, versatile and inexpensive, and are based upon extensive practical experience and development. Complementary to these are clays or earth materials which are valued particularly for their deformability, swelling properties and radionuclide sorption/fixation. Consolidation of salt, which is expected to constitute a major portion of bedded salt repository back-fill, has been discussed in other reports, and is discussed only briefly.

The cementitious seal materials investigated were designed for potential longevity, taking into consideration a number of properties and characteristics: 1) relative intrinsic thermodynamic stability; 2) feasible placement combined with adequate mechanical and physical properties; 3) minimizing permeability and implicitly radionuclide transport; and 4) other features relating to thermodynamics in the specific bedded salt environment, and kinetic factors used to

evaluate potential phase changes. Most of these same factors were also considered in investigations of clay or earth materials.

1.3 ORGANIZATION OF REPORT

The report is divided into sections, each dealing with a different aspect of seal materials. This first section is introductory, dealing with concepts, background, and the longevity problem. Section 2 provides information on characterization of rock from a bedded salt area in SE New Mexico. Section 3 treats specific seal materials containing salt, and additional seal materials which are probably compatible with other horizons and includes studies on concrete, solid-aggregate bonding, and interface characteristics. Section 4 deals with studies on the stability of earth materials in brine environments. Section 5 discusses various aspects of stability and durability. Section 6 provides conclusions and tentative recommendations.

2 REPOSITORY ROCK

2.1 LITHOLOGY

Lithology of the host rock is one of the important factors considered in siting a waste repository (DOE, 1980; Klingsberg and Duguid, 1980). Each potential host-rock type presents a unique set of problems and advantages. Requisite to a study of compatibility between rock and cementitious or other repository-seal materials is thorough characterization of repository rocks. Properties of the host rock will to a great extent determine or constrain the use of certain substances for closure and sealing.

Rocks recovered from subsurface drilling at the Los Medanos site in southeastern New Mexico are the focus of our study. These rocks, although specific to one area of evaporites, provide appropriate examples of the lithologies generally encountered in evaporite strata. The proposed repository horizon in this region is within the Salado formation. This unit is 213 to 610m thick and consists of beds of both relatively pure and clay-rich halite, and potassium-bearing minerals. With a thickness of over 1525m, the total evaporite sequence in this region includes several brine aquifers and complex interbeds of halide and sulfate minerals. Closure of a repository in this sequence will require sealing salt beds, anhydrite beds, aquifers, and carbonate and clastic units interlayered with and overlying the evaporites. The non-evaporite strata have physical and chemical properties very different to those of the Salado bedded salts.

Study of the repository rocks has not been limited to considering their sealing requirements. We have extended our efforts to include use of mined-out host rock as backfill or concrete aggregate. Using the mined-out rock as a component of sealing composites is advantageous for several reasons. Foremost among these are:

- 1) The aggregate itself would enhance compatibility between host rock and seal materials. Such composites might more readily be made to share the best properties of the host strata.
- 2) Using mined-out rock on-site minimizes expensive transportation and handling.

The rock removed from tunnels and shafts may not fulfill the requirements of the plugs at certain horizons. Commercial aggregate available from near the repository site might then be the best choice for maximizing compatibility while minimizing materials handling.

Table 2.1.1 is a summary of the mineralogy and lithology of the core segments studied. Some segments from the Santa Rosa, Dewey Lake, Salado, and Castile formations were crushed and sieved to provide coarse aggregate for cementitious composites. A commercial dolostone aggregate, mined at the surface in this region, was also studied and used. This served the dual purpose of allowing us to test compatibility of salt mixes with dolostone (there are dolostone beds in this sequence although we received no cores of it); and extending the scope of our study to include a near-site commercial aggregate, as mentioned above. Mineralogies and brief petrographic descriptions of the gravels used are given in Table 2.1.2.

2.2 CHARACTERIZATION

Many standard methods of characterization were used for core segments and aggregate. These tests and analyses are briefly described below, and the resulting data are presented in Tables 2.2.1 through 2.2.3. Additional detail of the methods of rock characterization was published previously (Wakeley et al., 1981a). Some methods were appropriate only to aggregates; others to rock as either host or aggregate.

X-ray diffraction was employed to identify the minerals present in all core segments (three or more samples per core) and of the specific gravels used in composites. In addition, water-insoluble residues were isolated from many segments, and analyzed by x-ray diffraction. Isolation of these residues was especially useful for identifying accessory components in halite rocks, where NaCl preponderates whole-rock diffraction patterns. This procedure also allowed us to determine the percentage of soluble salts in different horizons (Table 2.2.1).

Clay minerals isolated by settling techniques (Folk, 1968) from segments of Dewey Lake and Salado core were treated with ethylene glycol. This method expands the lattice of expandable clays, causing an identifiable peak shift on diffraction patterns. Special x-ray studies of the clay-sized fractions of these rocks revealed the presence of chlorite and mixed-layer illite/smectite in Dewey Lake mudstone; and mixed-layer chlorite/smectite (corrensite) in some beds of the Salado evaporites. The hydrophilic nature of these expandable clays foretells a potential for absorbing water from cement pastes (discussed in Section 3.5). Section 4 includes other considerations of clay minerals.

Additional details of the mineralogies and fabrics of these rocks derived from study of petrographic thin sections with an optical microscope and polarized

Table 2.1.1. Stratigraphy, lithology, and mineralogy of Los Medaños core segments.

Core and Depth	Formation	Apparent Lithology	(XRD) Mineralogy*	Remarks
AEC-8 065-067	Santa Rosa	sandstone	Qu Do Il Ha Ch He	coarse and porous; dolomite cement
068-070		sandstone	Qu Do Il Ha Ch(?) He(?)	
564-566	Dewey Lake	gypsiferous mudstone	Qu Gy Do Ha Mo Ch Il He	green nodules, and gypsum partings
618-619		gypsiferous mudstone	Qu Il Do Ch He Gy	
682-684	Rustler	coarse gray anhydrite	An Ha Do	very coarse gypsum locally
976-977		gray siltstone	Qu Ha An Ma Ch Il	unconsolidated
1013-1015	Salado	silty halite	Ha Qu An Do (+clays)	very "dirty" in lower part
[1065]		[mixed salts]	(blocks from recovered core segment -Potash Zone)	
AEC-7 1685-1687		silty halite	Ha Qu (+clays)	
1688-1690				
1691-1692				
2998-3000	Castile	fine white anhyd.	An Ma	
3003-3005		anhydrite and clear halite	An Ha Do Il	very light color, "clean"
3006-3008		halite	Ha Do	coarse clear xtls
3011-3013		halite and anhydrite	Ha An Ma	very light color
3014-3015		anhydrite with halite stringers	An Ha	white
3016-3018				
3924-3925		dark gray anhydrite	An Ha Ca	fine-grained, massive
3928-3930			An	
3933-3935			An	
3937-3940			An	
3942-3944			An Ca	
3947-3949			An	
3952-3954			An Ca	
3957-3959			An Ca	

*Mineral Abbreviations:

Qu - quartz	Do - dolomite	Gy - gypsum	He - hematite
An - anhydrite	Il - illite	Mo - montmorillonite	Ca - calcite
Ha - halite	Ch - chlorite	Ma - magnesite	

Table 2.1.2. Mineralogy and lithologic descriptions of gravels.

Rock Type	Depth	Formation	Mineralogy (XRD)*	Description (optical microscopy)
Dolostone	mined at surface	Dark Canyon	Do,Qu,Ca,He	(commercial gravel; no lithologic study)
Anhydrite	918 m (3013 ft)	Castile	An,Ma,Ha	granular texture, non-porous; remnants of massive halite
Mudstone	172 m (563-4 ft)	Dewey Lake	Qu,Gy,Do,Ha,Mo,Ch,Il,He,Sm,I/S	clay matrix with fine-grained quartz, chert, rock fragments; authigenic smectite filling fractures
Sandstone	20 m (66 ft)	Santa Rosa	Qu,Do,Il,Ha,He,Ch	dolomite-cemented quartz grains and rock fragments; Fe stain in cement; coarse and porous
Halite	515 m	Salado	Ha,Qu,Co	massive blocky halite with inclusions; some amorphous Fe-stained areas; traces of gypsum locally along crystal boundaries

*Mineral Abbreviations:

Qu - quartz	Ha - halite	Il - illite	Mo - montmorillonite	Sm - smectite
An - anhydrite	Do - dolomite	Ch - chlorite	Ma - magnesite	Ca - calcite
Co - corrensite	I/S - mixed layer illite/smectite	Gy - gypsum	He - hematite	

transmitted light. Some notable petrographic features of four rock types are listed in Table 2.1.2. Differential scanning calorimetry (DSC) and thermal analyses (TGS) confirmed mineral identification via other methods (Table 2.2.2).

Compressive strength was measured for core segments of three rock types: sandstone (Santa Rosa) and mudstone (Dewey Lake), each about 20 MPa; and anhydrite (Castile), >80 MPa. Having been cored twice, once when recovered from the subsurface and again in preparation for testing, the rocks had been subjected to multiple episodes of physical shock. Therefore we assume that these measured values indicate lower strengths than field performance would show.

Permeability of the dolostone, anhydrite, sandstone, and halite were measured to various media at pressures of 0.69 to 4 MPa. Measured permeability values are reported in Table 2.2.3.

Specific gravity and absorption (ASTM C-127) and packing density were determined for the commercial dolostone gravel and coarse aggregate of the same size range (12.7 x 4.75-mm) derived from sandstone and anhydrite core segments (Table 2.2.4). Pore sizes of samples of sandstone, anhydrite, and salt aggregates were determined by mercury (Hg)-intrusion porosimetry (Table 2.2.5). The very large pores of the sandstone were measured at low pressure; no pores were intruded at >15.0 psia. This porosity agrees well with the low specific gravity, low strength, and high permeability measured for this poorly cemented sandstone. The very low permeability of the anhydrite, as well as its high strength, are compatible with very small pore sizes. All measurements assume an Hg wetting angle of 140°.

The brine used most frequently for curing, and in some composites as the mixing water, is based on the average composition of water in which Salado bedded salt has been dissolved to saturation (WIPP-B, MRL number E17). These components in 1 liter of brine are summarized in Table 2.2.6. We used other types of brine in some specialized experiments. These are presented in discussions where appropriate.

Table 2.2.1. Data from separation of water-insoluble residues, Los Medaños core segments.

Formation	Core Segment Depths, Ft	Water-Insoluble Minerals, wt%	Mineralogy ³ (XRD)	No. of Samples Tested
Rustler	682-977	84 to 92	Qu, Il, Mo, Ma, He	5
Salado ¹	1013-1015	3	Do, An	1
	1685-1692	2 to 28	Qu, Il, Ch, Ma, Gy, Do	8
Castile ²	2998-3018	for halite 0.15 to 0.26 for anhydrite 83 to 92	An, Ma	10
	3924-3959	86 to 96	An	10

¹Source of halite aggregate used in this study.

²Source of anhydrite aggregate.

³See Table 2.1.1 for key to mineral abbreviations.

Table 2.2.2. Mineralogic changes determined by DSC and TGA
for rocks and grouts.

sample	change indicated
<u>A. DSC - SCANNED FROM 52 TO >450°C</u>	
dolostone	no peaks in range of scan, gradual energy increase (= endotherm)
sandstone	same
mudstone	energy input 90-130°C from dehydration of clays and gypsum
halite/mixed salt	energy input 100-115°C dehydration of clays many small changes suggest the presence of blodite, leon- ite, polyhalite, but range of scan inadequate for posi- tive identification
anhydrite	gradual energy increase (= endotherm) 270° to 400°C (end of scan)
<u>B. TGA - WEIGHT LOSS 25 TO 1000°C</u>	
anhydrite	3.3% weight loss (no gypsum indicated) break in slope ~550°C, clay dehydration
dolostone	1.9% weight loss before dolomite decomposition 11.6% weight loss 700° to 840°C with decomposition of dolo- mite 26.3% weight loss 840° to 916°C, no break in slope to indicate calcite

Table 2.2.3. Measured permeability values for evaporite-site rocks.

Rock Type	Test Medium	Permeability	
		(darcy)	(cm sec ⁻¹)
dolostone	deionized water	6×10^{-8}	6×10^{-11}
anhydrite	deionized water	$< 10^{-8}$	$< 10^{-11}$
sandstone	brine*	10^{-2}	10^{-5}
bedded salt	nitrogen	2×10^{-7}	2×10^{-10}

*Simulated WIPP-B brine. See Table 2.2.6.

Table 2.2.4. Specific gravity and absorption and packing density.

Gravel Type	Bulk Specific Gravity	Absorption, %	Packing Density, %
dolostone	2.74	0.5	48.3
sandstone	1.99	11.50	41.5
anhydrite	2.91	0.4	44.6

Table 2.2.5. Pore sizes of samples of sandstone, anhydrite, and salt aggregates.

Gravel Type	Size Range	Mode(s)
sandstone	1 to 50 μm	11.5 μm
anhydrite	33 to 2000 $\text{\AA}$	75 $\text{\AA}$
halite	7 to 35 μm	7.75, 8.25, 11.5 μm

Table 2.2.6. Composition of WIPP-B brine (E17)
(grams/liter).

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	0.016
$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$	0.045
NaHCO_3	0.13
KBr	0.045
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.101
CaCl_2	2.44
NaBr	0.474
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	11.46
NaCl	292.25

3 CEMENTITIOUS SEAL MATERIALS

A series of cementitious mixtures has been designed for potential longevity. These mixtures are blends formulated using four guiding principles.

1) A useful material needs to possess intrinsic thermodynamic stability. Lower free energy states and greater stability are caused in portland cements by reducing the amount of the relatively soluble free Ca(OH)_2 which remains as a by-product of the hydration of the calcium silicate components. Adding "pozzolans"* or silica-rich materials such as blast furnace slag or fly ashes accomplishes this. Thus the nature of pozzolanic reactions is important.

2) Feasible placement must be combined with adequate mechanical and physical properties. High strength is usually associated with durability. Strength increases when the remaining Ca(OH)_2 reacts with additional silica to produce more calcium silicate hydrate (C-S-H), the strength-producing component in hydrated cement. Reducing the water content of a mix also generates strength, by reducing residual porosity. Strength is inversely related to the amount of water added to the mixture. A conventional cement paste or mortar has a water/cement ratio in the neighborhood of 0.4 to 0.5. If the amount of water is reduced by effective use of water-reducing agents, the water requirement of a mixture of the same consistency can be reduced to 0.25 to 0.3g per 100g cement. This results in a substantial increase in strength.

3) The means for transport of water and/or radionuclides through seal materials can be reduced by decreasing the porosity and permeability of the final product. One way that this can be done is by using super water reducers and fine-grained pozzolanic materials.

4) Other features relating to stability in a particular bedded salt environment, and kinetics of phase changes are important. The stability of calcium aluminate components of cement, and their effects on the durability of a cement seal material is influential on the materials properties. Formation of ettringite, an Aft phase (aluminate/ferrite tri-substituted) causes the cement to expand. If Aft phases form after the concrete has hardened in an unrestrained state, the material may eventually lose strength through excessive expansion. Controlled expansion of this nature, however, is usually desirable in confined curing, such as in an underground borehole or shaft, whereby a seal which is both chemical and mechanical is produced.

*See Section 3.2.2 for definition.

The special properties of expansive phases made it important to study the relationship between AFt phases and AFm phases [aluminate/ferrite, mono-substituted, calcium monochloroaluminate (Friedel's salt), and calcium monosulfoaluminate]. Long-term curing of normal cement compositions converts AFt to AFm phases. This conversion could affect the volume stability of a mixture long after emplacement, and understanding or preventing it by compositional change therefore is important.

Studies of the chemistry of various cementitious mixtures are necessary in considering longevity. Long-term studies are under way, but their results are of necessity delayed. The approach we have adopted is dealing with the mechanisms of reaction within the cementitious materials. Important information from theoretical data will be combined with results from short, intermediate and long-term experiments, and those from accelerated tests to determine reaction mechanisms and evaluate kinetic factors. Various pozzolans have been investigated, and many types of reactions appear to have similar mechanisms. The kinetics of these reactions differ, however.

Two major aspects of the chemistry of the hydration process are addressed. These are: the pozzolanic reaction; and the stability of various aluminate phases, especially their bearing on the long-term behavior of a cement plug. Mechanistic studies should in part determine longevity, and will be followed by very long-term experiments with selected cementitious materials. Concurrently, we are investigating the thermodynamics of critical reactions and phase transitions. These studies are an additional source of information with a bearing on longevity.

3.1 SALT-CONTAINING SEAL MATERIALS AND DERIVATIVE MIXTURES

3.1.1 Introduction

Characterization of a 17-year-old borehole plug (Wakeley et al., 1981b) recovered from bedded evaporites demonstrated that salt-saturated cements were viable plugging materials for salt-dominated strata. Previous work at the Waterways Experiment Station (WES), Sandia (Gulick et al., 1980a), and The Pennsylvania State University (PSU) (Scheetz et al., 1980) on borehole sealing formulations also showed salt-containing cements to have adequate strength development and generally to be suitable for their intended use. Experimental work at WES led to the development of a formulation known as DHT-1. This was later modified by Dowell and resulted in the basic formulation known as BCT-1F (Gulick et al., 1980b). Although never used in field tests, the mixture (designated PSU #79-071) was

included as one of the test formulations in the present study. This mixture led to two derivative formulations BCT-1FF (PSU #79-091) and PSU "salt-free BCT-1F" (PSU #79-08). Subsequently, a new intermediate formulation (PSU #80-081), the so-called PSU/WES mixture, was also investigated. In addition to these formulations, work at PSU also pursued cement formulations containing salt, fly ash, and condensed silica fume (PSU #81-030 and 81-091).

All mixtures were designed to be expansive, and thus contained an expansive agent or additional calcium sulfate which would promote the formation of ettringite and encourage expansion. In theory, expansion would take up any space generated by the dissolution of salt by the plugging formulation and also restress the wall rock and thus prevent annular cracking in the borehole due to stress relief.

3.1.2 Viscosity

As a first step in designing and evaluating the suitability of various mixtures, rheologic properties were measured on fresh mixtures (Asaga and Roy, 1980). Shear stress was recorded as a function of shear rate and apparent viscosities were recorded. Results for the final mixtures used are given in Table 3.1.1. The mixtures BCT-1F (79-071), BCT-1FF (79-091), and PSU/WES (80-081) were very fluid, whereas mixtures 81-030 and 81-091 had higher apparent viscosities. Each mixture was susceptible to shear thinning with time and exhibited near plastic or pseudoplastic behavior. All mixtures exhibited a yield point, although the values for 79-071 and 80-081 were very small, and nearly insignificant.

3.1.3 Formulations

Table 3.1.2 gives the formulations of the six mixtures. The first of these mixtures (79-071) is nearly salt-saturated, containing 29.5g of NaCl per 100g of mixing water. Its formulation and subsequent testing is well documented elsewhere (Gulick et al., 1980a). The mixtures 79-091, 79-080, and 80-081 (PSU/WES) were derivatives of the original BCT-1F mixture, in which the salt content was reduced to zero (79-091, and 79-080) or cut to about 14g NaCl per 100g mixing water (80-081). This latter mixture, its formulation and testing is well documented (Roy et al., 1980; Roy et al., 1981). For the sake of brevity, the reader is again referred to these outside sources, for more complete data.

The PSU salt-free "BCT-1FF" samples (79-080) were mixed according to API

Table 3.1.1. Apparent viscosity (cP)[†] measured at 117 sec⁻¹
shear of salt and salt derivative mixtures.

mixture	time, hrs					
	0.11	0.5	1.0	2.0	2.5	5.0
79-071	180	300	460	---	665	1215
79-091	106	273	637	1042	---	---
79-080	---	---	---	---	---	---
80-081	158	203	206	322	---	---
*81-030	765	1000	1331	---	---	---
*81-091	599	843	1108	---	---	---
*81-030 } viscosity at 132 sec ⁻¹ . 81-091 }				[†] 1 cP = 10 ⁻³ Pa·s = mPa·s.		

Table 3.1.2. Formulations of salt-containing and derivative mixtures (grams).

	Code No.*	mixture					
		79-071 BCT-1F	79-091 BCT-1FF	79-080 PSU salt free	80-081 PSU/WES	81-030	81-091
class H cement	H-7, H-8	62.42	67.95	67.95	65.83	65.75	65.80
Litepoz	B15, B26	21.09	22.96	22.95	22.17	--	--
gypseal	A31	--	--	--	8.07	4.04	4.04
low lime fly ash	B25	--	--	--	--	11.12	11.10
ferrosilicon dust	B31	--	--	--	--	15.16	--
Ohio fume	B27	--	--	--	--	--	15.14
C109 sand	C15	--	--	--	--	49.31	49.24
NaCl	B8, B16	8.14	--	--	3.92	3.93	3.92
expansive additive A	A29	8.35	9.09	9.10	--	--	--
D-65	A28	0.25	0.27	0.22	1.06	--	1.0
D-47	A27	0.02	--	0.02	0.02	--	--
Mighty 150	A3, A36	--	--	--	--	1.36	--
water	E01, E11	27.56	25.07	24.75	28.46	29.89	30.00
w/c		0.44	0.37	0.36	0.43	0.45	0.46
w/reactive solid		0.27	0.25	0.25	0.28	0.30	0.30

*Multiple listings signify different batches of the same material. Differences in properties are small to insignificant. Compositions are given in Appendix A.

procedures, molded in glass vials and cured at temperature. The samples were broken free from the vials at 24 hours and curing continued in WIPP-A brine.* The BCT-1FF formulation was used in permeability and bond strength experiments and not tested for compressive strength, etc., as was the case for all other mixtures. It too was mixed according to API procedures.

Mixtures 81-030 and 80-091 included different pozzolanic materials and the amounts of salt and expansive additive were proportionally smaller than in previous mixtures. Also, these later mixtures contained ASTM C 109 sand and thus had the properties of dense grouts or mortars. Compositions of the starting materials are given in Appendix A.

Samples were cast as either 25.4-mm by 50.8-mm long cylinders or 50.8-mm cubes, cured at temperature, demolded at 24 hours and allowed to cure in saturated $\text{Ca}(\text{OH})_2$ solution, saturated $\text{Ca}(\text{OH})_2$ plus NaCl solution, or brine solution until the time of test. In addition, sample 81-091 was also cast in Teflon-coated glass vials which were cured in saturated relative humidity at specified temperatures. These were partially restrained low-water-content samples, used for microhardness and permeability determinations.

3.1.4 Results

Compressive Strength. Strength data are given in Table 3.1.3. The BCT-1F mixture (79-071) was cured at three temperatures (27°, 60°, and 90°C) as a function of time up to 180 days. These samples were cast as cylinders, nominally 25.4-mm by 50.8-mm long. Since the mixture was nearly saturated with salt, it was subsequently cured in a saturated NaCl brine solution also saturated with $\text{Ca}(\text{OH})_2$. Mixture (80-081) was cast as 50.8-mm cubes and cured in saturated $\text{Ca}(\text{OH})_2$ solution at one temperature (38°C).

The development of strength for the PSU/WES mixture (80-081) was nearly linear up to 56 days, after which time unrestrained expansion of the cubes caused the samples to weaken and strengthen in a cyclic pattern up to 365 days. The strength development for the BCT-1F cylinders was linear (based on only two points), but only up to 28 days, after which the same pattern of weakening and regain of strength is repeated. The rates of strength development of the two mixtures are similar, but setting of BCT-1F (79-071) was retarded.

*WIPP-A brine (PSU #E07): 11.14 wt % MgCl_2 , 8.98 wt % NaCl, 4.77 wt % KCl, 0.36 wt % MgSO_4 , 0.14 wt % CaCl_2 .

Table 3.1.3. Compressive strength of salt-containing and derivative mixtures (MPa).

specimen age (days)	cure temp. (°C)	mixture					
		79-071	79-091**	79-080	80-081	81-030	81-091
3	27						49.3
	35						
	38				50.5		
	45						63.7
	60						79.1
	90						76.1
7	27			70.8		37.3	53.4
	35			85.0			
	38				65.2		
	45					61.5	77.5
	60			90.6		64.9	76.9
	90			51.6		58.2	61.9
14	27	49.4		57.2		41.8	
	35			121.0			
	38						
	45					66.2	
	60	61.4		72.6		60.6	
	90	45.9		43.4		46.8	
28	27	63.4		87.0		79.3	77.8
	35			110.6			
	38				91.7		
	45					85.6	91.1
	60	65.5		102.2		88.2	80.0
	90	60.2		52.3		96.9	83.1
56	27	57.21		85.9			64.6
	35			118.8			
	38				107.7		
	45						74.9
	60	48.3		123.7			61.4
	90	35.8		54.4			84.7
90	27	79.0		122.1			23.8
	35			81.2			
	38				61.5		
	45						28.3
	60	68.0		97.0			26.2
	90	68.7		48.0			27.0
180	27	78.5					71.0
	35						
	38				93.2		
	45						76.1
	60	78.5					86.3
	90	61.1					76.8
365	38				83.2		

*Data set believed incorrectly recorded scale on chart.

**No data.

The compressive strength data for mixture 79-080 (PSU salt-free) also show relative consistency in the strength increases in the temperature range 27°- 60°C, with generally lower strengths of samples cured at 90°C. These salt-free samples when cured in WIPP-A brine after demolding at 24 hours would permit some diffusion of chlorides, in particular, into the samples.

Compressive strength development of mixtures 81-030 and 81-091 is very similar to the development of strength by 79-071, 80-081 and 79-080. However, the 81-030 and 81-091 samples cured at 90°C have consistently higher relative strengths than the mixtures in sets 79-071, 80-081 and 79-080.

Microhardness. Data for the above mixtures are given in Appendix B. These values are not directly proportional to strength, but samples having low strength have low microhardnesses.

Bulk Density. These measured values for all mixtures are given in Table 3.1.4. The slight decrease in bulk density of the BCT-1F mixture (79-071) with time may reflect the expansion of the sample. Changes in bulk density of the PSU/WES mixture (80-081), follow a pattern similar to compressive strength and apparently are related to the expansive mechanism. The data for mixture 81-091 except for one or two anomalies remain relatively high. The data for mixture 81-030 are relatively constant to 28 days, the last time measured.

Permeability. Limited data are available for permeability of mixtures 79-071, 79-091 and 79-080. Data for confined curing are included in section 3.5 on composite studies.

Permeabilities of the PSU/WES mixture (80-081) to water are given in Table 3.1.5. Data for three types of samples are presented. The permeabilities for the unrestrained samples cured at 38°C in Ca(OH)_2 solution show greater variability in flow than do the restrained (steel ring and sealed vial cured) counterparts. Apparently this is related to the expansion of the sample, which is unrestrained in one case, and partially restrained in the others (steel ring, lesser restraint, sealed glass vial). Since down-hole conditions are more nearly represented by the restrained condition and the presence or absence of excess water does not appear to be of concern, assuming no interface difficulties, this would suggest that expected permeabilities should be in the range of $<10^{-8} \text{ } \mu\text{m}^2$ ($<10^{-11} \text{ cm sec}^{-1}$ equivalent hydraulic conductivity or 10^{-8} darcy).

Table 3.1.4. Bulk density of salt-containing and derivative mixtures.

specimen age (days)	cure temp. (°C)	mixture					
		79-071	79-091**	79-080	80-081*	81-030	81-091
3	27						1.92
	35						
	38				0.006		
	45						1.93
	60						1.90
	90						1.92
7	27			2.15		1.85	1.90
	35			2.23			
	38				0.004		
	45					1.85	1.92
	60			2.54		1.87	1.89
	90			2.11		1.86	1.91
14	27	2.11		2.09		1.83	
	35			2.28			
	38						
	45					1.87	
	60	2.09		2.09		1.85	
	90	2.10		2.08		1.85	
28	27	2.07		2.19		1.84	1.94
	35			2.20			
	38				0.016		
	45					1.86	1.92
	60	2.11		2.20		1.85	2.24
	90	2.11		2.21		1.84	1.93
56	27	2.09		2.12			1.83
	35			2.06			
	38				0.028		
	45						1.83
	60	2.15		2.14			1.50
	90	2.07		2.06			2.11
90	27	2.05		2.12			1.83
	35			2.15			
	38				0.018		
	45						1.95
	60	2.06		2.11			1.84
	90	2.03		1.98			1.84
180	27	1.99					1.91
	35						
	38				0.006		
	45						1.90
	60	1.97					1.94
	90	2.00					1.97
365	38				0.005		

*Change in density.

**No data.

Table 3.1.5. Permeability to water of 80-081 expansive cement cured at 38°C (darcys, μm^2).

	unrestrained	restrained		
cure time (days)	Ca(OH) ₂ solution cure	50.8 mm cast in steel rings	glass vial cure	
3	<div><10⁻⁸</div>	<div><10⁻⁸</div>	<div><10⁻⁸</div>	
7				
28				
56	9.7x10 ⁻⁵			
90	<div><10⁻⁸</div>			
180				
365	1.8x10 ⁻⁶ *			

*Sample had an observable pre-existing crack when tested.

Permeabilities of mixtures 81-030 and 81-091 to water are given in Table 3.1.6. Although the samples 81-030 and 81-091 differ only slightly in composition, the permeability data do not attest to this fact. The 81-030 mixture cured in $\text{Ca}(\text{OH})_2$ solution and the 81-091 glass vial cured samples shows very low permeabilities at nearly all times and temperatures. Some anomalies in test procedures used with 81-091 cured in $\text{Ca}(\text{OH})_2$ solution prevent complete interpretation of the latter data. The permeabilities of all the samples were very low at 180 days.

X-Ray Diffraction Data. Data for mixtures 79-071 (BCT-1F) and 80-081 (PSU/WES) are given in Table 3.1.7. Apparently, the phases which are developed are related to the concentration of salt in the mixture, curing temperature, and curing environment. In nearly salt-saturated BCT-1F [cured in $\text{Ca}(\text{OH})_2 + \text{NaCl}$] the dominant aluminate phase at 90°C is Friedel's salt $[\text{Ca}_3\text{Al}_2\text{O}_6 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}]$, as might be expected. However, at 27°C ettringite and Friedel's salt coexist at 28 to 56 days, while ettringite is abundant at 90 to 180 days. In the PSU/WES (80-081) mixture, those unrestrained samples cured at 38°C in saturated $\text{Ca}(\text{OH})_2$ solution contained ettringite at all times up to one year, the chloride possibly leached out. In contrast, those samples cured in glass vials in a saturated humidity environment, first developed ettringite, then at 28 days to one year, also contained coexisting Friedel's salt. Apparently the substantial chlorine activity, the lack of $\text{Ca}(\text{OH})_2$ and abundant water moderated ettringite ($\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$) formation.

X-ray diffraction data for mixture 79-080 (PSU salt/free/"BCT-1FF") are given in Table 3.1.8. The brine curing solution has interacted with the sample and changed its phase chemistry. Some liberty has been taken with the data in order to reduce it to the simple terms shown in the table. Basically, the MgCl_2 in the solution must have diffused into the sample and produced $\text{Mg}(\text{OH})_2$ and CaCl_2 , the latter reacting to produce Friedel's salt. In addition, the chloride activity of the cement was also elevated by the NaCl present in the brine. This high activity is instrumental in changing the ettringite to Friedel's salt. Although not always present, $\text{Mg}(\text{OH})_2$ apparently formed in preference to $\text{Ca}(\text{OH})_2$. A problem which made interpretation more difficult was the depth of penetration of the solution, the resulting degree of conversion and the random sampling of the compressive strength samples subsequently used

Table 3.1.6. Water permeability of mixtures 81-030 and 81-091 as a function of temperature and curing conditions (darcys $\approx \mu\text{m}^2$).

time (days)	temperature, °C			
	27°	45°	60°	90°
<u>81-030: class H cement + silica fume + class F fly ash</u>				
14	3.4×10^{-8}	$<10^{-8}$		full flow
28				
<u>81-091: class H cement + silica fume + class F fly ash</u>				
saturated $\text{Ca}(\text{OH})_2$ cure	3	10^{-8}		
	7	full flow*		
	28			
	56	$\sim 10^{-5}$		
	90	$\sim 10^{-7}$		$<10^{-8}$
	180			
sealed glass vials	3	$\sim 10^{-7}$		
	7	full flow		
	28	full flow		
	56	$\sim 10^{-6}$		
	90	$<10^{-8}$		
	180			

*Excessive pressures (1000 psi) may have broken the samples. Repeat testing of different samples at 650 to 680 psi at 7, 28, and 56 days resulted in no flow which is equivalent to a permeability of $<10^{-8}$ darcy. Apparently the vial-cured samples were less prone to cracking due to the suppression of expansive character by the lack of excess water.

Table 3.1.7. X-ray diffraction data for expansive cement pastes containing varying amounts of salt.

79-071: BCT-1F			
time (days)	temperature, °C		
	27°	60°	90°
14	residual cement Ca(OH) ₂ quartz C-S-H		
28	residual cement Ca(OH) ₂ quartz		
56	ettringite Friedel's salt C-S-H		
90	residual cement Ca(OH) ₂ quartz ettringite		
180	C-S-H		

80-081: PSU/WES		
time (days)	38°C curing	
	Ca(OH) ₂ cure	glass vial cure
3	residual cement ettringite Ca(OH) ₂ quartz C-S-H*	residual cement ettringite Ca(OH) ₂ quartz C-S-H
7		
28		
56		residual cement ettringite Ca(OH) ₂ quartz
90		Friedel's salt C-S-H
180		
365		

*CaCO₃ sometimes detected in all of these samples.
Apparently these are extremely susceptible to carbonation.

Table 3.1.8. X-ray diffraction data for derivative mixtures.

time (days)	temperature, °C			
	27°	35°	60°	90°
<u>79-080: PSU salt-free ("BCT-1FF")</u>				
7	residual cement ettringite quartz Friedel's salt Mg(OH) ₂ C-S-H			
14				
28	residual cement ettringite quartz gypsum Mg(OH) ₂ * C-S-H			residual cement Friedel's salt quartz Mg(OH) ₂ C-S-H
56				
90	residual cement ettringite Friedel's salt Mg(OH) ₂ C-S-H quartz gypsum			residual cement Ca(OH) ₂ quartz gypsum C-S-H
180				
360				

*The Mg(OH)₂ apparently forms in the following fashion: $\text{Ca(OH)}_2 + \text{MgCl}_2 \rightarrow \text{Mg(OH)}_2 + \text{CaCl}_2$ liberating the CaCl₂ to take part in forming Friedel's salt (C₃A·CaCl₂·12H₂O) or AFt-substituted phases.

for x-ray diffraction work. The results, however, illustrate the influence of the curing solution (and hence, host rock chemistry) on the results of various tests and on the potential long-term behavior of the seal once emplaced in a geologic formation.

X-ray diffraction data for samples 81-030 and 81-091 [cured in sat. $\text{Ca}(\text{OH})_2$] are presented in Table 3.1.9. Ettringite apparently forms at lower temperatures in these mixtures, but above 60°C , at least in mixture 81-091, some sulfate is present as gypsum which, with time, seems to disappear altogether. Both the gypsum (which is secondary in nature, formed from $\text{CaSO}_4 \cdot 1/2\text{-H}_2\text{O}$ and the ettringite are potentially expansive. Mixtures 79-091 data (BCT-1FF) are not available. Only bond strength and permeability were determined for this material.

SEM Investigation. In an attempt to better interpret the mechanical and phase data, a series of scanning electron microscope images were taken for mixture 80-081 (PSU/WES). Representative images are presented in Figures 3.1.1 and 3.1.2 for 7- and 90-day vial-cured samples, respectively.

Prisms or needles of ettringite were most commonly observed having grown in pockets or void spaces in the cured grout samples (Figure 3.1.1B). These were most easily located in the youngest sample and were clearly evident at 3, 7, and 28 days. At ages beyond 56 days, with increasing completeness of hydration, these occurrences became scarcer, although some prisms could be found (see, for example, Figure 3.1.2--90-day results). Some ettringite-like material is observed at 180 days, but its habit is more massive. This latter massive material may be the more common form of ettringite. It is more difficult to recognize, but may be responsible for the abundance of ettringite in the x-ray diffraction pattern.

Fly ash spheres in various states of alteration were observed throughout the 365-day curing of the paste and are described in Roy et al. (1981) and Grutzeck et al. (1981b).

Densification of the paste seems to occur with time. Pockets of ettringite are being filled or replaced by other material. Fly ash spheres are hydrating and becoming part of the matrix material. In broken samples the fly ash spheres act as centers of weakness and therefore are involved in the breaking process, the glass-to-hydration product rims being a weak link in the younger pastes. In older pastes the fly ash spheres are hydrated and incorporated into the matrix, becoming less involved with the breaking process. In specimens cut with a diamond saw the void features which are so common in

Figure 3.1.1. SEM images of 7-day cured 60°C vacuum-dried shell-vial samples of mixture 80-081.

- a) Overall view of typical surface at 1060X showing fly ash spheres, fly ash voids and dense matrix. A collapsed fly ash shell with internal crystallites is visible.

- b) Ettringite detail in two hexagonal gypsum casts and dense matrix material. These features may be precursors of Hadley grains (5050X).

- c) Ettringite growing in a void space surrounded by C-S-H type matrix material (5050X).

Figure 3.1.2. SEM images of 90-day "as-cured" shell-vial cured samples of mixture 80-081.

- a) Overall view of typical surface at 1050X showing fly ash spheres and voids in various states of hydration. Some ettringite in pockets and massive matrix is also evident.

- b) Detail of fly ash and ettringite (3070X).

- c) Detail of fly ash/matrix contact. Fly ash sphere surface is on left. Blade-like crystals in center of photograph are typical hydration products of the glassy fly ash sphere (30700X).

Table 3.1.9. X-ray diffraction data for silica and class F fly ash-substituted cements.

time (days)	temperature, °C			
	27°	45°	60°	90°
<u>81-030: class H cement + ferrosilicon dust + class F fly ash</u>				
7	quartz residual cement Ca(OH) ₂ Friedel's salt (tr.) C-S-H (tr.) (a)	quartz residual cement ettringite C-S-H (a)		quartz residual cement C-S-H (a,b)
28				
(a) traces of aluminate hydrates and/or gehlenite hydrate (b) trace amounts of anhydrite sometimes present				

<u>81-091: class H cement + ferrosilicon dust + class F fly ash</u>				
3			quartz remnant cement ettringite gypsum C-S-H	
7				
28				
56	quartz remnant cement ettringite C-S-H [†]	quartz remnant cement ettringite gypsum C-S-H		quartz remnant cement gypsum C-S-H
90				
180			quartz remnant cement C-S-H ± gypsum	
360				

[†] a duplicate sample at 38°C hydrated for 7 days showed slight evidence of gypsum.

broken samples are generally lacking. Cross sections of fly ash spheres show hydration in various stages, and the hydration rim is continuous from the glass surface to the matrix. There is very little evidence to indicate a gap of any kind between glass spheres and hydration rim. The matrix is very dense and the actual void features attributed to the presence of fly ash spheres are few.

A similar SEM study was made for mixture 81-091 (Grutzeck et al., 1981b). Representative SEM images are presented in Figure 3.1.3. Views (a) and (b) show a generally dense matrix, presumably due to the silica fume and partially reacted fly ash spheres typical of 3 days. By 28 days (view c) the fly ash is significantly reacted. Bonding to the matrix is stronger and features, showing breakage of the fly ash in cross section, are more common. At 90 days (view d) the matrix is still very dense and fly ash spheres are more highly reacted. Views (e) and (f) at 180 days re-emphasize that some fly ash spheres are fully reacted (view e) while others are still in the process of reaction. In both cases at 180 days bonding of the fly ash to the matrix is very good (view f), which correlates well with the low permeabilities measured.

Other Tests. Early volume change measurements (Setter and Roy, 1978; Perez, 1981) to 24 hours were made using the BCT-1F formulation, with and without salt. Typical results of these measurements are shown in Figure 3.1.4, which shows for contrast, measurements made on the pure Incor "H" cement paste. The reduced shrinkage during the early stages for the sample containing salt, is consistent with previous findings. Similar data are given for mixture 81-091 in Figure 3.1.5. Volumetric data are compared to longitudinal change. The percent unidimensional change approaches a constant value of minus 0.08%. The volumetric change is approximately ten times as big.

Dynamic Young's modulus data for bars of mixture 81-091 cured in saturated Ca(OH)_2 solution are given in Figure 3.1.6. Data for bars cured at 27°, 38°, and 60°C are given. There is a general increase in modulus with time up to 180 days curing for each temperature. The drop in modulus values at 60°C beyond 80 days is attributed to the expansive character of the paste.

Thermal conductivity measurements on mixture 81-091 as a function of time and temperature were also completed. These data are presented in Table 3.1.10. At a given temperature, most values increase with time, reflecting a "normal" progression of hydration. As pore space previously occupied by gas or water becomes bridged or filled by the developing hydration products, the thermal conductivity tends to increase.

Figure 3.1.3. SEM images of mixture 81-091 cured at 60°C.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3.1.4. Unidimensional change of mixtures 79-071 and 79-080 compared to a neat cement paste. Room temperature hydration.

Figure 3.1.5. Unidimensional and volumetric change of mixture 81-091. Room temperature and 55°C hydration.

Figure 3.1.6. Dynamic Young's modulus for mixture 81-091 as a function of temperature.

Table 3.1.10. Thermal conductivity of mixture 81-091 as a function of time and temperature (W/mK).

specimen age (days)	curing temperature, °C	
	27°	38°
7	1.800	1.529
14	2.103	1.512
28	2.122	1.599
56	2.494	2.270

Compressive strengths reported previously for mixture 81-091 would lead one to believe that higher temperature curing at a given time would also result in higher Young's modulus and thermal conductivity. However, this is not the case. Relative to the 27°C curing condition, both Young's modulus and thermal conductivity data are reduced for the 38°C cure. These discrepancies are apparently due to differences in sample preparation from one day to another.

3.1.5 Discussion and Conclusions

Four salt-containing and two salt-free derivative mixtures were investigated. All were sulfated and all eventually expanded. Each of the mixtures exhibited adequate strength development, and related physical and mechanical properties. One compositional feature appears to correlate with compressive strength: the percentage of salt saturation of the mixing water. In Figure 3.1.7 the appropriate percentages of salt saturation of five of these mixtures have been plotted against compressive strengths of the mixtures at 28 days (before any onset of cracking due to unrestrained expansion had taken place) and 60°C (a median temperature). The correlation is good, with most of the variation in compressive strength explained by the salt content of the mixing water. The salt (NaCl) content controls the phase content (relative proportion of Friedel's salt vs. ettringite), and affects the reactivity of the water. It also affects the morphology of the ettringite which is present. In the salt-free mixture, the ettringite is needle-shaped and may exhibit greater stress and contribute a reinforcing effect acting as fibers in the paste. In the salt-saturated mixture the ettringite/Friedel's salt is more stubby (Ogawa and Roy, 1981, 1982) and cannot impart this same effect. Furthermore, Friedel's salt has a platy, rather than needle-like morphology.

Results have shown that permeabilities of both salt-containing and salt-free mixtures are generally very low, especially in restrained specimens. Infiltration of water and migration of salt out of the samples was significant in specimens exposed to curing solutions after only one day hydration. Two distinctive modes of behavior were observed when such "wet" cured samples were compared with "dry" cured samples. It is apparent that accurate control of the initial chemical composition of a mixture is necessary to produce the desired properties of a seal material optimized for a specific environment.

In addition to temperature, the availability of water in a particular expansive salt-containing mixture probably controls the rate of formation and continued expansion of ettringite or an AFt phase. If water is restricted or its activity lowered by raising the chloride concentration, ettringite formation $[C_3A \cdot 3CaSO_4 \cdot 32H_2O]$ which requires 32 molecules of water, will be slowed or even reversed while a competing reaction to form Friedel's salt $[C_3A \cdot CaCl_2 \cdot 10H_2O]$ or an AFm phase which contains only ~10 molecules of water will play an increasingly more prominent role. Thus, balancing the total chemical composition including the

Figure 3.1.7. Correlation of compressive strength with % salt saturation of mixing water (28 days, 60°C).

water and salt content of the mixture and the environment is desirable to control the phase formation and the amount of expansion.

Expansiveness is not the only goal, but the nature of the contact of the wall rock with the mix solution during placement and long time curing is important. Chemical compatibility is necessary so that no undesirable phase changes will take place, as discussed later, in section 3.5.

3.2 FRESH WATER MIXTURES WITH POZZOLANIC ADMIXTURES

3.2.1 Introduction

The mixtures in this section all contain some type of "siliceous" material(s) often termed a "pozzolan." These materials partially replace the cement and are used to reduce free Ca(OH)_2 and subsequently increase the strength. The nature and definition of pozzolans and pozzolanic reactions are discussed briefly in the following section.

3.2.2 Nature of the Pozzolanic Reaction

Many historical cultures knew about pozzolans. They found that the addition of certain naturally occurring volcanic ashes or pottery shards would enhance the properties of their early cements. By present-day convention, there are two types of pozzolans: those that occur naturally and those that are products or by-products of some industrial process; the latter are termed "artificial" pozzolans. The present work has emphasized the utilization of artificial pozzolans in combination with various commercial portland cements.

By definition, pozzolanic materials are ones "...which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" (ASTM C 618). According to this definition, ASTM class C fly ashes and blast furnace slags are not true pozzolans, since they are somewhat self-cementitious even though free lime reduction in cement pastes and concretes is achieved through use of these materials; however, the reduction is less than that achieved by adding equal amounts of ASTM class F fly ash or silica fume. In the stricter sense, they are cements. In addition to these materials, relatively unreactive finely-divided quartz or at the extreme, ASTM C 109 sand, have also been used in the experimental program. Using the broader definition, they

too exhibit pozzolanic character; and given enough time, could enter into the reaction to a small extent.

Normally, siliceous materials which are relatively reactive are termed pozzolans, whereas very slow reacting materials such as quartz sand are termed inert aggregate. In the present situation these kinetic limitations are less important over the extraordinarily long time frame in which a repository seal must function. Therefore, the broader definition of pozzolanicity has been adopted in this report.

Artificial pozzolans such as fly ash, blast furnace slag, silica fumes and gels can be roughly classified into two groups. The first consists predominantly of "glassy" materials (fly ash and granulated blast furnace slag) which have formed from a melt and resemble super-cooled liquids. The glasses are metastable and thus possess excess free energy when compared with the crystalline anhydrous or hydrated counterparts. The second group consists of cryptocrystalline to amorphous materials with very high surface areas. They have either condensed from a vapor phase or at some time were sols or gels. This group of materials is best typified by the silica fumes, which are by-products of silicon metal or ferrosilicon alloy manufacture. Earlier research incorporated silica gels or calcined colloidal silicas (Roy et al., 1978). The mechanisms of reaction of the silica fume or silica gel in portland cement are slightly different from the glasses. The fumes and gels have very large surface energies associated with an extremely small particle size which is on the order of 0.1 μm or smaller.

Recent work on fly ash-substituted cements has demonstrated a mechanism of localized dissolution followed by topochemical and precipitative growth of C-S-H (Grutzeck et al., 1981b). The mechanism of silica fume incorporation in cement pastes is one in which a sol- or gel-like coating first forms which is very reactive, and thus the fume quickly becomes coated by C-S-H as it reacts with the calcium hydroxide in solution (Grutzeck et al., 1982).

3.2.3 Design of Experimental Cementitious Mixtures

Materials have been designed for ultimate reduced free-calcium hydroxide content by incorporating pozzolanic materials, and for reduced water/cement (w/c) ratio by using water-reducing dispersants. Pozzolans obviously differed in reactivity, hence mixtures often included combinations of rapidly and slowly reacting materials together to lengthen the duration of the pozzolanic reaction. Such

combinations have generated potential seal materials which have adequate strength combined with permeabilities of less than 10^{-8} darcys (10^{-11} cm sec⁻¹).

Since a good contact between the host rock and the seal is thought to be important, slightly expansive seal formulations were also evaluated. A mechanism of expansion common to all mixtures was based on the formation of ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$). To achieve this expansion, various calcium sulfates were added to the mixtures (which included lime and alumina) in their contents. Both salt and non-salt strata are penetrated in a potential repository site in bedded salt, hence both salt-containing and salt-free mixtures were investigated. The results of the salt-free experiments are detailed in the text of this section.

3.2.4 Viscosity

To determine the proper water and admixture proportions for feasible emplacement, the rheological properties of potential mixtures were measured (Asaga and Roy, 1980). Shear stress was recorded as a function of shear rate, and apparent viscosities were recorded. Summary results for all mixtures are given in Table 3.2.1. All seven mixtures in Table 3.2.1 are very fluid. All mixtures showed a small and nearly insignificant yield point and each mixture exhibited shear thinning with time, with near plastic or pseudo-plastic flow behavior.

3.2.5 Formulations

Formulations for the eight mixtures in this section are given in Table 3.2.2. Compositions of starting materials are given in Appendix A. Additional details regarding some of these mixtures are given elsewhere (Roy et al., 1982). The most important features are highlighted here.

The behavior of the fumes and dusts (collectively called silica fume) were found to be relatively similar in nature, due to their high surface areas. Reactivity was partially related to their state of agglomeration, which effectively increased their particle size above the nominal 0.1 μm particle size which is common to all fumes and dusts. These agglomerations were partly dispersible under certain cement mixing conditions. Since these fumes were very high surface area, it was necessary to use a high-range water reducer to reduce the water demand of the formulated pastes.

The addition of fly ash to a cement paste or concrete usually causes a slower development in strength, but often results in physical and chemical property

Table 3.2.1. Apparent viscosity (cP)[†] at 117 sec⁻¹ shear of pozzolanic cements.

mixture	time, hrs		
	0.5	1.0	2.0
81-141*	-	-	-
81-101	394	507	563
80-020*	-	-	-
80-030	216	273	334
80-040	212	364	486
81-050	182	273	425
81-121 ^{††}	-	406	-
81-111	183	1240**	2578

[†] 1 cP = 10⁻³ Pa·S

*These mixtures were not tested.

^{††}81-121 viscosity at 132 sec⁻¹.

**1.2 hours.

enhancement at later ages. However, the reaction mechanisms and stages in achieving the superior properties are not fully understood. Thus, fly ash-containing mixtures appear to be candidate seal materials if their mechanisms of reaction are better understood so that their long-range properties can be predicted.

Table 3.2.2. Formulations of pozzolan-containing mixtures (weights in grams).

	Code No.	mixture							
		81-141	81-101	80-020	80-030	80-040	81-050	81-121	81-111
class H cement	H-8,H-7	74.81	68.57	69.4	69.4	64.9	65.81	64.47	69.4
Litepoz	B44	25.19	23.09	--	--	--	--	--	--
gypseal	A31	--	8.41	--	--	--	4.03	2.23	--
ferrosilicon dust	B31	--	--	--	--	15.3	15.13	8.37	--
Ohio fume	B27	--	--	15.3	--	--	--	--	15.3
fly ash	B25	--	--	--	--	--	--	--	15.3
Alabama fume	B24	--	--	--	15.3	--	--	--	--
Min-u-sil (30 μ m)	B23	--	--	15.3	15.3	15.3	--	--	--
slag	B19	--	--	--	--	--	15.03	24.93	--
C 109 sand	C14,C16	--	--	--	--	--	49.25	65.04	--
Mighty	A36	--	1.12	--	--	--	--	1.98	--
Mighty 150*	A3	--	--	1.4	1.40	1.4	2.09	--	1.8
defoamer	A27	0.02	0.02	--	--	--	--	--	--
water	E01,E05	27.50	29.63	25.0	25.0	30.15	30.01	27.50	30.0
w/c		0.37	0.43	0.36	0.36	0.43	0.46	0.43	0.43
w/s		0.28	0.30	0.30	0.30	0.35	0.30	0.25	0.30

*liquid contains 41% solids.

A fly ash selected for mixtures in this section was one of the high-lime varieties because of greater availability in the western United States. This ash in itself is slightly cementitious when mixed with water.

The first two fly ash formulations (81-141, 81-101) were mixed and molded as either cylinders (25.4 by 50.8-mm long) or cubes (50.8-mm). Molds were sealed with grease and immersed in 38°C tap water for 24 hours. After demolding, the samples continued curing at 38°C in saturated Ca(OH)_2 solution until time of testing. Based on expected underground temperatures, the temperature chosen for hydration was 38°C, which was found to accelerate hydration reactions, but not significantly alter reaction products. Compressive strengths and x-ray diffraction data were primary evaluation instruments, along with the SEM microstructural studies. Samples used for SEM examination were freeze-dried.

Three of the mixtures were formulated specifically to compare the performance of different silica sources. Mixtures bearing PSU numbers 80-020, 80-030, and 80-040, contained equal portions of reactive silica "dust," and the less reactive coarser quartz. These mixtures were prepared as slurries according to API mixing procedures, molded as cylinders (25.4 by 50.8-mm long); precured in the sealed molds at selected temperatures, demolded at 24 hours and cured at temperature in Ca(OH)_2 -saturated water until tested.

The final three mixtures in this section contain combinations of silica fume and slag or silica fume and class F fly ash. All mixtures were formulated with high-range water reducers. Formulations PSU 81-050, 81-121, and 81-111 were mixed as pastes/grouts/sandy grouts according to API procedures, molded as cylinders (25.4 by 50.8-mm long), precured at temperature in Teflon-coated sealed brass molds, demolded at 24 hours and cured as a function of time at temperature in saturated Ca(OH)_2 solution. These mixtures were tested for compressive strength, microhardness, bulk density and also examined by x-ray diffraction and SEM analysis. As before, samples were tested either "as-cured" or freeze-dried.

3.2.6 Results

Compressive Strength. Values for the mixtures studied in this section are given in Table 3.2.3. The strength of the cement + fly ash mixture (81-141) increased with time, reaching the very high strength of 123 MPa at 56 days. The strength increase began similarly with the sulfate-containing mixture (81-101), but the rate diminished between 28 and 56 days. Since the compositions of mixture

Table 3.2.3. Compressive strength of pozzolanic mixtures (MPa).

specimen age (days)	cure temp. (°C)	fly ash		fumed			fume + slag		fume + fly ash
		81-141	+ CaSO ₄ 81-101	80-020	80-030	80-040	81-050	81-121	81-111
3	27							76.4	18.0
	38	59.7	51.7						
	45							98.8	28.6
	60							108.4	51.3
	90							94.7	91.5
7	27			46.2	87.8	78.7	76.7	61.2	72.8
	38	89.1	81.6						
	45			90.6	92.1	101.5	83.1	74.1	92.0
	60			92.4	91.8	82.6	117.0	108.2	86.6
	90			93.8	74.3	100.7	89.7	100.4	98.7
14	27			52.7	107.2	52.7	85.7		70.0
	38		88.5						
	45			74.3	109.9	70.8	87.6		88.2
	60			92.7	119.3	27.1	84.7		95.3
	90			62.7	106.2	110.8	68.2		50.3
28	27			113.2	98.8	99.1	90.4	80.5	70.5
	38	109.5	90.7						
	45			112.1	97.7	94.7	103.6	80.7	76.6
	60			107.0	99.7	119.2	99.1	96.1	85.3
	90			116.2	92.4	95.5	64.3	116.3	72.9
56	27							87.6	117.3
	38	123.0	91.8						
	45							82.3	97.4
	60							120.5	130.3
	90							114.7	106.8
90	27							130.2	
	38								
	45							138.0	
	60							136.1	
	90							121.7	

81-141 and 81-101 are otherwise similar it appears that the sulfate content of mixture 81-101 was influential.

The compressive strengths achieved by mixtures 80-020, 80-030 and 80-040 through 28 days of curing are relatively high in comparison to what has already been discussed, having strengths between 75 and 100 MPa at 7 days. All mixtures achieved a 28-day compressive strength between 95 and 120 MPa.

Mixtures 81-040 and 81-121 are similar mixtures containing sand, both designed to be somewhat expansive (81-050 more so than 81-121). Also, mixture 81-121 contains about half as much ferrosilicon dust (~8% based on cementitious solids) as 81-050. Both developed high strengths at an early age (7 days was the earliest test age for 81-050, and 3 days for 81-121). The highest fume-content mixture, 81-050, showed the most steady strength development between 7 and 28 days when cured at 27° and 45°C. The higher-temperature 60° and 90°C samples developed high 7-day strengths, leveling off later. Longer-term data are required to determine if this trend continues. Mixture 81-121 showed very high strengths at 45°, 60°, and 90°C even at 3 days, probably reflecting the higher slag contents, and the 90°C sample showed a very steady pattern of strength increase with time. As expected, the 27° sample had the lowest strength at 3 days. It is not clear at this stage whether the pattern of strength development is controlled to a greater extent by ettringite formation (see Roy et al., 1981; Wakeley et al., 1981a; and Ogawa and Roy, 1981, 1982, for discussion of effect of ettringite formation on expansion and strength) or other factors, such as porosity and pore structure (Parker and Roy, 1982).

Mixture 81-111 was a grout containing a low-lime class F fly ash as well as silica fume. It was similar to the formulations for mixtures 80-020, 80-030, and 80-040 (closest to 80-040), but with the 30 μ m quartz being replaced by a class F fly ash. A more consistent strength gain pattern is shown by 81-111, compared to its counterpart, 80-040. The greatest rate of strength gain of mixture 81-111 is again between 3 and 7 days, except for the 90°C samples, at which temperature the reactivities of the fume and/or fly ash are high even at 3 days. Strengths were high at all temperatures by 7 days, and were highest at 56 days.

Microhardness. These values which are more closely correlated with Young's modulus than compressive strength, are useful particularly for study of small specimens and in the absence of replicates. The current results (Appendix B) show relatively high values for the materials at all temperatures and curing

times. An occasional unusually high microhardness value was observed, which correlated with a high compressive strength measurement, having a low standard deviation. The microhardness values for mixtures 81-050, 81-121, and 81-111 tend to gradually increase with time.

Bulk Density. The values given in Table 3.2.4 relate to constituents, porosity, degree of expansion, and provide general quality control. Compared with the total series, mixture 81-121 shows higher densities, reflecting the higher slag content relative to fume, and higher sand content. Generally, densities increase with time and temperature of hydration, signifying a conventional hydration sequence.

The silica fume + class F fly ash mixture (81-111) generally does not have the same high early strength as do the mixtures containing slag, since the slag is initially more reactive than the fly ash. By 56 days the strengths of the fly ash mixture and the slag mixture are very much the same, reflecting the later reactivity of the fly ash. However, comparisons are not directly applicable between sand-containing (81-121) and sand-free (81-111) mixtures, since mortars usually have lower strengths than sand-free mixtures. The slag and sand-containing mortars (81-121) however, were found to have about the highest strengths of any of the materials investigated.

Permeability. Water permeability data for the three silica fume-substituted cements (80-020, 80-030 and 80-040) are given in Table 3.2.5 as a function of time and temperature. The fume-substituted cements have very low permeabilities. Mixture 80-040 had very low permeability (below detection limit) under all conditions of curing, which is surprising since it had such a wide variation in compressive strength. Water permeabilities of mixtures 81-050, 81-121 and 81-111 are given in Table 3.2.6. Generally, the values are very low, with only one value falling at $\sim 10^{-7}$ darcys. No permeability measurements were made on mixtures 81-141 and 81-101, which were formulated primarily for studies of reaction mechanisms.

X-ray Diffraction. Summaries of phase data for mixtures 81-141 and 81-101 are given in Table 3.2.7. Phases are given in decreasing order of relative intensity, as applicable. Hydrated calcium aluminate phases were often present throughout the hydration history of the samples, which is not entirely unexpected since the fly ash contains more than 17 wt % Al_2O_3 . In addition, the molar Ca/Si ratio of the fly ash is comparable to that in C-S-H and therefore it is

Table 3.2.4. Bulk density of pozzolanic mixtures.

specimen age (days)	cure temp. (°C)	mixture							
		81-141	81-101	80-020	80-030	80-040	81-050	81-121	81-111
3	27							2.08	1.71
	38		1.76						
	45							2.17	1.70
	60							2.02	1.69
	90							2.12	1.76
7	27			1.84	1.87	1.71	1.96	2.19	1.74
	38		1.76						
	45			1.85	1.89	1.69	1.99	2.18	1.74
	60			1.86	1.89	1.72	2.01	2.21	1.81
	90			1.90	1.94	1.73	2.04	2.20	1.85
14	27			1.85	1.89	1.68	1.99		1.77
	38		1.79						
	45			1.85	1.89	1.67	2.00		1.78
	60	n		1.86	1.91	1.68	2.01		1.81
	90	o		1.91	1.96	1.71	2.03		1.89
28	27	d		1.82	1.83	1.70	1.92	2.10	1.70
	38	a	1.94						
	45			1.85	1.85	1.68	1.91	2.11	1.66
	60	a		1.85	1.97	1.73	1.92	2.16	1.74
	90			1.87	1.99	1.77	1.92	2.14	1.78
56	27							2.07	1.78
	38		1.87						
	45							2.09	1.85
	60							2.10	1.91
	90							2.13	1.90
90	27							2.13	
	38								
	45							2.15	
	60							2.18	
	90							2.16	

Table 3.2.5. Water permeabilities of fume- and dust-substituted cements (darcy $\simeq \mu\text{m}^2$).

cure time (days)	temperature, °C			
	27°	45°	60°	90°
80-020: class H cement + Ohio silica fume				
7	--	--		
14	$\sim 10^{-4}$			$\sim 10^{-5}$
28		$< 10^{-8*}$		
80-030: class H cement + Alabama silica fume				
7	$\sim 10^{-5}$			
14	$\sim 10^{-4}$	$< 10^{-8}$	$\sim 10^{-5}$	
28				$\sim 10^{-5}$
80-040: class H cement + Icelandic ferrosilicon dust				
7		--		
14				--
28		$< 10^{-8}$		--

*

-- (missing data).

Table 3.2.6. Water permeability of complex fume- and dust-substituted cements (darcys $\approx \mu\text{m}^2$).

cure time	temperature, °C				
	27°	45°	60°	90°	
<u>81-050: Class H cement + ferrosilicon dust + slag</u>					
7	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">$<10^{-8}$</div>			missing data	
14					
28					
<u>81-121: class H cement + ferrosilicon dust + slag</u>					
7	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">$<10^{-8}$</div>				
28					
56					<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">$10^{-6.5}$</div>
90					<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">10^{-3}</div>
180					
<u>81-111: class H cement + silica fume + fly ash</u>					
7	$\sim 10^{-8}$	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">$<10^{-8}$</div>			
28					
56	<div style="border: 1px solid black; width: 100%; height: 100%; display: flex; align-items: center; justify-content: center;">$\sim 10^{-7}$</div>				

Table 3.2.7. X-ray diffraction phase data for samples cured at 38°C in Ca(OH)_2 solution.*

hydration days	81-141 class H + fly ash	81-101 class H + fly ash + sulfate
3	<div> unhydrated PC Ca(OH)_2 quartz ettringite C_2ASH_8 C_2AH_8 (Tr) </div>	no data
7	<div> unhydrated PC Ca(OH)_2 quartz C_2ASH_8 C-S-H ettringite (Tr) monosulfate (Tr) </div>	<div> unhydrated PC Ca(OH)_2 ettringite quartz C_2ASH_8 C-S-H C_4AH_{13} (Tr) </div>
14	no data	<div> unhydrated PC ettringite Ca(OH)_2 quartz C-S-H </div>
28	<div> unhydrated PC Ca(OH)_2 quartz C_2ASH_8 C-S-H C_4AH_{13} monosulfate (Tr) </div>	<div> unhydrated PC Ca(OH)_2 ettringite quartz C-S-H C_2ASH_8 (Tr) </div>

*Conventional cement nomenclature is used: C = CaO
A = Al_2O_3 , $\bar{\text{S}}$ = SO_3 , S = SiO_2 , H = H_2O , F = Fe_2O_3 .
In addition, PC = portland cement, Tr = trace.

likely that much alumina will be removed from the reaction zone. In mixture 81-141, ettringite ($C_3A \cdot 3\bar{C}\bar{S} \cdot H_{32}$) and C_2AH_8 were formed early, but later reacted to form monosulfoaluminate ($C_3A \cdot \bar{C}\bar{S} \cdot H_{12}$) and C_4AH_{13} . In addition, C_2ASH_8 (Stratling's compound) was always present throughout the history of hydration of this sample. In the sulfated mixture (81-101), the trisulfoaluminate, ettringite, was dominant. Small amounts of C_2ASH_8 were also detected from time to time. All mixtures contained $Ca(OH)_2$, C-S-H and unhydrated portland cement phases.

The x-ray diffraction summary data for mixtures 80-020, 80-030 and 80-040 are presented in Table 3.2.8. In all three formulations at temperatures above $27^\circ C$ the free $Ca(OH)_2$ had reacted with the fume or dust to produce additional C-S-H, and was no longer detected by x-ray diffraction. At $27^\circ C$, the free $Ca(OH)_2$ still present tended to decrease with time. Its presence at 27° and not at higher temperatures reflects the kinetics of reaction.

X-ray diffraction data for mixtures 81-050, 81-121 and 81-111 are given in Table 3.2.9. Mixture 81-121 is a modification of 81-050, having increased sand and slag, and lesser percentages of ferrosilicon dust, calcium sulfate, and water. However, the x-ray data are still similar except that the mixture 81-050 with the higher dust content proved to be more effective at reducing the free $Ca(OH)_2$ content at an earlier time than 81-121. (It had a slightly higher w/c ratio and lower slag content, also.) Ettringite was present in 81-050 mixtures through $45^\circ C$, while in 81-121 ettringite was also found at $60^\circ C$ at some test dates. X-ray diffraction data for mixture 81-111 were relatively straightforward, giving very similar results to those presented for other fume- and dust-containing cements given in Table 3.2.7. Free $Ca(OH)_2$ reduction was relatively rapid, having taken place even in the $27^\circ C$ samples at 28 and 56 days. Both silica fume and fly ash may have an effect in reducing free lime, the latter probably at later ages. Ettringite was found as an additional phase at all times at 27° and $45^\circ C$.

SEM Data. SEM examination was carried out on six of the eight mixtures. Since some data for these mixtures (81-141, 81-101, 80-020, 80-030, 80-040, and 81-050) are presented elsewhere (Roy et al., 1982), only a summary of the findings is given here.

The pattern of fly ash hydration which evolves in fly ash-containing mixtures 81-141 and 81-101 is one of in situ hydration of the fly ash spheres, which are gradually consumed in the hydration reaction. The glass spheres are replaced by radiating clusters or bundles of fibrous C-S-H, which in cross-section has a typical honey-comb appearance. As the spheres are consumed, radiating

Table 3.2.8. X-ray diffraction data for fume- and dust-substituted cements.*

cure time (days)	temperature, °C			
	27°	45°	60°	90°
<u>80-020: Class H Cement + Ohio Silica Fume</u>				
7	quartz residual cement C-S-H Ca(OH) ₂	quartz residual cement phases C-S-H		
14				
28				
<u>80-030: Class H Cement + Alabama Silica Fume</u>				
7	quartz residual cement C-S-H Ca(OH) ₂	quartz residual cement phases C-S-H		
14				
28				
<u>80-040: Class H Cement + Icelandic Ferrosilicon Dust</u>				
7	quartz residual cement C-S-H Ca(OH) ₂	quartz residual cement phases C-S-H		
14				
28				

*Conventional cement nomenclature is used: C = CaO, S = SiO₂, H = H₂O.

Table 3.2.9. X-ray diffraction data for ferrosilicon dust + slag- and silica fume + fly ash-substituted cements.*

cure time (days)	temperature, °C			
	27°	45°	60°	90°

<u>81-050: Class H Cement + Ferrosilicon Dust + Slag + CaSO₄ + Sand</u>				
7	<div>quartz residual cement Ca(OH)₂ ettringite (tr) C-S-H</div>			
14				
28	<div>quartz residual cement ettringite (tr) C-S-H</div>			<div>quartz residual cement C-S-H</div>

<u>81-121: Class H Cement + Ferrosilicon Dust + Slag + CaSO₄ + Sand</u>				
3	<div>quartz residual cement Ca(OH)₂ ettringite C-S-H</div>	<div>quartz residual cement ettringite C-S-H</div>		<div>quartz residual cement C-S-H</div>
7				
56				
90				

<u>81-111: Class H Cement + Silica Fume + Fly Ash</u>				
3	<div>residual cement Ca(OH)₂ ettringite C-S-H</div>			
7				
14	<div>residual cement ettringite C-S-H</div>			<div>residual cement C-S-H</div>
28				
56				

*Conventional cement nomenclature is used: C = CaO, S = SiO₂, H = H₂O, Tr = trace.

fibers grow inward to fill the space. At first, bonding of the C-S-H material to the sphere is necessarily weak, becoming progressively stronger with time as the C-S-H densifies with progressive hydration.

Mixture 81-101 also shows progressive hydration of the fly ash, but since excess sulfate is present, the potential for substantial ettringite formation exists. The x-ray diffraction data confirm the presence of ettringite and it is assumed that the rod-like or prismatic crystals present in the matrix are mainly ettringite (also see Grutzeck et al., 1981b).

SEM images for the fume- and dust-substituted cements (80-020, 80-030 and 80-040) contained features which were nearly identical from formulation to formulation. Recent work with ferrosilicon dust with $\text{Ca}(\text{OH})_2$ solutions and cement mixtures has resulted in the postulation of a mechanism of reaction whereby the fume or dust first consumes water to form a silica sol or "gel," which in turn combines with $\text{Ca}(\text{OH})_2$ available in solution to form C-S-H (see Figure 3.2.1). The application of this mechanism of gel formation and subsequent agglomeration of the fume and dust spheres into larger silica-rich particles, has been used to explain the majority of behavioral features of the silica fume and dust-substituted cements. Details of the mechanism and implications drawn from this model are presented in Grutzeck et al. (1982).

SEM data for mixture 81-050 are similar to those presented for mixture 81-141 and 81-101. The influence of temperature and time on reaction rate is obvious. The higher temperature or longer duration specimens show effects of densification and tendency to produce less ettringite and more C-S-H from the ferrosilicon dust.

Other Tests. Dynamic Young's modulus data are presented for mixture 80-020 at 60°C in Figure 3.2.2. As in the compressive strength data, the modulus data tend to plateau at 7 to 14 days with a gradual nearly linear (log) increase thereafter.

Dimensional change data for mixture 81-111 for the first 24 hours of curing are given in Figure 3.2.3. Three plots for different samples of varying length are given. If rates of change are plotted, these are nearly identical. A rapid rate of shrinkage is observed through 6-8 hours, followed by a plateau lasting through 12 hours followed by another stage of renewed shrinkage through 19-20 hours. Compared with the expansive mixture 81-091 reported on in section 3.1, this mixture shows nearly twice as much shrinkage. However, other features of the curves are very similar.

Figure 3.2.1. Mechanism of hydration of a normal paste and a "silica-fume-enhanced" paste.

Figure 3.2.2. Dynamic Young's modulus for mixture 80-020 hydrated at 60°C in saturated $\text{Ca}(\text{OH})_2$ solution.

Figure 3.2.3. Unidimensional change of mixture 81-111 as a function of sample length.

3.2.7 Discussion

Overall behavior of the mixtures presented in this section are satisfactory. Permeability values are very low, nearly always in the 10^{-8} darcy (10^{-11} cm sec⁻¹) range. Consequently, any apparent increases due to expansion of the "gel" related mechanism particular to the silica-fume-substituted cements do not seem to be of consequence. In addition, the use of these mixtures usually will involve restraint of borehole or shaft walls and effects related to expansion will serve to enhance the bond between rock and seal material. Thus, some expansion is deemed desirable. On the short term, the fumed cements or slag cements tend to give the highest compressive strengths.

A model of high-lime fly ash hydration based on the foregoing data as well as data by Scheetz et al. (1981a) and Grutzeck et al. (1981a) was presented by Grutzeck et al. (1981b). Basically, composition of the paste seems to play a relatively minor role in the hydration of these fly ash spheres. Hydration appears to begin at the surface of the glass sphere and progress inward, leaving in its wake a network of radiating bundles of fibrous C-S-H. Thickness of the glass sphere, age of the honey-comb network, and development of bond strength with time account for observable phenomena.

Reaction rates of fly ash spheres differ due to varying compositions of glasses. Even though the chemical composition of a mixture is fixed, the composition of species in solution and crystals present in the matrix may vary as a function of time. Finally, should a fly ash sphere be completely surrounded by calcium hydroxide, interaction will be inhibited. Water will be excluded except due to very slow diffusion, resulting in insignificant hydration.

The mechanism of slag hydration is not fully understood, but the effects of temperature on its activation and development of properties of granulated slag-cement mixtures has been explained (Roy and Idorn, 1982; Wu et al., 1982; Parker and Roy, 1982).

Evidence has been presented that silica fumes (including ferrosilicon dusts) are very effective pozzolanic materials, reacting with free Ca(OH)_2 to minimize or eliminate it, at temperatures from room to 90°C. Some irregular compressive strength variations have been observed by others when fume or dust substitutions above 10 wt % have been made, and recent work at this laboratory has also found this to be the case. However, other properties such as microhardness or permeability show no such effects. Nevertheless, current mixture using fume substituting for cement are now formulated to keep the content below 10 wt %. Strength

gain, reduction of free Ca(OH)_2 , densification, and low permeabilities are routinely expected when small silica fume contents are incorporated.

3.3 EXPLORATORY MIXTURES

3.3.1 Introduction

This section presents information on early mixtures or experimental mixtures used to explore reactivity of silica fumes in the non-plasticized state. The data are often preliminary in nature; however, the results obtained acted as foundation for runs already reported upon.

3.3.2 Viscosity

The mixture 81-010, which contained cement and sand, was thick and behaved much like the thick pastes discussed previously. Data for mixture 81-010 are given in Table 3.3.1. Most of the older mixtures in this section were prepared before a viscometer was available, and no in-depth study of rheology was completed. However, mixtures were formulated with as little water as possible and tended to have the consistency of thick pastes.

3.3.3 Formulations

The mixtures described in this section were formulated to investigate the effects of replacing approximately 30-50 wt % of the cement portion of the mixture with various silica-rich materials, such as C-109 sand (81-010), class F fly ash (79-010, 79-020 and 79-030), silica fume (79-060 and 80-010), and class C fly ash and/or slag (79-040 and 79-050).

The formulations of the mixtures are given in Table 3.3.2. Composition of starting materials are given in Appendix A. Mixture 80-010 was formulated as a reference for comparing other mixtures. It is a sandy, thick grout, containing 70 wt % class H cement and 30 wt % ASTM C 109 sand. It may be compared with many of the mixtures discussed in the report in which approximately 30-50 wt % of the mixture consists of sand with various reactive additives in part substituting for the cement. The composition of the sand was assumed to be essentially pure SiO_2 .

Mixtures 79-010, 79-020 and 79-030 each contain class C cement and a class F fly ash. The fly ash is rich in SiO_2 and Al_2O_3 and relatively poor in CaO . As a result, the calcium oxide to silica molar ratio of the various mixtures varies from approximately 1.25 (79-020) to 0.83 (79-030) as more fly ash is added to the

Table 3.3.1. Apparent viscosity (cP)[†] at 132 sec⁻¹ shear of exploratory mixture 81-010.

mixture	time, hrs					
	0.11	0.5	1.0	2.0	2.5	5.0
81-010	1233	1530	1784	1873		

*contains sand.

[†]1 cP = mPa.s.

Table 3.3.2. Formulation of exploratory mixes.

code no.		mixture							
		81-010	79-010	79-020	79-030	79-060	80-010	79-050	79-040
class H cement	H-4,H-7,H-8	100.0	--	--	--	--	69.4	--	--
class C cement	C-2,C-5	--	54.35	61.44	45.05	69.4	--	35.15	51.0
fly ash	B3	--	45.65	38.56	54.95	--	--	--	19.6
ferrosilicon dust	B17	--	--	--	--	15.3	15.3	--	--
slag	B19	--	--	--	--	--	--	35.15	29.4
Min-u-sil	B5,B7,B23	--	--	--	--	15.3	15.3	29.70	--
sand C 109	C15	42.86	--	--	--	--	--	--	--
Mighty C150	A3	1.18	--	--	--	--	--	--	--
water	E01	26.11	33.0	33.04	33.0	37.5	32.5	45.00	35.0
w/c		0.26	0.61	0.54	0.73	0.54	0.47	1.28	0.69
w/reactive solids		0.26	0.33	0.33	0.33	0.38	0.32	0.45	0.35

mixture. This study was made to illustrate the effects of replacement of relatively large amounts of cement by fly ash.

Mixtures 79-060 and 80-010 were formulated from a class C and a class H cement, respectively. Both contained equivalent amounts of cement and a 50:50 mixture of ferrosilicon dust and 30 μm quartz. Since these did not contain a high range water reducer, the water required to formulate an equally consistent paste varied from 37.5g for the finer class C cement to 32.5g for the coarser class H cement. The results of these experiments gave insight into the effect of adding 15.3 wt % ferrosilicon dust to a paste (as compared to the sandy grout discussed earlier), the effect of reducing the w/c ratio, and the effect of changing the cement reactivity by changing the particle size of the cement.

Rather than risk volume instability from excessive silica fume additions, the silica replacement of some of the cements were made by a 50:50 mixture of fume and 30 μm quartz. The results have shown that even 15.3 wt % may have been too much.

Mixture 79-040 contained class C cement blended with slag and a class F fly ash. It contained a relatively large proportion of slag and a moderate amount of fly ash. Of the replacements, the slag was expected to react fastest, whereas the fly ash would be expected to react much more slowly, but contribute to strength development over the long term.

Blast furnace slag was again used in formulating the mixture (79-050). Because no high-range water reducer was used in this formulation, it has a relatively high water content (w/s ratio) ranging from 0.69 and 0.45 if only the cement and slag, or if all solids, cement, slag and quartz are considered. The mixture is very rich in silica, having a bulk SiO_2 content of approximately 55 wt %. Some lime reduction was anticipated, and as will be seen in the report, actually occurred.

3.3.4 Results

Compressive Strength, Microhardness and Bulk Density. Compressive strength and bulk density data for all eight mixtures are given in Tables 3.3.3 and 3.3.4, respectively. Microhardness data are given in Appendix A. Compressive strengths of mixture 81-010 increase with time, reaching values between 69 and 86 MPa in 28 days.

Data for mixtures 79-010, 79-020 and 79-030 represent curing behavior at 90°C for each mixture. In addition, data for 27° and 60°C for mixture 79-030, with the least amount of fly ash substitution, are also given. Relatively high strengths at all temperatures are characteristic of the latter at 90 days.

Table 3.3.3. Compressive strength of exploratory mixtures (MPa).

specimen age (days)	cure temp. (°C)	mixture							
		81-010	79-010	79-020	79-030	79-060	80-010	79-050	79-040
7	27	51.0				53.4	53.1	43.2	56.4
	45	77.6				42.6	48.2	42.9	64.6
	60	54.6				46.8	40.3	44.0	65.9
	90	59.5				41.9	39.6	57.4	76.9
14	27	38.8			37.2	62.6	67.4	60.4	70.8
	45	36.9				68.1	67.8	61.2	71.0
	60	53.4			52.1	70.7	46.6	62.4	87.6
	90	41.3	65.6	62.0	25.3	41.5	42.1	87.3	72.3
28	27	81.8			42.1	--	62.5	68.4	64.2
	45	74.9				66.2	72.1	55.3	73.1
	60	85.9			57.4	58.9	5-9	52.1	63.3
	90	68.5	49.7	38.2	30.3	60.4	68.6	88.2	79.5
56	27				19.6				
	45								
	60				51.7				
	90		42.6	51.4	61.8				
90	27				42.4				
	45								
	60				65.9				
	90		81.3	59.6	67.3				
180	27				62.3				
	45								
	60				65.3				
	90		48.8	50.0	34.8				

Table 3.3.4. Bulk density of exploratory mixtures.

specimen age (days)	cure temp. (°C)	mixture							
		81-010	79-010	79-020	79-030	79-060	80-010	79-050	79-040
7	27	2.07				1.82	1.79	1.80	2.01
	45	2.04				1.83	1.81	1.81	2.03
	60	2.06				1.77	1.84	1.78	2.08
	90	2.06				1.70	1.74	1.78	2.01
14	27	2.10			1.89	1.84	1.76	1.86	1.95
	45	2.06				1.93	1.85	1.86	1.94
	60	2.07			1.89	1.85	1.83	1.88	1.98
	90	2.09	1.83	1.81	1.84	1.79	1.88	1.84	1.93
28	27	2.13			1.90	1.75	1.83	1.83	2.00
	45	2.13				1.73	1.83	1.82	2.01
	60	2.01			1.89	1.70	1.84	1.84	1.97
	90	2.14	1.99	2.04	1.82	1.78	1.89	1.81	1.99
56	27				1.92				
	45								
	60				1.89				
	90		1.93	1.95	1.87				
90	27				2.04				
	45								
	60				2.02				
	90		1.99	2.01	1.97				
180	27				1.52				
	45								
	60				1.53				
	90		1.91	1.89	1.55				

Contrary to conventionally accepted correlations of compressive strength to w/c ratio, mixtures 79-060 and 80-010 attain similar compressive strengths independent of water content. Apparently, the gain in strength due to the reduction in water due to the coarser grind of the class H cement balances the corresponding loss in strength of the less reactive, lower surface area class H cement. All sets have reasonably high strengths at 28 days.

The compressive strength and microhardness data for mixture 79-050 tend to show a clustering of the 27°, 45°, and 60°C data in a distinct grouping separate from the 90°C data. In both compressive strength and microhardness, the 90°C data prove to be the stronger. Apparently, this mixture would benefit from the addition of superplasticizer. Mixtures containing silica fume and superplasticizer already discussed tend to bear this out.

The mixture 79-040, comparable to other slag-containing mixtures, shows relatively high strengths at 7 days, particularly for the 45°, 60°, and 90°C samples.

Permeability. Since most samples were quite exploratory, no routine permeability measurements were made. The two exceptions were mixtures 81-010 and 80-010. Data are presented in Table 3.3.5 for 81-010 and 80-010. Values for 81-010 were calculated to be less than 10^{-8} darcys at all times and temperatures with the exception of 14 and 28 days at 90°C. A very small flow was observed at these times and temperature. This suggests that curing at temperatures above 90°C tend to change the hydration process somewhat, often causing larger pore sizes and perhaps greater associated permeability. Parker and Roy (1982) have shown this phenomenon for cements, particularly at higher w/c ratios. Data for mixture 80-010 reflect these same general findings.

X-ray Diffraction. Data for mixture 81-010 are presented in Table 3.3.6. Mixture 81-010 shows a normal progression of hydration. Ca(OH)_2 is present at all times and temperatures. Some ettringite is formed early, being replaced by AFm phases at later times.

X-ray diffraction data for mixtures 79-010, 79-020 and 79-030 are given in Table 3.3.7. Ettringite is present at all times at 27°C in mixture 79-030. It is also present at 60°C up to 28 days, after which its presence or absence is sporadic. The low-lime fly ash used in mixtures 79-010, 79-020 and 79-030 is reactive at higher temperatures, since Ca(OH)_2 is absent at 90°C at all times, and at 60°C at 180 days.

X-ray diffraction data for mixtures 79-060 and 80-010 are given in Table

Table 3.3.5. Water permeability data for mixtures 81-010 and 80-010 (darcy $\approx \mu\text{m}^2$).

cure time (days)	temperature, °C			
	27°	45°	60°	90°
<u>81-010: class H cement + sand</u>				
7	no data		no data	$<10^{-8}$
14				
28		$<10^{-8}$		$\sim 2 \times 10^{-8}$
<u>80-010: class H cement + ferrodust + quartz</u>				
7		$\sim 10^{-7}$	10^{-6}	failure*
14	$<10^{-8}$	$<10^{-6}$	$<10^{-8}$	$\sim 10^{-4}$
28	missing data			failure*

*These failures may be related to the relatively low compressive strengths of these samples due to their relatively high w/s ratio.

Table 3.3.6. X-ray diffraction data for sandy grout 81-010.

81-010: class H cement + sand				
cure time (days)	temperature, °C			
	27°	45°	60°	90°
7	Ca(OH) ₂ residual cement quartz tr. ettringite		Ca(OH) ₂ residual cement quartz tr.alum-hydrate	
14	Ca(OH) ₂ residual cement quartz C-S-H	Ca(OH) ₂ residual quartz quartz tr. monosulfate C-S-H	Ca(OH) ₂ residual cement quartz C-S-H	
28				

Table 3.3.7. X-ray diffraction phase data for samples cured in a saturated Ca(OH)_2 solution.

hydration days (at 90°C)	79-010 class C + fly ash C/S = 1.06	hydration days (at 90°C)	79-020 class C + fly ash C/S = 1.25
14	residual cement quartz C-S-H* **	14	residual cement quartz, Ca(OH)_2 C-S-H*
28		28	residual cement quartz C-S-H* **
56		56	
90		90	
180		180	

79-030
class C + fly ash
C/S = 0.83

hydration days	temperature, °C		
	27°	60°	90°
14	<div>residual cement Ca(OH)₂, quartz ettringite C-S-H*</div>		<div>residual cement quartz C-S-H* **</div>
28			
56			
90	<div>residual cement Ca(OH)₂, quartz C-S-H*</div>		
180			

*All samples also contained residual mullite from the ash.

**Occasionally trace amounts of "ettringite", gypsum or Ca-Al-monosulfate hydrate were also detected. The presence or absence of these phases appeared to be random in nature.

3.3.8. They develop ettringite as one of their earliest aluminate phases. The role of the various aluminous phases and their bearing on the overall stability is yet unclear. Ettringite forms rather quickly and is often converted to monosulfoaluminate depending upon the total sulfate content, temperature and other factors.

X-ray diffraction data for mixture 79-050 and 79-040 are given in Table 3.3.9. These data show that the hydration of these pastes progresses normally. Some residual cement is present throughout, although of reduced magnitude with abundant C-S-H development at nearly all ages. In mixture 79-050, ettringite and calcium monosulfoaluminate are present at early ages and low temperatures. Free $\text{Ca}(\text{OH})_2$ is absent at 60°C and higher temperatures at 28 days, and absent at 90°C at all times (7, 14, and 28 days). This behavior is probably explained by the slag reacting with excess $\text{Ca}(\text{OH})_2$ to form additional C-S-H and also by partial reaction of lime with quartz.

The presence of the class F fly ash was not very effective in reducing free $\text{Ca}(\text{OH})_2$ in mixture 79-040 at all times up to 28 days. The x-ray determined phases present at all temperatures are $\text{Ca}(\text{OH})_2$, residual cement, quartz (from the fly ash), and C-S-H.

SEM Studies. Representative SEM photographic images for mixture 81-010 are given in Figures 3.3.1 to 3.3.3. An interesting observation was that the sand, which was assumed to be non-reactive, did show some reaction, confined to the surfaces of the sand grains. Because of their large size, however, the magnitude of the reaction is limited. Figure 3.3.1 depicts the starting material sand. It has been ultrasonically washed in water and shows characteristically smooth rounded surface features. Chemically, it was essentially pure SiO_2 . Figure 3.3.2 gives images of samples of the sandy grout (81-010) hydrated for 7 days at 45°C (view a), 60°C (views b, c, and d), and 90°C (views e and f). View (a) is representative of the type of C-S-H forming in the paste matrix at 7 days. It is typical of all temperatures. The chemistry of this material is dominantly Ca with lesser Si and minor K. Views (b) through (d) represent a partially encrusted sand grain (a), a close-up of the sand grain surface (b) whose chemistry is predominantly Si with traces of Ca, and a close-up of the C-S-H-to-quartz grain interface (c), showing C-S-H development, respectively. The chemistry of the latter C-S-H is dominated by Ca and Si with minor K and trace amounts of Al. Reaction of the sand with the surrounding matrix material is evident. Views (e) and (f) are features typical to the 90°C sample. View (e) gives edge detail for a sand grain and shows C-S-H as

Table 3.3.8. X-ray diffraction data for ferrosilicon dust-substituted cements.

time (days)	temperature, °C			
	27°	45°	60°	90°
<u>79-060: class C cement + ferrosilicon dust + quartz</u>				
7	residual cement Ca(OH) ₂ quartz gypsum ettringite C-S-H			residual cement quartz gypsum monosulfoaluminate C-S-H
14	residual cement Ca(OH) ₂ quartz C-S-H			
28	residual cement Ca(OH) ₂ quartz monosulfoaluminate C-S-H	residual cement Ca(OH) ₂ quartz gypsum monosulfoaluminate C-S-H		residual cement quartz C-S-H monosulfoaluminate
<u>80-010: class H cement + ferrosilicon dust + quartz</u>				
7	residual cement Ca(OH) ₂ quartz gypsum ettringite monosulfoaluminate C-S-H	residual cement Ca(OH) ₂ quartz gypsum ettringite C-S-H		residual cement quartz gypsum monosulfoaluminate
14	residual cement Ca(OH) ₂ quartz ettringite C-S-H			residual cement quartz C-S-H
28	residual cement Ca(OH) ₂ quartz monosulfoaluminate C-S-H			

Table 3.3.9. X-ray diffraction phase data for samples cured in saturated $\text{Ca}(\text{OH})_2$ solution.

time (days)	temperature, °C			
	27°	45°	60°	90°
<u>79-050: class C cement + slag + fly ash</u>				
7	residual cement $\text{Ca}(\text{OH})_2$ quartz ettringite monosulfate C-S-H	residual cement $\text{Ca}(\text{OH})_2$ quartz monosulfate C-S-H	residual cement quartz C-S-H	
14				
28	residual cement $\text{Ca}(\text{OH})_2$ quartz monosulfate C-S-H	residual cement quartz monosulfate C-S-H	residual cement quartz gypsum C-S-H	
<u>79-040: class C cement + slag + fly ash</u>				
7	$\text{Ca}(\text{OH})_2$ residual cement quartz (a)			
14				
28				

(a) Traces of AFt and AFm at 27° and 60°C at 7 days and at all temperatures at 90°C at 14 days.

(a)

(b)

Figure 3.3.1. SEM images of ASTM C 109 sand.

Figure 3.3.2. Seven-day hydration of mixture 81-010.
(a) 45°C; (b,c,d) 60°C; (e,f) 90°C.

(a)

(b)

(c)

(d)

(e)

(f)

well as thin disk-shaped crystals, consisting compositionally of mostly Ca and Si. View (f) is a close-up of a sand particle surface showing etch or solution features and the development of resistant "stack"-like features.

Figure 3.3.3 gives images of 14-day samples. View (a) represents the surface features developed on a 45°C reacted sand grain which has pulled free from the matrix on breakage for SEM examination. The rounded edges of the quartz grain are evident at the edges of the photo, with remnant C-S-H adhering to the particle at the middle of the photograph. View (b), at 60°C, represents an interfacial region between a quartz grain, upper right-hand (URH) corner, and interfacial region, mid-section of photo, and an open structured C-S-H material, LLH corner. Calcium content of the interfacial region increases from right to left, from the quartz grain to the C-S-H. Views (c) and (d) at 90°C are a pair. View (d) is an enlargement of the central portion of view (c) of what appears to be radiating networks of C-S-H surrounding a void from which a particle of some sort has been plucked. Views (e) and (f) at 90°C are views of an etched sand grain and a pocket filled with needles (Ca, Si, with traces of Al, S, Fe) and rounded disk-shaped particles (Ca, Si, Al, S, Fe). Twenty-eight-day features were similar to those already described. General matrix densification was observed.

Representative SEM images for mixtures 79-060 and 80-010 cured for 7 days at 27°C are given in Figure 3.3.4, views (a-c) (79-060) and (d-f) (80-010). View (d) is typical of the low magnification microstructure of these samples. The silica fume/quartz matrix is dense, with large angular quartz grains showing. Pockets are filled with ettringite/thaumasite (containing Si). View (b) is a detailed view apparently of thaumasite (left-hand side) and ettringite or gypsum (right-hand side). Views (a) and (c) are views of matrix showing remnant ferrodust spheres, cemented with fibers and foils of C-S-H. In addition, view (e) has monosulfate plates near the center of the photograph. Finally, large remnant ferrodust spheres are shown for each mixture in views (c) and (f). These show possible drying shrinkage effects. If a gel or sol intermediate reaction stage exists for silica fume-substituted cements, as postulated, it is possible that some volume instability and structural weaknesses which could affect compressive strength could result from both gross features as these (views c and f), or from the same type of behavior on the microscale.

SEM images for 7-day 27°C-cured samples of mixture 79-040 are given in Figure 3.3.5. Views (a-c) show details of AFt-type phases (ettringite) surrounded by C-S-H honey-comb (view a) and typical AFm hexagonal plates (views b

Figure 3.3.3. Fourteen-day hydration of mixture 81-010.
(a) 45°C; (b) 60°C; (c-f) 90°C.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 3.3.4. SEM images of 7-day, 27°C cured samples of mixtures 79-060 (a-c) and 80-010 (d-f).

(a)

(d)

(b)

(e)

(c)

(f)

Figure 3.3.5. SEM images of 7-day, 27°C cured samples of mixture 79-040.

(a)

(b)

(c)

(d)

(e)

(f)

and c). View (d) gives details of some massive Ca(OH)_2 which is common in the sample. Views (e) and (f) show some details of the reaction of fly ash. In view (e) the fly ash sphere is somewhat attacked, showing a pocked surface, which seems to have some crystals adhering to it. View (f) shows a typical pull-out feature, a fly ash void produced during sample preparation. The hydrated material in the void gives the impression of blade-like crystals with some occasional rounded crystals on this surface. The former may be AFt or AFm phases produced by the aluminate from the fly ash. The rounded disks are of unknown origin. The presence of many hexagonal plates and ettringite fibers at various early stages is pronounced.

3.3.5 Summary and Discussion

The cementitious materials discussed in this section all exhibited more than adequate strength development, and permeabilities typically less than 10^{-8} darcys. The compressive strengths of the silica-substituted mixtures usually exceeded the values for the sandy mixture (81-010) used as a baseline. Variations in compressive strength from the general pattern of increase with time are not directly correlatable with other measured properties such as permeability. This seems to indicate that such variations in compressive strength are transient features without long-term effects.

The observed reaction of sand grain surfaces at early ages, apparently weakening the cement is a transient one, and all other data indicate that it does not impair overall long-term performance. If the cement is partially replaced by a pozzolanic reactive silica source, such as a class F fly ash, slag, or silica fume, modified performance might be expected. In order to explore this concept, additional mixtures were formulated which contained pozzolans as partial replacement for cement and sand. The mixtures discussed in this and previous subsections contained silica fume, slag, class F fly ash, and finely divided quartz.

Although the data are incomplete, they suggest that a viable seal might be formulated from all the materials studied. All appear to have adequate strengths at 28 days. The mechanism of reaction for the glassy materials may possess similarities, dependent upon dissolution and precipitation of C-S-H. However, the blast furnace slag, though having the larger percent Ca, is much more reactive and apparently more effective in lime removal, whereas the lime-poor fly ash reacted only very slowly (they had approximately the same SiO_2 content).

In addition to the relative reactivity of the two glasses, possibly the 5 μm SiO_2 included in the former mixture also entered into the reaction. Additional work is needed on slag and class C fly ash-substituted cements.

Reactions of the above mixtures from 27° to 60°C are of the same general type. Temperature accelerates the reaction, but the phases remain generally the same as at room temperature. At 90°C, hydration mechanisms and products appear to be somewhat different.

Class F fly ash and quartz react very slowly. They often give a low compressive strength value at early stages, but this seems to have little bearing upon the final properties.

The conversion of ettringite to monosulfate with time, characteristic of portland cement hydration, occurs because the materials normally have insufficient sulfate to keep ettringite stable; furthermore, sulfate also enters the C-S-H phase. In most cements, there is not even enough gypsum to maintain monosulfate, and thus the final phase assemblages in mature cementitious materials probably consist of monosulfate and C_4AH_x , along with C-S-H which incorporates sulfate in solid solution.

The series of mixtures discussed in this and the previous sections contained what are commonly accepted as artificial pozzolans and/or quartz as 5 μm or 30 μm quartz. By definition, pozzolanic materials are those which reduce free $\text{Ca}(\text{OH})_2$ through reaction and develop strength by forming C-S-H. In this report, we have adopted a broader definition which is free of kinetic limitations, taking the position that given the time of reaction in a repository environment, even sand may be pozzolanic in nature.

If selected 28-day strengths are plotted against w/c ratio [Figure 3.3.6 (a)], most mixtures appear to obey the commonly-accepted inverse relationship between compressive strength and w/c ratio. All mixtures except for the cement + sand (81-010), cement + fly ash (79-030), and cement + slag + quartz (79-050) mixtures appear to fall within a narrow shaded area. Apparently, the water content is not totally responsible for the observed variations in compressive strength, implying that in some instances there must be a different mechanism in operation.

In the plot of w/reactive solids vs. 28-day compressive strength [Figure 3.3.6 (b)], two facts become apparent: 1) all plasticized mixtures are nearly always stronger than non-plasticized mixtures of the same w/s ratio; and 2) the reactivity of the pozzolanic material influences compressive strength (the fumes are more reactive than the fly ashes). Rather than the relationship seen in the

Figure 3.3.6. A comparison of compressive strength vs. water/cement (w/c) ratio to compressive strength vs. water/reactive solids (w/s) ratio for selected cementitious mixtures.

w/c plot with exceptions, now the compressive strength behavior can be explained by a single plot with a slightly steeper slope than the plot seen in view (a).

Another generality noted when viewing the data in Figure 3.3.6 (b) is that mixes containing fume generally had lower permeabilities than their non-fumed counterparts. Densities did not vary in any meaningful way, mainly due to differences in starting materials. Therefore, the lower permeabilities must be related to the reduced water content and resulting higher compressive strengths.

It is concluded that unquestionably better performance can be expected from superplasticized cement formulations. Furthermore, in formulating cementitious mixtures, the w/reactive solid ratio should be taken into account, rather than simply the w/c ratio, which often gives less meaningful results.

3.4 CaCl_2 + NaCl MIXTURES

3.4.1 Introduction

The mixture BCT-1FF appeared to be a feasible grout for use in an anhydrite-rich environment; salt-saturated portland cement grouts, such as BCT-1F, though less expansive, appeared to be adequate as matrix for cementitious seal materials for some salt-saturated environments; while mixtures such as 80-081 had intermediate properties and higher versatility. Nevertheless, because of some uncertainties regarding stabilities, it is worthwhile investigating other alternative materials designed to be stable in specific environments. The previous expansive mixtures were based upon formation of ettringite as the expansive agent. However, most bedded salt repository horizons, except for anhydrite members, are typified by sulfate activities in the rocks and associated brines which are much lower than those of the chlorides, giving rise to the potential for metastabilities of sulfate-containing phases. Field performance could be a problem if the expansive stress generated by a sulfate-containing phase is degraded with time. In a related study (Ogawa and Roy, 1981) we also established the effects of temperature on limits of expansive phase formation and stability, over a limited pressure range.

The approach in design of typical oil well cements has been to saturate cementitious mixing liquids with sodium chloride to counterbalance the high activities of sodium chloride in such salt-rich horizons. Slight expansive properties are typical of such cementitious materials. Mixtures studied previously in the laboratory, which contained both NaCl and CaSO_4 , usually formed

ettringite, and after extended curing began to develop some calcium monochloroaluminate hydrate, Friedel's salt (Roy et al., 1981, mixture 80-081). The high-lime fly ash used in these mixtures was reactive, containing significant amounts of alumina beyond the alumina (and Fe_2O_3) in the cement phases available for formation of AFt (ettringite) or AFm (Ca monosulfoaluminate and/or Friedel's salt) phases, gehlenite hydrate or other calcium aluminate hydrates (see also Grutzeck et al. (1981b)). The initial curing solution used for mixture 80-081 was saturated calcium hydroxide solution (Roy et al., 1981), and because of the apparently high negative free energy of formation of ettringite, the latter phase persisted despite the presence of chloride ions [which were also partly depleted through diffusion into the curing solution (Goto and Roy, 1981)]. After longer periods (56 to 90 days) some Friedel's salt was also apparent in the product of curing in sealed vials. Particularly when exposed to a brine having high NaCl activity, extensive Friedel's salt was present in the product (Wakeley et al., 1981a,b).

The probable relations of phases may be expressed in a schematic composition diagram of the system $\text{C}_3\text{A}-\text{CaSO}_4-\text{CaCl}_2$, as presented in Figure 3.4.1. Projections of phases containing water are shown on this base composition triangle. At all times in the cementitious mixtures studied, sufficient water is usually present to form the named hydrates rather than anhydrous phases, at moderate temperatures.

Conventional portland cement pastes normally contain insufficient SO_3 for complete reaction of an alumina (and iron oxide)-containing phase to form ettringite or even monosulfoaluminate (shaded area in Figure 3.4.1 labeled conventional cement). As the aluminate phases in cement (including C_4AF) react, ettringite is formed at an early stage on surfaces; later, as the sulfate (gypsum) is depleted, reacting with additional aluminate to form monosulfate. Long-term cement hydration products usually contain mixtures of the monosulfate with other calcium aluminate hydrates (some of which are partially carbonated); and alumina and iron oxide are also contained as a solid solution component in C-S-H.

The second area of interest is labeled in Figure 3.4.1 as a sulfate-chloride-rich cement. The mixture is typical of what has been described in this report for aluminate-enriched experimental mixtures containing both fly ash (or, to a lesser extent, blast furnace slag) and salt. The obviously preferred chloride "salt" as a component of Friedel's salt is CaCl_2 , which may be used directly, or it may be obtained indirectly from the reaction of $\text{NaCl} + \text{Ca}(\text{OH})_2$, in which case Friedel's salt and NaOH are reaction products.

Figure 3.4.1. Schematic composition diagram of potential phase relations in the system C_3A - $CaSO_4$ -'"chloride'".

The mixture 80-081 was such a "sulfate-chloride-rich" cement, as discussed above. The calcium trichloroaluminate hydrate equivalent of ettringite (shown as an "end-member" on the composition triangle, Figure 3.4.1) is not stable at temperatures much above normal room temperature, and was not identified in 80-081 products. In fact, even the ettringite formed in 80-081 after long curing periods in contact with $\text{Ca}(\text{OH})_2$ solution was depleted in sulfate, and contained appreciable silica, apparently as partial replacement for sulfate, but very little chloride. In order for phases such as ettringite to form, proper proportions of the constituents must be available: i.e., CaSO_4 , C_3A (or Ca^{++} + aluminate, ferrite, etc.), and water.

3.4.2 Rationale for Mixtures

In order to design seal materials having the greatest potential for stability, or more particularly, for long-term durability, it is necessary both to understand the phase relations, and to determine the effects of any likely phase transformations on physical and mechanical properties. This has been discussed partly in the previous sections. Since slightly expansive materials have been formed from NaCl-saturated mixtures, it is possible that expansion will be generated from CaCl_2 -containing mixtures as well. Referring to the diagram of Figure 3.4.1, CaCl_2 appears to be the preferred constituent to NaCl, from the standpoint of phase stabilities, if the potential for rapid setting can be controlled. Furthermore, it is likely that the high chloride activities present in CaCl_2 -containing mixtures would be in equilibrium with the Cl^- activities in the surrounding rock and brines, enhancing interfacial stability of such a system.

As the Friedel's salt forms slowly from the CaCl_2 in solution in the pore fluids, the Ca ions, and the liberated aluminate ions from the fly ash or slag, slight expansion should be generated. The formation of an AFm phase, and absence at elevated temperatures of a stable chloride end member AFt phase (see Figure 3.4.1) would enhance the above product's volume stability, since no AFt (Cl-ettringite-like phase) to AFm transformation would occur. After the mixture is placed, it should expand slightly as available water is used by the calcium aluminate and calcium silicate hydrate processes. Expansion would eventually cease in the dry environment which typically might be found in a salt repository. Should brine begin to intrude into the interfacial region between rock and seal material, it would cause the mixture to swell slightly as additional Friedel's salt was formed via continuing hydration. This expansion would fill any annular

space; the potential for self-sealing of annular spaces is therefore built into the cement. Even though the expansive forces due to Friedel's salt formation are less than those of ettringite formation, such materials have the potential advantage that in a chloride environment the expansive stress will not be lost. There are, however, some uncertainties about the mechanical properties characteristic of the platy microstructures of Friedel's salt compared with needle-like habit of ettringite, the latter generally considered superior.

In design of all three mixtures described below, nearly the entire aluminate content of the mixtures has been taken into account. The cements have been designed to produce either the room-temperature stable $3\text{CaCl}_2\text{-AFt}$ (ettringite-like) or $1\text{CaCl}_2\text{-AFm}$ (Friedel's salt) phase. In addition to these mixtures, others have been designed which are intermediate to pure CaSO_4 and have been designed which are intermediate to pure CaSO_4 and pure CaCl_2 mixtures.

3.4.3 Formulations

The compositions of the three mixtures under study are given in Table 3.4.1. The source and/or percent of chloride present differ in the three mixtures. Compositions of the starting materials are given in Appendix A.

The amounts of CaCl_2 required to produce either the AFt or AFm phases described previously were calculated from the percentage alumina in the mixtures as follows:

<u>constituent</u>	<u>wt, g</u>	<u>% Al_2O_3</u>	<u>total wt Al_2O_3, g</u>
cement	60	(3.5)	2.1
silica fume	10	(0.05)	negligible
class C fly ash	15	(17.4)	2.61
class F fly ash	15	(27.0)	4.05
			<hr/>
			8.76g total

For the purpose of this calculation the rest of the contents were assumed to be inert fillers. The number of moles of Al_2O_3 present per 100g of the constituents above is approximately 0.086; for complete conversion to ettringite or a CaCl_2 equivalent AFt phase, 0.258 moles of either CaSO_4 or CaCl_2 is required. In this case, 28.6g of CaCl_2 would be required for the AFt phase and 9.53g for the AFm (Friedel's salt) phase. Because 100% reaction of Al_2O_3 is not expected, the mixtures in Table 3.4.1 deliberately contain slightly less than the required

Table 3.4.1. Mixtures for salt repository strata.

		mixture		
	code no.	82-02 3X CaCl_2	82-13 1X CaCl_2	82-14 NaCl
class H cement	H-9	49.02	55.83	53.78
Litepoz	B15	12.27	14.00	13.44
Ohio fume	B51	8.17	9.30	8.96
fly ash	B25	12.25	14.00	13.44
C 109 sand	C38	89.87	102.35	98.59
NaCl	P05			10.37
CaCl_2 (anhydrous)	P07	18.30	6.95	
citric acid	P27	0.20	0.93	
superplasticizer	A41	0.82	0.93	0.90
defoamer	A27	0.3*		
water	E01	23.0	32.57	25.21
w/c		0.47	0.58	0.47
w/s		0.23	0.33	0.25

*drops

amounts of CaCl_2 or Cl derived from NaCl to produce the required phases. The C-S-H should incorporate some of the alumina while additional sulfate and carbonate ions would probably enter into solid solution with the Cl in the AFt or AFm phases, thereby requiring less chloride.

For the same reason, iron oxide was neglected in the calculation, to keep the mixture slightly deficient in $\text{CaCl}_2 \cdot x\text{H}_2\text{O}$. A strong retarder, citric acid, was used in order to counteract the accelerating effects of large amounts of CaCl_2 . Interestingly, the 3X CaCl_2 mixture (82-02) needed much less citric acid than the 1X CaCl_2 mix (82-13) to prevent rapid setting. The NaCl functioned as a retarder in mixture 82-14.

Samples of the three mixtures were cast as 50.8-mm cubes and cylinders 25.4 by 50.8-mm long, after mixing according to modified ASTM C 305 procedures (see section 3.5.3). The CaCl_2 was first dissolved in the water and allowed to cool to room temperature. The high-range water reducer was added next, followed by the silica fume, the other solid materials, and sand in sequence, with specified mixing between additions. These samples were cured for 1-2 days at temperature in sealed molds. Upon demolding, samples were cured in either WIPP-B brine* or at the vapor pressure of water above the same brine solution.

Additional samples of each mixture were cast in 50.8-mm diameter stainless steel cylindrical molds (rings) to gain information on expansion, and for restrained permeability tests. These samples were also aged in brine or water vapor at the vapor pressure above brine, as before.

3.4.4. Results

Compressive Strength and Bulk Density. Compressive strength and bulk density for the three mixtures are given in Tables 3.4.2 and 3.4.3. The strengths of mixture 82-02 (3X CaCl_2) are strongly temperature-dependent, being higher at higher temperatures, as are the initial rates of strength development. Mixture 82-13 (1X CaCl_2) has similar strength development, but the strengths of the 90°C samples are slightly lower than their 60°C counterparts. The data for mixture 82-14 (containing NaCl) also show strength increase with time, but at a much lower rate than either 82-02 or 82-13 (NaCl is a retarder when used in high concentrations). However, the results are not entirely straightforward, as some samples apparently have a dip in strength development at 14 days. Values at

*see Table 2.2.6 for composition of the brine.

Table 3.4.2. Compressive strength of chloride mixtures (MPa).

specimen age (days)	cure temp. (°C)	mixture		
		82-02	82-13	82-14
3	38	11.8	17.4	28.7
	60	21.6	52.5	60.7
	90	43.6	35.9	31.8
7	38	19.0	33.7	35.4
	60	32.5	72.7	51.7
	90	64.4	64.6	34.9
14	38	17.3	34.7	30.6
	60	32.9	45.2	43.2
	90	26.9	71.8	36.8
28	38	38.8	50.8	46.9
	60	40.0	47.5	60.0
	90	53.5	47.1	45.1

Table 3.4.3. Bulk density of chloride mixtures (g/cm³).

specimen age (days)	cure temp. (°C)	mixture		
		82-02	82-13	82-14
3	38	1.81	1.90	--
	60	1.89	1.85	--
	90	1.95	1.82	1.77
7	38	1.85	1.77	2.02
	60	1.95	1.74	2.06
	90	1.98	1.82	1.75
14	38	1.91	1.79	1.72
	60	1.96	1.78	2.05
	90	2.00	1.81	1.74
28	38	1.92	1.82	1.96
	60	1.92	1.83	1.96
	90	2.00	1.84	1.72

28 days seem to cluster between 38 and 60 MPa, which seems to suggest a relative lack of sensitivity of the mixtures to the source and of chloride present.

Permeability. Two preliminary studies of permeability of the 82-02 mixture were carried out after about one week of curing. One sample consisted of a solid 50.8-mm specimen cast in a stainless steel ring and subsequently cured in saturated WIPP-B brine. The second sample consisted of the 3X CaCl_2 mixture mixed with half as much halite aggregate of 4.75 x 2-mm size. This sample was cured in air with >95% rh. After one week the solid disk was laced with surface cracks. However, this sample's permeability to brine was quite low. No liquid had permeated the sample. After approximately two days at 100-300 psi brine pressure, the pressure was increased to 400 psi. Once established, the flow rate was very low. In contrast, the salt aggregate sample showed immediate flow to brine once pressure was applied, possibly due to the solubility of the aggregate at elevated pressure. The fact that the flow rate decreased with time was encouraging. At the termination of the experiment the flow was $\sim 6 \times 10^{-2}$ darcys and falling. This was the first salt aggregate sample to give a flow rate slow enough to be measurable (others failed immediately under pressure). Additional data for all three mixtures are given in Table 3.4.4. The impermeability of mixture 82-02 was reconfirmed. The salt mixture (82-14) also had a low permeability. The 1X CaCl_2 mixture designed to produce Friedel's salt, on the other hand, showed rapid flow.

Microstructures: SEM. SEM images of the 3X CaCl_2 paste hydrated in E17 brine for 5 to 7 days at 38°C are given in Figure 3.1.2. The mix was expansive (could see macro effects in the sample), and the abundance of Friedel's salt (x-ray diffraction confirmed) lends support to this expansive character, which is strongly suggested by the crystal development shown in Figure 3.4.2. View (a) is comprised of the single needle, blade- or plate-shaped area found in the sample. However, rather than approximate an ettringite composition, these crystals are rich in Ti, S, and Ca, with minor amounts of Si and Cl. The hexagonal plates shown in views (b) and (c) are more typical of the developing AFm phases. In view (b) one sees the development of Friedel's salt having a massive irregular platy nature, with patches of C-S-H honey-comb between the plates. A fly ash void can be seen in the upper left hand (ULH) corner of the photograph. The AFm chemistry is predominantly Ca, Cl, Al, Fe, and Si. The Friedel's salt pictured in view (c) has the more classic development of hexagonal plates. Here crystal

Table 3.4.4. Permeability data for salt strata mixtures
cured at 60°C in WIPP-B* brine (darcy $\approx \mu\text{m}^2$).

cure time (days)	formulation		
	82-02	82-13	82-14
29	--	rapid flow	$\sim 10^{-7}$
41	$<10^{-8}$	--	--
45	--	--	$\sim 10^{-7}$
48	$<10^{-8}$	--	--

*See Table 2.2.6 for composition.

Figure 3.4.2. SEM images for 38°C brine-cured samples of mixture 82-02.

(a)

(b)

(c)

growth probably occurred in an open space or pocket. Its chemistry is also Ca, Cl, Si, Al and Fe. Again, C-S-H can be seen binding some of the plates together. In Figure 3.4.3 are presented additional data for the 3X CaCl_2 mixture, but for samples cured for five days at room temperature at the rh above saturated E17 brine (views a-c), and at 38°C in saturated NaCl brine (views d-f), respectively. In each case the morphology of the AFm crystals is nearly the same. The hexagonal plate development in (views a-c) is ubiquitous, but this sample was taken from near the surface. Most everything in the pocket shown in view (a) is covered by some crystals. The round fly ash spheres are evidently covered by these crystals and in some instances are being held together by them. Close-ups of various areas are shown in views (b) and (c). C-S-H is again evident between the hexagonal plates, holding them together. In all cases, the chemistry of the plates is as follows: Ca, Cl, Si, Al, Fe, with occasional traces of K and Ti. The development of the hexagonal Friedel's salt in views d-f is less striking. This may be due in part to the area of the sample investigated. The previous sample was taken from near the surface, while this one, which was cured in NaCl brine, was taken from deeper in the sample. All three views show hexagonal plates development ranging from the very crystalline rosettes in view (d) to the more massive matrix material view (e), and containing C-S-H (view f). The chemistry of the view (e) crystals, presumably laths and plates on edge, is Ca, Cl, and Si. This may be an AFm phase. The chemistry of the plates in view (f) consists of Ca, Cl and Al, as expected for Friedel's salt formation.

Phases Present: X-ray Diffraction. X-ray results show the presence of significant Friedel's salt (PDF #19-201) at all times in the CaCl_2 mixtures. The reduced relative intensity of peaks for Friedel's salt in samples of the NaCl salt mixture indicate that the amount is greatly reduced relative to CaCl_2 mixes. Its presence is questionable in all samples of mix 82-14 cured at 90°C. Gypsum (PDF #21-816) appears in 3-day samples of 82-02, disappearing at longer times; and in 38° samples of 82-14, diminishing with both higher curing temperatures and longer time. Tetracalcium aluminate carbonate (PDF #14-83) formed in CaCl_2 mixes only, increasing with both higher temperature and longer time as calcium chloride 6-hydrate (PDF #26-1053) decreases. Ettringite remains until 28 days at 38° in 82-02 and 82-13 samples, but is not detectable at increased time or temperature, nor in NaCl samples. $\text{Ca}(\text{OH})_2$ is minor but detectable in samples of 82-02 and 82-14 only at 38° up to 14 days hydration. C_2SH (PDF #29-372), a phase which imparts

Figure 3.4.3. SEM images of mixture 82-02 cured in various environments at room temperature and 38°C.

(a)

(d)

(b)

(e)

(c)

(f)

low strength to cured pastes with a high Ca:Si ratio, appears to be a constituent of all samples, especially those from higher temperatures, but its identification is tentative. See Table 3.4.5 for a summary of phases detected by x-ray diffraction.

Restrained Samples. Mixtures 82-02, 82-13, and 82-14 cast in 50.8-mm ID stainless steel cylindrical molds (rings) were allowed to cure one day at temperature, after which they were immersed in simulated WIPP-B brine (E17) or placed in the air environment at the relative humidity over the brine to continue curing.

Table 3.4.6 presents observations of both the restrained rings and equivalent brine-cured bars for mechanical properties tests. Of the three mixtures cured in the air environment, only the 1X CaCl_2 mixture (82-13) exhibited shrinkage (the 38° and 60°C samples were loose in their rings). All brine-cured samples, with the exception of the 41-day cured 82-13 samples, were still tightly held in their respective rings. Of the unrestrained bars, only the bar of 82-02 cured in brine at 38°C showed visible cracking at the time of observation. These data demonstrate that an expansive formulation will seal, and that the degree of sealing is a function of the degree of expansion. Apparently the 82-13 samples shrink somewhat with time or do not expand very much even when immersed in brine.

Dynamic Young's Modulus. Data for the dynamic Young's modulus of mixtures 82-02, 82-13 and 82-14 are presented in Table 3.4.7. The values generally increase in magnitude with both time and temperature. The single exception is the temperature dependence of mixture 82-13 at 90°C. Its values increase with time, but are lower than the 60°C counterpart. This behavior was not observed at such low temperatures but occurred in other materials at 250°C.

3.4.5 Discussion

An expansive cement should be an asset in plugging salt strata since the host rock salt is deformable. For this reason a series of conventional potentially expansive cementitious materials (containing 7-18% CaCl_2) were formulated and tested, in parallel with a high-NaCl content mixture.

The high chloride ion activity of such cements should also inhibit the dissolution of NaCl from the host rock. Mixtures containing sufficient CaCl_2 to react with nearly all of the aluminate to form either Aft or AFm phases have

Table 3.4.5. X-ray diffraction phase data for salt strata mixtures.

cure time (days)	temperature, °C		
	38°	60°	90°
<u>82-02: cement + fly ash + fume + 3CaCl₂</u>			
3	quartz remnant cement Friedel's salt ettringite NaCl AFm* C-S-H CaCl ₂ ·6H ₂ O Ca(OH) ₂ gypsum	quartz remnant cement Friedel's salt NaCl gypsum C-S-H AFm*	no data
7			
14	quartz Friedel's salt remnant cement C-S-H NaCl AFm* ettringite CaCl ₂ ·6H ₂ O gypsum	Friedel's salt quartz remnant cement C-S-H NaCl AFm* quartz CaCl ₂ ·6H ₂ O	quartz Friedel's salt remnant cement AFm* C-S-H CaCl ₂ ·6H ₂ O NaCl gypsum
28			
<u>82-13: cement + fly ash + fume + CaCl₂</u>			
7	Friedel's salt quartz remnant cement C-S-H ettringite NaCl CaCl ₂ ·6H ₂ O	Friedel's salt quartz remnant cement NaCl CaCl ₂ ·6H ₂ O gypsum	
14	Friedel's salt quartz remnant cement C-S-H ettringite NaCl CaCl ₂ ·6H ₂ O gypsum AFm**	Friedel's salt quartz remnant cement C-S-H NaCl CaCl ₂ ·6H ₂ O gypsum AFm**	
28			
<u>82-14: cement + fly ash + fume + NaCl</u>			
7	quartz remnant cement C-S-H NaCl Friedel's salt gypsum Ca(OH) ₂		quartz remnant cement C-S-H halite Friedel's salt
14		gypsum remnant cement C-S-H NaCl Friedel's salt gypsum Ca(OH) ₂	
28			

*C₄A $\bar{C}$ H₁₁. **AFm--tentative presence of C₄A $\bar{C}$ H₁₁ at 28 days.

Table 3.4.6. Restrained and unrestrained curing of salt strata mixtures.

time (days)	temp. °C	82-02			82-13			82-14		
		bars	rings		bars	rings		bars	rings	
			wet	dry		wet	dry		wet	dry
18	38	longitudinal*	ok**	ok						
	60	cracks								
	90	ok	ok	ok						
22	38				ok	ok	moves ***			
	60				ok	ok	in ring			
	90				ok	ok	moves in ring ok			
24	38								ok	ok
	60							ok	ok	ok
	90							ok	ok	ok
29	38							ok		
	60							ok		
	90									
37	38	longitudinal	ok	ok						
	60	cracks	ok	ok						
	90	ok	ok	ok						
41	38				ok	ok	moves in			
	60				ok	moves in	ring			
	90				ok	moves in	ring			
43	38						moves in		ok	ok
	60						ring	ok	ok	ok
	90						ring	ok	ok	ok
48	38							ok		
	60							ok		
	90									

*Cracking due to expansion.

**Signifies that sample is tight in ring--apparently due to expansion.

***Sample has shrunk.

Table 3.4.7. Dynamic Young's modulus (10^6 psi)* of NaCl and CaCl₂ mixtures.

mixture	curing temp. (°C)	curing, days									
		1	5	8	15	17	21	23	28	32	43
82-02	38	longitudinal cracks, no reasonable measurements									
	60					3.77			3.84		
	90					3.98			3.99		
82-13	38						3.65			3.82	
	60						4.27			4.26	
	90						4.12			4.21	
82-14	38	3.36	3.93	4.02	4.28				4.40		
	60	4.17	4.51	4.60	4.73				4.82		
	90							3.31			3.33

* 10^6 psi = 6.8 GPa.

produced materials with reasonable properties. The addition of large quantities of CaCl_2 has not significantly compromised the mixtures' properties; permeability is low in the basic materials. An expansive mixture designed to produce Friedel's salt (chloroaluminate) as the expansive agent seems to hold considerable promise, and in ways may be superior to the expanding cementitious mixtures discussed in part one of the report. Longer term studies with additional mixtures containing varying amounts of CaCl_2 , NaCl , and CaSO_4 should provide a more full evaluation, establishing phase relationships between the AFt and AFm phases, and determining the effects of activities of component ions from the host environments. This understanding will help to better predict and control the long-term behavior of such expansive cements.

3.5 CEMENT-BASED COMPOSITES/CONCRETE CONTAINING AGGREGATE FROM EVAPORITE STRATA

3.5.1 Selection of Aggregates

Coarse aggregates representing five different lithologies were chosen for their specific properties to simulate mined-out rock in cementitious composites/concretes. Mineralogy and physical and mechanical tests of these rocks were summarized in section 2.0. Preliminary experiments included all five types of coarse aggregate.

Properties of early samples showed that the composites with mudstone and sandstone from the Los Medanos site were the least promising, although the cement-based grout did form a bond to these aggregates. After confined curing, which avoided cracking via expansion of clays, the mudstone composites had low permeability to brine. We were unable to test the compressive strength of composites of mudstone from confined curing, however. The very low strength and high permeability of the Santa Rosa sandstone made it unsuitable for aggregate in concrete to be used as structural backfill.

Our experiments showed that it was possible to bond tailored cements to these rocks, so that any penetrations through such soft clastic units can be filled and sealed to the equivalent of the host formation. But additional experiments concentrated on bedded salt and anhydrite, more representative rock types; and on dolostone aggregate, composites of which, not surprisingly, exhibited the highest strength (Wakeley and Roy, 1982a). Data from tests of the low-strength composites were reported previously (Wakeley et al., 1981a).

3.5.2 Concrete Mixture Formulations

Of the many mixtures we have tested for use in evaporite strata, two mortars and two grouts were chosen as matrix for composites. Each cementitious formula contained either NaCl (3 of the 4) or CaCl_2 , added to the mixing water. One of the grouts in fact was mixed with E17 brine (simulated WIPP-B). Components of each mix are listed in Table 3.5.1. The NaCl grout was introduced in section 3.1. NaCl and CaCl_2 mortars are described more fully in section 3.4. As mentioned previously, most of the experimental composites were made with one of three coarse aggregates: dolostone, mixed with both mortars and both grouts; crushed bedded salt, with the salt-containing mortar and brine-mixed grout; and anhydrite, with grout. Table 3.5.2 summarizes these combinations.

The design and testing of mixes B, C, and D were discussed in previous sections. The brine-mixed mortar was included to represent a standard field practice. Naturally-occurring brines are used routinely for mixing cementitious materials for plugging boreholes in evaporites (Wakeley et al., 1981b).

3.5.3 Casting and Curing Composites

Composites in row B of Table 3.5.2 were cast as pre-placed aggregate concrete. The aggregate was rodded into standard 51X 102-mm bronze molds, the inner surfaces of which had been coated with a Teflon^(TM) releasing agent. ASTM-mixed grout was slowly poured into each gravel-filled mold, with the molds on a vibrating platform at low speed. After curing in the molds for 48 hours, the cylinders were demolded and transferred to E17 brine at the required curing temperature.

All other composites in this study were prepared as normally mixed concrete, the coarse aggregate mixed by hand into grout or mortar prepared by modified ASTM mixing methods (ASTM C 305, modified by stirring the silica fume, if any, into the mixing liquid before combining the liquid with the other cementitious components; this modification is necessary due to the very high surface area and surface charging of this material, and is a routine procedure in our laboratory when fumed silica is used). Concretes were tamped into the molds. Mold size and preparation, precure, and other practices were as described above.

Additional samples of most composites were cast in prepared stainless steel sleeves (no releasing agent) of 51 x 51-mm. Containing salts, these mixes were expansive enough to seal themselves into these restraining sleeves as they cured. Samples were designed to fit the apparatus for measuring permeability. Use of

Table 3.5.1. Components of grouts and mortars used for composites with evaporite-sequence aggregate.

A) <u>Brine-mixed grout, 82-08</u>			B) <u>NaCl grout, 81-G81</u>
<u>Component</u>	<u>weight, g</u>	<u>Code No.</u>	Same as A), using 29.4g deionized H ₂ O instead of brine (see section 3.1).
class H cement	68.0	(H-09)	
class C fly ash	22.9	(B44)	
calcium sulfate	8.34	(A40)	
reagent NaCl	4.05	(P05)	
plasticizer (D-65)	1.10	(A50)	
defoaming agent	0.04	(A27)	
E17 brine (WIPP-B)	42.7	(E17)	
C) <u>NaCl mortar, 82-14 (see section 3.4)</u>			D) <u>CaCl₂ mortar, 82-02</u>
<u>weight, g</u>	<u>Component</u>	<u>Code No.</u>	<u>weight, g</u>
48.0	class H cement	(H-08)	48.0
12.0	class C fly ash	(B15)	12.0
12.0	class F fly ash	(B25)	12.0
8.0	silica fume	(B51)	8.0
88.0	sand (ASTM C-109)	(C38)	88.0
9.26	reagent NaCl	(P05)	--
--	reagent CaCl ₂	(P07)	17.92
0.80	plasticizer	(A41)	0.80
--	defoamer	(A27)	0.05
--	citric acid	(P26)	0.20
21.6	deionized water	(E01)	22.5

Table 3.5.2. Combinations of aggregates and cementitious formulations.

	dolostone	halite	anhydrite
A) brine-mixed grout, 82-08	X	Y	
B) NaCl grout, 81-091	Y		Y
C) NaCl mortar, 82-14	X	X	
D) CaCl ₂ mortar, 82-02	X		

x = samples at 38° and 60°C; y = samples at 38°C.

El7 brine as the permeating fluid for these composites avoided much dissolution of water-soluble components.

Cylinders of each mix were cured at 38°C until the desired test date. Additional cylinders of both salt-mortar concretes, of brine-grout concrete with dolostone aggregate, and of CaCl_2 -mortar concrete were cured at 60°C (see Table 3.5.2).

3.5.4 Testing Composites: Methods and Results

The first focus of the studies of these cement/rock materials was the strength of the composites. Compressive strength of the cylinders, measured according to ASTM C 39, indicates in a relative way the strength of the bonds between grout or mortar and rock. Of course the measured strength value depends on many factors. Sample size and shape; the strength of the cured mortar and the rock individually; the shape and distribution of aggregate particles; and testing-machine settings all affect the quantification of compressive strength. The variables were minimized by using one sample size, one range of aggregate size, etc., and one operator to complete these tests. Values for compressive strength of grout concretes (A and B above) and mortar concretes (C and D above) are given in Table 3.5.3.

Bulk density was measured and porosity calculated for some composites on material derived from the cylinders after compression testing. Samples of the cured grout or mortar fraction of each composite were prepared for x-ray powder diffraction, ground and sieved to -100 mesh. Some samples were mounted for study as a slurry with collodion; most were packed dry into specially made sample holders in an attempt to avoid preferred grain orientation. Table 3.5.4 lists bulk density values. Crystalline phases identified by x-ray diffraction are essentially the same as those recognized in diffraction patterns from the mortars or grouts alone (see section 3.1 for discussion of phase composition relative to curing time and temperatures). Samples of brine-mixed grout containing dolostone aggregate also included Ca(OH)_2 .

Thin sections were prepared for optical microscopy of NaCl grout and mortar with dolostone aggregate. After one month of curing, the grouted dolostone showed an extensive zone of crystal growth at the interface between grout and rock. This zone was not obvious in the mortar concrete, although the contacts were continuous. [The latter sample had been cured in a Ca(OH)_2 solution, not in brine as had the others, so we had not expected the interaction to be the same.]

Permeabilities to brine were tested for many of the composites. In general,

Table 3.5.3. Compressive strength (MPa) measured for composites with NaCl and CaCl_2 .

		curing time* (days)			
		7	14	28	56
A)	brine-mixed grouts				
	82-02 dol		17.2	31.6	
				30.3 (60°)	
	82-08 hal		9.4	9.5	10.8
B)	NaCl grout				
	81-081 dol		26.1	20.0	38.2
	81-081 anh			21.3	28.6
C)	NaCl mortar				
	82-14 dol	25.1		21.9	
				30.3 (60°)	
	82-14 hal			14.0	
				11.7 (60°)	
D)	CaCl_2 mortar				
	82-02 dol	13.3		24.5	
				22.4 (60°)	

*in E17 at 38°C unless other temperature noted.

dol = dolostone aggregate; hal = halite aggregate; anh = anhydrite aggregate.

Table 3.5.4. Bulk density (g/cc) and porosity of composites.

	dolostone	halite
A) brine-mixed grout, 82-08	2.10 (14d)* 0.178	1.75 (14d) 0.204
B) NaCl grout, 81-081	2.16 (14d) 0.172	
C) NaCl mortar, 82-14	2.11 (7d) 0.135	
D) CaCl ₂ mortar, 82-02	2.25 (7d) 0.125	

*values differed very little at 28d.

Table 3.5.5. Measured permeability of concrete composite samples (38° curing)

composite type	age (days)	average permeability (darcy, μm^2)
NaCl grout + dolostone 81-081	14	4.3×10^{-7}
	28	4.0×10^{-7}
	56	$<10^{-8}$
	90	8.2×10^{-7}
NaCl grout + anhydrite 81-081	28	$<10^{-8}$
	56	7.8×10^{-8}
	90	6.9×10^{-8}
brine grout + halite		(failed)

the values for permeability of these samples approached those of the aggregate included in them. This indicated no preferred flow pathways along grout/rock interfaces, although the aggregates were not necessarily in grain-to-grain contact except in samples with pre-packed aggregate (row B in tables). Table 3.5.5 is a summary of measured permeability values.

3.5.5 Special Combinations of Cements and Rocks

In addition to the concrete-type composites described above, we have also designed and tested another type of sample, which permits measurement of flow at the interface between mortar or grout and rock (Wakeley and Roy, 1982b). The rock which is the focus of interest is cut into slabs the thickness of the desired finished sample. Using a drill press with a coring bit, cylinders of the diameter of the desired test specimen were cut from the slab. Either oil or water is appropriate for cooling during sawing and drilling, depending on the rock type in question (we used oil for evaporite rocks).

To create the surface that will become the interface, cut the rock cylinders or discs in half by cutting parallel to the side walls of the cylinder, splitting the circumference from top to bottom of the cylinder. If the diameter is greater than the height, and rock specimens thus disc-shaped, this is like splitting an aspirin tablet. Seal each half-cylinder of rock with epoxy into a sleeve or ring tooled to the required inside diameter. Avoid applying epoxy to any surface of the rock other than curved surface in contact with the sample sleeve. It plugs the pores and changes the effective pressurized area. We have used brass and stainless steel sleeves.

After the epoxy has cured, interface samples are created by filling the empty halves of the rings with the desired grout or mortar. The interface is then planar and parallel to the pressurized flow, if any. We have used this configuration with dolostone and anhydrite in contact with NaCl grout (Table 3.5.1, B). The values obtained were compared to permeabilities of grout and rock individually. We assumed that if the grout/rock interface provided a preferred flow path, the permeability values obtained would be greater than values measured for either grout or rock. Experimentally rapid flow (on the order of 10^{-3} darcy or greater) was assumed to represent sample failure, either from epoxy failure, or from shrinkage of the mortar.

All groups of samples gave permeability values in line with those of their components individually. By this method, we have determined that the interface

between these rock types and some specially designed cementitious mixes does not provide a preferred pathway for water flow (Wakeley and Roy, 1982b). Permeability values for rocks are given in Table 2.2.3; those of interface samples are given in Table 3.5.6.

3.5.6 Summary

In general, the concrete composites with the highest strength and lowest porosity are those including dolostone aggregate. Strength at 28 days is not strongly affected by temperature (38° vs. 60°). Of the grout-based composites, those mixed with brine and 81-081 matrix achieved higher strength at 28 days than do the others, the latter surpassing them with longer curing times. The CaCl_2 mortar samples gain strength slowly, but at 28 days they are comparable to the NaCl grout with either dolostone or anhydrite. At longer curing times, the CaCl_2 -containing samples lose strength through self-cracking, but the presence of coarse aggregate seems to mitigate strength loss. This is true to some extent for all composites. The strengths attained and low porosities and permeabilities of these composites suggest that under confined curing their behavior would be improved.

Table 3.5.6. Measured permeability: interface samples.

sample type	age (days)	permeability (darcy, μm^2)
NaCl grout (81-081) + dolostone	56	2.6×10^{-7}
	120	1.4×10^{-6}
NaCl grout (81-081) + anhydrite	120	$<10^{-8}$
	120	$<10^{-8}$

4 EARTH MATERIALS

4.1 INTRODUCTION

Clay minerals and mixtures of clays with other materials have been proposed as a major backfill material in radwaste repositories and their adjoining shafts primarily for the sealing properties and their ability to adsorb large amounts of radionuclides from solution (D'Appolonia, 1980b, DOE, 1980). Clay minerals that expand in the presence of water have received much attention as a potential means of sealing a borehole, especially at the rock-seal interface, thereby effectively reducing fluid flow (Pusch, 1978; Pusch et al., 1980). At the same time, the ability of these clays to adsorb various radionuclides has attracted its proponents for inclusion in the backfill area of a repository.

Despite the attractiveness of clay minerals as an effective sealant, it is recognized that the ability to attain an effective seal with clays is not nearly as feasible as with many impermeable concretes. Therefore the attention on clay minerals has shifted from short-term clay function to that of stability and longevity in the repository environment (D'Appolonia, 1980a). While clay minerals may not provide as effective a seal as many concretes, it is expected that because they are natural materials, still relatively close to their conditions of formation, that certain clays can persist for very long periods of time, providing the long-term seal required for radioactive waste repositories. Most clay minerals form at or very near the earth's surface, which is reflected primarily by their hydrous nature, and have been observed to persist for long periods of time under diagenetic, low-grade metamorphic conditions.

It is possible that proper emplacement methods reduce the differences in physical and chemical behavior between clay types, such that with sufficient forethought a satisfactory seal can be produced from virtually any clay or mixture of clays. The overriding concern is that of stability and longevity of these various clay minerals under repository conditions, for diagenetic changes in the chemistry and structural configuration of the clays have profound effects on their sealing properties. Along with the considerations of stability it is very important to determine the rates at which these clays will transform; a clay mineral outside its stability field may nonetheless alter so slowly that it retains its essential properties for the anticipated lifetime of the repository seal.

The same concerns may be raised about the potential use of zeolites in repository room and tunnel backfill. Because of their high sorptive capacities

for many cations including fission products and actinides, their potential use is considered primarily for this purpose, rather than for their capacity to restrict water movement.

Specific questions of longevity for these two main types of earth materials, the rates at which alteration can take place, and the effects on their properties are being addressed. Natural analog mineral occurrences are synthetic laboratory experiments are principal means of study.

4.2 NATURAL ANALOGS--CLAY MINERALS IN SALT

The occurrence of clay minerals in various types of evaporite deposits reflects both the influence of original mineralogy due to source and distribution along with post-depositional diagenetic alteration and neoformation reactions. Stability relationships among clay minerals deposited within these hypersaline environments have been determined primarily by earlier studies on mineral identification (characterization), while detailed geochemical work on the clays has lagged behind. Despite the unevenness of available data, several generalizations regarding the relative stability of common clay minerals can be inferred from the abundant, if somewhat dated, geological descriptions of clays in evaporites (see Droste, 1963; Millot, 1970, for reviews). One of the problems of using older studies is that perceptions of interstratified clays and methods for their characterization have changed considerably over the past 20 years.

Distribution of clay minerals in evaporite deposits of various ages mirrors the overall clay mineral distribution through time (Weaver, 1958; Droste, 1963). Carboniferous and older deposits contain a predominantly illite and chlorite assemblage while younger evaporites include smectite, and lesser amounts of chlorite. It is still uncertain as to whether this distinctive distribution of clays through time in both "normal" shale and evaporite reflects a change in provenance around Carboniferous time or is due to rate-controlled post-depositional diagenetic processes.

One problem requiring resolution is whether the clay minerals observed in evaporites are detrital in origin, precipitates from solution and deposited on the sediment surface, or authigenic precipitates that form within the interstitial voids after deposition. The cases of neoformational precipitation satisfy certain requirements for chemical equilibrium and thereby suggest a stable assemblage with the surrounding evaporite. On the other hand, even if a detrital

clay mineral flake is not in chemical equilibrium with the evaporite its continued persistence for hundreds of millions of years suggests a certain degree of long-term metastability. Nevertheless, it would be nice to resolve the question of detrital vs. authigenic origin for the clay minerals in evaporites inasmuch as it may provide some insight into alteration and precipitation mechanisms.

Clay minerals occur in evaporites as part of "mud seams," "clay partings," or "shale breaks." These layers contain only 10-35% true clay minerals, while the rest of the fine-grained material consists of dolomite, quartz, feldspars and other less common minerals (Droste, 1963). The origin of these clay seams may either result from deposition onto shallow-water sabkha deposits which is a commonly observed phenomenon in recent shallow-water evaporites, or from the slow accumulation of insoluble residues during pressure solution, as commonly seen in carbonates.

Along with the illites and chlorites that dominate the clay seams in Paleozoic evaporite deposits, random mixed-layer clays, corrensite, talc, and vermiculite have also been identified. Since most of these geologic studies pre-date the recent developments in mixed-layer clay identification it is unclear as to the type of mixed-layering present in many of these samples. It is presumed that in these studies that random mixed-layer clays are identified solely by non-integral basal spacing. These unspecified randomly interstratified clays are observed in the Salina Formation of the Michigan Basin (Droste, 1963; Lounsbury, 1963), the Paradox Basin, the Salado Formation of New Mexico (Droste, 1963), and the Permian salts of the Zechstein Basin (Fuchtbauer and Goldschmidt, 1959). Corrensite, a regularly interstratified chlorite-smectite, is present in salt deposits of Western Canada and the Permian Salado Formation of New Mexico (Droste, 1963; Grim et al., 1960; Wakeley et al., 1981a). In the Salado the corrensites are associated with the sylvite and other K-bearing ores (Grim et al., 1960). Vermiculite is identified along with interstratified illite-smectite in the Paradox Basin while talc is recognized in anhydrite beds in the Zechstein.

Smectite is a major clay mineral in Tertiary salt deposits. Usually it is referred to as montmorillonite, but there is no indication whether previous workers implied a dioctahedral expanding clay as in current nomenclature or were using montmorillonite as a generic term for all $17\text{\AA}$ expanding clays. The

di- or trioctahedral character of the interbedded smectites would be expected to shed additional light upon alteration reactions and stability relationships. Smectites are found in numerous desert basins in California and Nevada of which Searles Lake is probably the most intensively studied. Illite is the other major clay mineral found in Searles Lake drill holes, far exceeding the minor amounts of chlorite and kaolinite. Clay seams in the Miocene-Pliocene lacustrine borate deposits of California are also dominated by smectite, with lesser amounts of illite and kaolinite (Droste, 1963).

Regardless of the clay mineral assemblage, virtually all of these studies emphasize a detrital origin for the clay minerals, with minimal post-depositional alteration. Occasional minor constituents, such as talc, are believed to be authigenic. A detrital origin is supported by observable source areas, whether derived by weathering from nearby pelitic rocks or like much of the smectite formed from volcanic ash. Many of these studies also pre-date much of the recent advances in diagenesis research, such that their interpretation of clay minerals in evaporites is essentially one of minor chemical readjustment once deposited, e.g., reconstruction of "degraded" weathering products, and relative long-term stability.

More recent studies on clay minerals in evaporites which have utilized more detailed geochemical and mineralogical data suggest greater mineral reactivity within the diagenetic environment. Chlorites in the Silurian Retsof Formation of New York are higher in Mg and Si than composite "shale" chlorites which lead the authors to assume an authigenic origin (Bodine and Standaert, 1977). The homogeneity in chlorite analyses for several separate flakes suggests that the chlorite precipitates out of the hypersaline solution and is deposited (hyperhalmyrolysis) rather than diagenetic reconstitution of degraded detrital chlorites. The few analyses of other evaporite chlorites available also indicate a high-Mg clinocllore variety (Bodine and Standaert, 1977).

In contrast, the compositional heterogeneity between illite flakes in the Retsof Formation indicates diagenetic transformation ("metasomatic recrystallization") of detrital micaceous clays. These illites are also compositionally distinct from "shale illites" in that they have high tetrahedral Al, which would influence layer charge, and a high interlayer K content. The variability in the illite compositions suggests that equilibrium between the clays and interstitial brines has not been reached. Most of the compositional changes in the clays are

believed to have occurred early in the burial history, since they assume that the brine composition is constant through time, while later-stage diagenetic effects are restricted to "increasing crystallinity" (Bodine and Standaert, 1977). If brine compositions do vary through time, especially on a micro environment scale that chemical alteration need not be restricted to early diagenesis.

The clay minerals in the Salado Formation in the Permian Basin of New Mexico also indicate diagenetic alteration. The overlying shales and siltstones of the Dewey Lake redbeds are predominantly composed of interstratified illite-smectite which is 85% smectite layers (Wakeley et al., 1981a). In contrast are the regularly interstratified chlorite-smectites, or corrensites, that are found in the halite and sylvite beds (Grim et al., 1960; Wakeley et al., 1981a). These corrensites consist of 40% chlorite layers, and 60% smectite layers that are regularly intercalated with each other. The interpretation of these corrensites is that they are diagenetic transformation products of the original illite-smectite clays. The mechanism of transformation has yet to be deciphered as to whether smectite or illite or both types of layers are reacting with the brines and forming chlorite.

Geochemical studies of clay mineral stability indicate that chlorites and illites would be the relatively more stable clay assemblage at the expense of smectites in highly saline evaporite fluids. Activity diagrams of MgO , K_2O , and H_4SiO_4 systems indicate that in solutions of increased salinity and higher K and Mg activities that micas and chlorites are stable relative to smectites (Figure 4.2.1; Kastner and Siever, 1979). The effect of increased salinity is also apparent in natural analogs where in the Paris Basin, illite-smectites are found on the edge of the basin while corrensites populate the basin center, reflecting an increase in salinity during progressive desiccation (Millot, 1970). The smectites are thermodynamically unstable with respect to illites and chlorites in highly saline waters at room temperature, and even more so as temperature increases. The occurrence of detrital smectites in recent evaporites reflects the very slow rates of diagenetic transformations at surface temperatures.

The conclusion is that smectites are unstable in an evaporite system with high salinity interstitial fluids, and alter to illite or chlorite depending upon the actual fluid activity. The rates of these transformations appears to be slow, millions of years at low temperatures, though actual rate constants have not been determined.

Figure 4.2.1. Stability relationship diagrams for several common low-temperature clay minerals calculated for the activity of several cations (K^+ , Na^+ , Mg^{+2} , H^+) against silica activity (after Garrels and Christ, 1965).

4.3 ALTERATION OF CLAY MINERALS AND ZEOLITES IN BRINES AT ELEVATED TEMPERATURES AND PRESSURES

4.3.1 Introduction

Clay minerals and zeolites are candidate seal materials for any nuclear waste repository located in geological formations. While clays may be used in primary seals, both clays and zeolite minerals may be constituents of backfill: that material used to fill boreholes, mine shafts and tunnels of a repository when the repository is sealed. Backfill is also a component of the waste package in a multibarrier system of nuclear waste disposal. The primary functions of various types of backfill are as follows: a) to minimize or exclude the migration of ground water between the host geology and the waste canister system, b) to control the Eh, pH and chemical composition of the ground water within the repository environment, and c) to retard the migration of waste elements in the ground water. The list of potential backfills include expanding clays such as sodium or calcium bentonite (montmorillonite), natural and/or synthetic zeolites, desiccants such as CaO and MgO, quartz sand mixed with bentonite, powdered metals, etc. These backfills may be used singly or in combination and the nature of the backfill varies with the geological formation.

In a salt repository, geochemical and thermodynamic interactions of the rock, backfill and water may take place during the thermal period (Cohen, 1977). These interactions may take place under hydrothermal conditions if water intruded into the mined repository during the thermal period. If the sorptive backfill minerals alter by interaction with brine, prior to leakage of radioactive ions, the very purpose of using them may be lost. Therefore, the potential alteration of backfill minerals in brines of a salt repository have been investigated under certain elevated temperature conditions. These are closed-system type experiments in which the solid-liquid reactivity was investigated. Intrinsic variables such as Eh and pH varied with the bulk chemical composition and temperature conditions. These experiments of short duration will provide trends in the alterations of backfill barriers.

4.3.2 Experimental

Materials. Ten different backfill samples of clay minerals and zeolites were used in the present study. The sources and/or locations and particle sizes of these backfill samples are given in Table 4.3.1.

Table 4.3.1. Names, locations, sources, particle sizes of potential backfill samples.

Na-montmorillonite. Wyoming (WY). Source Clays Repository, The Clay Minerals Society. Pulverized.

Ca-montmorillonite. Texas (TX). Source Clays Repository, The Clay Minerals Society. Pulverized.

Vermiculite. Poole property, Enoree, South Carolina (SC). Zonotlite Divison, W.R. Grace and Company. 50-177 μm .

Phillipsite. Pine Valley, Nevada (NV). Reference zeolite 27154. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Mordenite. Union Pass, Arizona (AZ). Reference zeolite 27134. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Mordenite. Levelock, Nevada (NV). Reference zeolite 27144. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Clinoptilolite. Castle Creek, Idaho (ID). Reference zeolite 27034. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Clinoptilolite. Hector, California (CA). Reference zeolite 27024. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Erionite. Shoshone, California (CA). Reference zeolite 27104. Minerals Research, PO Box 591, Clarkson, New York 14430. <75 μm .

Chabazite. Christmas, Arizona (AZ). Reference zeolite 27124. Minerals Research, PO Box 491, Clarkson, New York 14430. <75 μm .

Methods. The montmorillonites were pulverized and homogenized by the supplier. The vermiculite sample was wet ground in a blender and sieved to obtain 50-177 μm size fraction. The zeolites were supplied as -200 mesh ($<75 \mu\text{m}$) powders. X-ray diffraction (XRD) analysis of dried suspensions of the untreated samples was carried out with a Philips diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation.

To simulate the interactions of brine with backfills in a salt repository, 100 mg of each backfill mineral was loaded into a gold capsule, 200 μl of a Mg-rich brine (designated as NBT-6a brine and composed of 10% MgCl_2 , 10% CaCl_2 , 5% KCl , 5% NaCl , and 70% H_2O) or saturated NaCl brine were added, sealed (Komarneni et al., 1979) and treated hydrothermally in autoclaves at 200° and 300°C for 4 and 12 (a few runs) weeks under a confining pressure of 30 MPa. The Mg-rich brine and NaCl brine used here are similar to the brines for Waste Isolation Pilot Plant (WIPP) experimentation, WIPP 'A' and WIPP 'B' brines, respectively (Nowak, 1980).

After the hydrothermal treatment, the gold capsules were weighed to check for the integrity of these closed-system type experiments. The gold capsules devoid of any leaks were cut and opened with a scissors in a glass vial, 25 ml of distilled water were added while washing the scissors, then the gold capsules with samples were shaken to free the sample from the gold capsule. The gold capsule, free of sample, was removed from the vial, the solid and solution phases were separated by centrifugation and the solutions were analyzed for Si and Al by atomic emission spectroscopy (AES) using a computer interfaced SpectraMetrics SpectraSpan III instrument. The solid samples were washed free of excess salts with water and 95% acetone, dried in an oven at 45°C and subjected to XRD analysis to determine the mineralogical alterations by the hydrothermal treatments.

The XRD detection limit is too high to detect minor alterations in the cation exchangers. A more sensitive way to detect alteration is probably a total cation exchange or a selective cation sorption measurement. Total cation exchange measurements are somewhat time-consuming and not as relevant as selective cation sorption measurements in the case of a salt repository. Therefore, selective cation sorption measurements were made in this study. Selective Cs and Sr sorption is defined here as the partial uptake of Cs and Sr from a 0.04N NaNO_3 solution. Twenty-five milliliters of 0.04N NaNO_3 solution containing 0.0002N CsCl and 0.0002N SrCl_2 was added to the untreated or hydrothermally altered samples,

Figure 4.3.1. X-ray powder diffractograms of hydrothermally altered zeolites in Mg-rich brine. A) Phillipsite from Nevada altered to 12Å clay mineral; B) same as A) but expanded to 17Å upon exposure to ethylene cylcol which indicated that it is smectite; C) chabazite, Arizona, altered to ~12Å clay mineral; D) same as C) but expanded to 17Å upon exposure to ethylene glycol which indicated that it is smectite.

and the mixtures were equilibrated for 24 hours at 25°C. The solid and solution phases were separated by centrifugation. The amounts of Cs and Sr adsorbed were estimated by determining the Cs and Sr remaining in solution. Cesium in solution was determined by atomic absorption spectrophotometry (AAS) using a Perkin Elmer PE703 instrument with electrode-less discharge lamp. Strontium in solutions was determined by AES.

4.3.3. Results and Discussion

Alterations of Clay Minerals and Zeolites in Saturated NaCl Brine. The mineralogical alterations of clay minerals and zeolites under hydrothermal conditions of 200° and 300°C in NaCl are presented in Table 4.3.2. At 200°C, no alteration of the two montmorillonites and vermiculite could be detected in hydrothermal NaCl brine by XRD. Among the zeolites, phillipsite completely altered to analcime while erionite altered only slightly in this brine at 200°C (Table 4.3.2). No mineralogical changes could be detected with mordenites, clinoptilolites and chabazite NaCl brine at 200°C. At 300°C, only the montmorillonite from Texas seemed to be altering to albite (Figure 4.3.2), but not the other montmorillonite. Albite may have formed by the reaction of the amorphous component in this montmorillonite with NaCl. Vermiculite did not seem to change in this brine even after treatment at 300°C. Most of the zeolites seem to be altering to albite via analcime. In fact, this type of alteration has been reported earlier (Surdam, 1977; Boles, 1977). This is not surprising because the structures of zeolites are similar to those of feldspar (Breck, 1974). Mordenites which are more siliceous than the other zeolites seem to be somewhat resistant to alteration (Breck, 1974).

Specific Sorption of Cs and Sr by Minerals Altered Hydrothermally in NaCl Brine. Clay minerals and zeolites specifically sorb ions such as Cs and Sr (Komarneni and Roy, 1980) and therefore, their alteration can also be detected by a change in their selective ion sorption properties. Specific sorption of Cs and Sr by the various hydrothermally altered minerals is given in Table 4.3.3. Selective Cs sorption decreased only in the case of phillipsite among all the minerals which were hydrothermally treated at 200°C. This is because phillipsite, an open zeolite, altered to the non-porous analcime (Table 4.3.2) which does not easily exchange its cations. The Cs sorption K_d decreased from 11,700 in the

Table 4.3.2. X-ray diffraction analyses of untreated and hydrothermally altered minerals.

Sample	Mineralogy of untreated samples	Mineralogical changes in saturated NaCl brine		Mineralogical changes in Mg-rich brine	
		200°C/30MPa	300°C/30MPa	200°C/30MPa	300°C/30MPa
Montmorillonite, WY	Montmorillonite, quartz, albite, mica and calcite	No obvious change	No obvious change	No obvious change	No obvious change
Montmorillonite, TX	Montmorillonite, cristobalite, quartz, K-feldspar and talc	No obvious change	Slightly altered to albite	No obvious change	Cristobalite formed; randomly interstratified montmorillonite/illite formed
Vermiculite, SC	Vermiculite	No obvious change	No obvious change	Some randomly interstratified vermiculite/mica (12.56Å) formed	Collapsed to form mica
Phillipsite, NV	Phillipsite	Completely altered to analcime	Completely altered to albite and analcime	No obvious change	Smectite and boehmite formed
Mordenite, AZ	Mordenite	No obvious change	No obvious change	No obvious change	No obvious change
Mordenite, NV	Mordenite and cristobalite	No obvious change	No obvious change	Some cristobalite formed?	Some cristobalite formed?
Clinoptilolite, ID	Clinoptilolite	No obvious change	No obvious change	No obvious change	Some smectite formed
Clinoptilolite, CA	Clinoptilolite	No obvious change	Moderately altered to albite and analcime	No obvious change	Some smectite formed
Erionite, CA	Erionite and quartz	Slightly altered to analcime	Albite	No obvious change	Smectite and unidentified phase formed
Chabazite, AZ	Chabazite and quartz	No obvious change	Albite + quartz	No obvious change	Smectite and quartz (?) formed

Figure 4.3.2. X-ray powder diffractograms of untreated and hydrothermally altered TX montmorillonite at 300°C/30 MPa. A) untreated; B) altered partially to albite in NaCl brine after 12 weeks; C) altered to randomly interstratified montmorillonite/illite after 4 weeks; D) altered to randomly interstratified montmorillonite/illite after 12 weeks.

Table 4.3.3. Specific sorption of Cs and Sr as affected by the hydrothermal alteration of backfills in saturated NaCl brine.

Sample	Cs sorption K_d^1 (ml/g)			Sr sorption K_d^1 (ml/g)		
	untreated	200°C/30MPa	300°C/30MPa	untreated	200°C/30MPa	300°C/30MPa
Montmorillonite, WY	410	400	510	170	200	310
Montmorillonite, TX	310	685	740	310	370	370
Vermiculite, SC	8,900	10100	990	2000	980	230
Phillipsite, NV	11700	240	15	460	25	10
Mordenite, AZ	8300	9500	7900	310	670	400
Mordenite, NV	6400	6700	30	170	370	25
Clinoptilolite, ID	3900	4800	5000	3000	6100	3500
Clinoptilolite, CA	5600	5600	4600	4700	4700	590
Erionite, CA	9500	11700	40	490	590	40
Chabazite, AZ	6600	8900	70	310	400	50

K_d^1 is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram to the amount of unsorbed Cs remaining per milliliter of the solution.

case of untreated phillipsite to 240 in the case of phillipsite treated at 200°C because of analcime formation after hydrothermal treatment. With the rest of the minerals, specific sorption either remained the same or increased slightly. The increase of specific sorption by these minerals can be attributed to a change in the nature of the exchangeable ions in these minerals by the hydrothermal treatment in NaCl brine, i.e., the natural cations such as K, Ca and Mg in these minerals were displaced by Na which competes less with Cs than either K or Ca or Mg (Ames, 1960, 1961, 1963; Tamura and Jacobs, 1961). Therefore, Cs sorption increased in these minerals which were treated at 200°C.

Specific Cs sorption increased in both the montmorillonites which were hydrothermally treated in NaCl brine at 300°C for the same reason as given above. Specific sorption of Cs decreased from 8900 K_d in the untreated vermiculite to 990 in the vermiculite which altered hydrothermally at 300°C probably because of partial chloritization by the hydrolysis of natural Mg^{2+} in the interlayers. This is a case where XRD did not reveal any mineralogical alteration while specific Cs sorption measurement indicated alteration of this mineral by hydrothermal treatment at 300°C. Specific Cs sorption decreased (Table 4.3.3) with most of the zeolites which were hydrothermally treated in NaCl brine because of alteration to analcime and/or albite. The latter minerals do not undergo cation exchange readily and therefore, Cs sorption decreased. Results of Sr specific sorption (Table 4.3.3) by the hydrothermally altered minerals closely parallel with those of the Cs sorption and can be explained similarly. Thus, the results of Cs and Sr specific sorption as well as the results of mineralogical alterations revealed by XRD of the hydrothermally altered minerals indicate montmorillonites are more resistant to alteration in NaCl brine than vermiculite or zeolites.

Alterations of Clay Minerals and Zeolites in Mg-rich Brine. The alterations of clay minerals and zeolites in Mg-rich brine under hydrothermal conditions are given in Table 3.4.4. Among the clay minerals, montmorillonites do not seem to alter in this brine at 200°C as detected by XRD. The vermiculite which has a high total layer charge (Komarneni and Roy, 1978) selectively adsorbed K from the Mg-rich brine (which contained substantial KCl) and transformed to randomly interstratified vermiculite/mica with an average c-axis spacing of 12.56 Å. The transformation of vermiculite to mica would decrease the cation exchange capacity and selective ion sorption because interlayer K from mica is not easily exchangeable. No alteration could be detected by XRD in any of the zeolites which were treated hydrothermally in this brine at 200°C.

Table 4.3.4. Concentrations of Si and Al in the capsule fluids after hydrothermal treatments.

Sample	Saturated NaCl brine				Mg-rich brine			
	200°C		300°C		200°C		300°C	
	Si (μgs/ml)	Al (μgs/ml)	Si (μgs/ml)	Al (μgs/ml)	Si (μgs/ml)	Al (μgs/ml)	Si (μgs/ml)	Al (μgs/ml)
Montmorillonite, WY	150	35	15	40	60	370	60	290
Montmorillonite, TX	45	25	<1.3	35	50	360	80	280
Vermiculite, SC	<1.3	<0.13	30	<0.13	25	180	20	<0.13
Phillipsite, NV	40	<0.13	6	<0.13	80	360	60	300
Mordenite, AZ	35	90	10	120	65	380	40	290
Mordenite, NV	70	40	30	80	35	370	50	280
Clinoptilolite, ID	15	1	15	15	65	350	35	270
Clinoptilolite, CA	50	15	<1.3	40	60	360	50	285
Erionite, CA	70	45	60	95	65	380	60	310
Chabazite, AZ	25	30	<1.3	120	80	380	60	320

Montmorillonite from Texas seems to be altering slightly in the Mg-rich brine at 300°C by forming mainly cristobalite and randomly interstratified montmorillonite/illite (Eberl et al., 1978) (Figure 4.3.2, Table 4.3.4). On the other hand, montmorillonite from Wyoming did not seem to alter by hydrothermal treatment at 300°C for 4 weeks (Table 4.3.4) or even after 12 weeks. The difference in reactivity between the two montmorillonites is not clear but may be attributed to a difference in the chemical composition (Van Olphen and Fripiat, 1979). The high charge vermiculite collapsed to form mica by selective uptake of K^+ ions from the Mg-rich brine. Most of the zeolites altered to montmorillonite (Table 4.3.2, Figure 4.3.2) in the presence of Mg-rich brine as a result of acidic conditions generated by the hydrolysis of Mg to form brucite (Komarneni, 1981), H^+ saturation of zeolite and decomposition of the zeolitic framework, followed by recrystallization to form smectite. Experiments are presently under way to test this hypothesis of smectite formation. Acidic pH develops in highly saline solutions at elevated temperatures because of changes in hydrolysis constants and the association of ion pair complexes and the pH may go down to about 3 in Mg-rich brine at 300°C (Claiborne et al., 1980; Braithwaite and Molecke, 1980). There is indirect evidence for the development of acidic conditions in the Mg-rich brine as revealed by the release of substantial concentrations of Al into solution (Table 4.3.4) when these minerals were treated in the brines. More Al was released in the Mg-rich brine than in the NaCl brine under these hydrothermal conditions because the Mg-rich brine is much more acidic than the NaCl brine (Braithwaite and Molecke, 1980). On the other hand, when these backfills were treated under hydrothermal conditions the concentrations of Si in solution are very low in the acidic hydrothermal brines (Table 4.3.4) because silica is less soluble in acidic conditions.

Specific Sorption of Cs and Sr by Minerals Altered Hydrothermally in Mg-rich Brine. The specific sorption of Cs by all the minerals excepting montmorillonite decreased (Table 4.3.5) because of mineralogical alterations (Table 4.3.2) and/or change in the negative charge balancing ions in these minerals treated hydrothermally at 200°C. For example, K^+ was selectively sorbed from the Mg-rich brine by the vermiculite and collapsed to form mica which is randomly interstratified with vermiculite at this temperature. Formation of mica led to a decrease in the specific Cs sorption because interlayer ions in mica are not easily exchangeable. Zeolites are also selective for K^+ ions (Ames, 1961) and

Table 4.3.5. Specific sorption of Cs and Sr as affected by the hydrothermal alteration of backfills in Mg-rich brine.

Sample	Cs sorption K_d^1 (ml/g)			Sr sorption K_d^1 (ml/g)		
	untreated	200°C/30MPa	300°C/30MPa	untreated	200°C/30MPa	300°C/30MPa
Montmorillonite, WY	410	-	180	170	-	250
Montmorillonite, TX	310	350	160	310	270	170
Vermiculite, SC	8900	7800	400	2000	440	130
Phillipsite, NV	11700	4200	220	460	120	330
Mordenite, AZ	8300	5100	6300	310	170	160
Mordenite, NV	6400	4400	2600	170	160	130
Clinoptilolite, ID	3900	2100	1700	3000	1400	270
Clinoptilolite, CA	5600	3600	2900	4700	1400	200
Erionite, CA	9500	5200	520	490	270	220
Chabazite, AZ	6600	3100	200	310	310	250

1K_d is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram to the amount of unsorbed Cs remaining per milliliter of the solution.

therefore they may have been mainly exchange-saturated with K^+ during the hydrothermal treatment with the Mg-rich brine at 200°C. The K^+ ions in the hydrothermally treated zeolites compete much better with Cs^+ than the natural cations (mainly Na^+ , Ca^{2+} , and some K^+) present in the untreated zeolites (Ames, 1960, 1961, 1963) and therefore the selective Cs sorption may have decreased at this temperature.

At 300°C, selective sorption of Cs^+ by all the hydrothermally altered minerals decreased (Table 4.3.5) because of the mineralogical alterations (Table 4.3.2). For example, formation of mica drastically reduced the Cs sorption by the vermiculite sample. Cs sorption K_d decreased from 8900 in the untreated to 400 in the altered vermiculite. Zeolites such as phillipsite, erionite and chabazite altered almost completely to montmorillonite in this Mg-rich brine and that is why the Cs sorption did not decrease as much as it did when these zeolites altered in NaCl brine to form albite. Albite has little cation exchange capacity while montmorillonite has high cation exchange capacity and the latter can sorb Cs. The case of phillipsite is really interesting because it altered completely to crystalline montmorillonite at 300°C and this montmorillonite has about the same specific Cs sorption capability as the untreated montmorillonites (Table 4.3.5).

The specific sorption of Sr by the untreated and hydrothermally altered minerals closely paralleled with the specific sorption of Cs at both the temperature of hydrothermal treatment and can be explained in the same fashion.

4.3.4 Conclusions

Montmorillonites appear to be more stable than vermiculites or zeolites in either saturated NaCl brine or Mg-rich brine under hydrothermal conditions which may be expected in a salt repository for nuclear waste, based upon experiments up to 84 days duration. Vermiculites altered to interstratified vermiculite/mica or mica in brines containing K. Zeolites altered to analcime and/or albite in the saturated NaCl brine but altered to montmorillonite in the Mg-rich brine. Between montmorillonites and zeolites, the former should be preferred for a back-fill in the waste package in a salt repository. However, these are at best short-term accelerated tests, and long-term stability of montmorillonite in saturated NaCl or Mg-rich brines expected in a salt repository need to be established, particularly in view of the thermodynamic considerations and natural analog occurrences previously discussed.

4.4 SALT CONSOLIDATION

It is considered that a major portion of the repository room backfill of a bedded salt repository will consist of mined-out salt from the repository, consolidated to various degrees. However, there are major difficulties in achieving consolidation in a short time, to approach the theoretical density which would be necessary to prevent substantial liquid transport through the rooms and tunnels. This necessitates that the major sealing for at least hundreds of years will probably depend upon the contribution of structures consisting of the previous categories of seal materials.

Jenks (1979) used an approach of earlier workers to develop equations describing effects of temperature, temperature gradient, and irradiation damage on migration velocity. Brine migration experiments have been conducted with salts consolidated artificially from carefully sized particles to varying densities (Biggers and Dayton, 1979; White, 1981) and upon natural cores (Baes, 1981). Biggers and Dayton demonstrated that in salts having >99% theoretical density that significant brine migration took place, primarily along grain boundaries. Therefore, the "permeability" to brine even in consolidated salts is not limited to that indicated by earlier theories and in some studies of migration of brine inclusions in single crystal halite (Olander et al., 1980).

It is expected to address the problem of salt consolidation and brine migration further in future studies.

5 STABILITY: OBSERVATIONS AND IMPLICATIONS

5.1 INTRODUCTION

The determination of potential stability of seal materials in a repository environment can be approached in a number of ways, each having factors in its favor, as well as limitations. First are experiments in which specimens of seal material are subjected to various environmental treatments. These experiments are usually accelerated tests of extreme case potential reactions in which the sample is subjected to specific solutions, temperatures and pressure. Often a shorter time exposure at elevated temperatures simulates a much longer time at lower temperatures. Actual ground water compositions may be less concentrated than the ones used, and the results may be more subtle. Nevertheless, the data are useful in postulating mechanisms of alteration, property enhancement or deterioration. A second source of information is thermodynamic data. Stability relations calculated from enthalpies and entropies of formation can give indications of ultimate long term reaction products in a relatively closed system. Experimental confirmation support the conclusions. Third are thermodynamic calculations of stable phases based on equilibrium with known groundwaters of lesser activities. Fourth are detailed kinetic studies and observations which give information on probable rates of change. The studies summarized in the following section have begun to address such different approaches.

5.2 EFFECT OF VARIOUS ENVIRONMENTS ON PROPERTIES OF CEMENTITIOUS MIXTURE 80-081

In order to evaluate the performance of potentially expansive cementitious mixtures in various environments, samples of a representative formulation (mixture 80-081) were cast as 50.8 mm cubes for unrestrained curing, as well as others cast inside 50.8-mm diameter ~40-mm high stainless steel cylindrical molds (rings) and cured in the restrained condition.

The effects of four solutions and a high-humidity air environment upon the properties of the material were investigated. These environments were thought to represent extreme conditions which might be encountered in various geologic media. The curing conditions are summarized in Table 5.2.1.

Cubes and restrained cylinders were exposed to each of the five environments listed above, at 38°C. Samples were examined after 24h, and periodically thereafter up to 180 days, to monitor the following: inception of macroscopic cracks, pH of curing solution; mineralogy via x-ray diffraction; and microstructure via

Table 5.2.1. Curing environments of mixture 80-081.

brine
saturated CaSO_4 solution
saturated $\text{Ca}(\text{OH})_2$ solution
humid air
deionized water

Table 5.2.2. Compressive strength $\pm \sigma$ of 50.8-mm cubes cured in various environments at 180 days (MPa)

curing conditions	compressive strength	$\pm \sigma(n)$
brine	101.1	1.19(3)*
CaSO_4	106.9	4.85(5)
$\text{Ca}(\text{OH})_2$	107.5	3.99(5)
humid air	89.3	5.32(5)
deionized water	109.9	3.46(5)

*Two samples were discarded due to the requirement of the $\pm 10\%$ rule. These values were 84.5 and 84.7 MPa.

SEM. Samples were photographed at 24h, at the onset of cracking and/or at 90 days of curing, and after 180 days.

The cubes cured in saturated CaSO_4 , saturated Ca(OH)_2 , and deionized water were observed to have surface cracks beginning at 7 to 14 days of curing. Cracking usually occurred parallel to cube edges, starting at an edge and progressing inward towards the center of the cube face, forming cross-shaped cracks. However, at 180 days, no cracking was observed in similar samples exposed to brine or to air. No cracking occurred in restrained-cylinder counterparts of all samples, although a volume increase was indicated by swelling of the upper (unrestrained) surface in some of the samples.

Cubes from all five curing conditions were still very strong when tested at 180d even though some had cracks. Values of compressive strength for the cubes cured ~180 days are delineated in Table 5.2.2. The samples which had shown surface cracking were also the samples with the highest values of compressive strength (saturated CaSO_4 = 106.9 MPa, saturated Ca(OH)_2 = 107.6 MPa, deionized water = 110.0 MPa). Compressive strength of one cube cured in brine was not significantly lower (101.22 MPa) but two samples had strengths of 84.5 and 85.7 MPa. The mean of the three specimens was $94.5 \text{ MPa} \pm 9.1$. The air-cured sample had partially dehydrated during curing, and its lower compressive strength (89.4 MPa) is consistent with this dehydration.

The restrained counterparts of the unrestrained cracked cube samples (CaSO_4 , Ca(OH)_2 and deionized water) were tested for permeability to water at ~180 days. These exhibited no flow of water under the test conditions employed ($p \sim 400$ psi, $t \sim 2$ to 3 days), indicating a permeability of less than 10^{-8} darcys. The air-cured sample was allowed to dry, and due to shrinkage was no longer sealed in the restraining ring.

One cube from each curing condition was reserved for x-ray diffraction studies. A small piece was removed from one corner of each of these cubes at each test date, and was freeze-dried, intended to prevent further hydration. Slurries of powdered samples were mounted on glass slides and scanned at $2^\circ 2\theta/\text{min}$ with $\text{CuK}\alpha$ radiation. Phases identified by x-ray diffraction are listed in Table 5.2.3.

These data show the similarities of phase development between the cracked samples on the one hand and the uncracked samples on the other. Notable is the nearly identical phase development in all cracked samples regardless of the curing solution. Ettringite formation requires several ingredients: lime,

Table 5.2.3. X-ray diffraction data.

time (days)	cracked			uncracked	
	CaSO ₄ -cured	Ca(OH) ₂ -cured	DI water	brine cured	high humidity
3		Ca(OH) ₂ ettringite remnant cement gypsum quartz			Ca(OH) ₂ ettringite remnant cement NaCl gypsum quartz
7				Ca(OH) ₂ ettringite NaCl remnant cement Friedel's salt gypsum quartz C-S-H**	Ca(OH) ₂ ettringite remnant cement NaCl quartz C-S-H
28					Ca(OH) ₂ ettringite remnant cement NaCl Friedel's salt C-S-H
56		Ca(OH) ₂ ettringite remnant cement quartz C-S-H*		Ca(OH) ₂ NaCl remnant cement Friedel's salt gypsum quartz C-S-H	Ca(OH) ₂ ettringite remnant cement Friedel's salt C-S-H
90					

*Small amounts of gypsum and NaCl were found at 28 days in Ca(OH)₂ and DI water-cured samples, respectively.

**C-S-H was more prominent at 28 and 56 days. Assumed to be present at 3 and 7 days.

alumina, sulfate and water. The degree of resulting expansion appears to be most related to the availability of water. However, if salt is added to the water or if the sample is allowed to cure in an environment where water is not abundant, ettringite formation is retarded or prevented; in one case the high chloride activity of the solution favors chloroaluminate formation, and in the other it lacks water. As a result, ettringite first coexists with the chloroaluminate phase (Friedel's salt) and eventually, in the case of the brine cure, completely converts to Friedel's salt by 90 days. In the air-cured sample, the conversion of early formed ettringite to Friedel's salt is slower, and both are seen to coexist at 90 days. Also of interest is the fact that gypsum is present in all of the solution-cured cements, which disappears after 3 days, except in the CaSO_4 -cured sample where it persists to 7 days. This gypsum apparently is converted to ettringite and thus is absent beyond 7 to 28 days. In the case of the brine-cured samples, gypsum persists throughout the curing history of the sample. Apparently chloroaluminate formation is favored over ettringite formation. In the air environment, gypsum is present at 3 days, but not beyond. It would seem that the air cure environment nearly mirrors the brine-free solution cure for 28 days, except that NaCl is present. At 56 days, chloroaluminate (Friedel's salt) begins to develop, and by 90 days free NaCl is no longer present.

5.3 EFFECT OF TEMPERATURE/PRESSURE AND NaCl ON ETTRINGITE STABILITY AND CHLOROALUMINATE (FRIEDEL'S SALT) FORMATION

5.3.1 Introduction

No systematic study of ettringite stability under high temperature and pressure or in salt solutions has been reported previously; however, several studies revealed the stability of ettringite in dry and moist (autoclave) conditions.

From thermodynamic studies, Mchedlov-Petrosian (1965) calculated the free energies of formation of the tricalcium aluminate mono- and trisulfate hydrates, and indicated that above 70°C at 1 atm pressure monosulfate hydrate was more stable than trisulfate hydrate (ettringite).

In separate studies in this laboratory, experiments therefore were carried out to determine the stability of ettringite under different conditions. A stationary cold-seal type hydrothermal furnace was used to examine the stability

of ettringite in both deionized water and NaCl solution, under high temperatures and pressures. The solid phases of reaction products were analyzed by x-ray diffraction and SEM. The starting material was pure ettringite prepared from solution in the laboratory. Two kinds of liquids were used: freshly decarbonated deionized water and a 20% NaCl solution. The solid phase, suspended in the liquid phase, was put into a Teflon tube, one end of which had been sealed. The other end was then sealed, and the capsule was placed in the autoclave and pressurized. Temperature was raised, keeping the pressure constant, and the sample was cured for one week after temperature and pressure became constant. After curing, the Teflon capsule was taken out of the pressure tube. The contents were filtered and the solid phase was dried in a desiccator.

5.3.2 Results and Discussion

Stability of Ettringite in Deionized Water. Figure 5.3.1 is the phase diagram for the stability of ettringite in deionized water. Closed circles show ettringite which was not decomposed, and open circles indicate decomposition to other phases. In deionized water, the decomposition temperature was between 145° to 150°C at pressures above 400 psi. This was lowered slightly at lower pressure and reached 130°C at 100 psi.

Monosulfate hydrate was a major phase formed by decomposition of ettringite, and hemihydrate ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) also was recognized by x-ray diffraction. At higher temperatures, that is 150°C, 600 psi and 150°C, 400 psi, a small amount of anhydrite was detected.

Scanning electron micrographs of the solid phase showed characteristic ettringite rods at 105°C, while at 150°C, 600 psi, pseudo-hexagonal outlines of monosulfate hydrate plates with many hexagonal holes were observed.

Stability of Ettringite in 20% NaCl Solution. In a 20% NaCl solution, ettringite was decomposed at a lower temperature, as shown in Figure 5.3.2. Though the decomposition temperature had a certain width, throughout the pressure range examined, ettringite was decomposed between 95° to 105°C, which was lower than that in deionized water by about 40°C. Decomposition product phases were mainly gypsum and Friedel's salt, and almost no monosulfate was recognized by x-ray diffraction. Scanning electron micrographs of decomposition products show large rod-like gypsum crystals and very fine irregular particles which are probably Friedel's salt.

Figure 5.3.1. Stability of ettringite under high temperature and high pressure in deionized water. Closed circles: ettringite is stable. Open circles: ettringite is decomposed.

Figure 5.3.2. Stability of ettringite under high temperature and high pressure in 20% NaCl solution. Closed circles: ettringite is stable. Open circles: ettringite is decomposed.

Detailed study is still necessary to determine the process of the decomposition of ettringite in NaCl solution, but apparently at temperatures above about 100°C at elevated pressures the combination Friedel's salt ($C_3A \cdot CaCl_2 \cdot H_{10}$) + calcium sulfate + NaOH is more stable than the combination ettringite + NaCl.

5.3.3 Conclusions

1) Ettringite was decomposed at 130° to 150°C in the range 100 psi to 600 psi in deionized water, yielding monosulfate hydrate as the main decomposition product. Hemihydrate and anhydrite were also formed. The morphology of the monosulfate hydrate thus formed was different from that in cement paste, that is, hexagonal holes and frace crystal growth were observed in the crystalline mass.

2) In a 20% NaCl solution, ettringite was decomposed at a temperature about 40°C lower than that required for decomposition in deionized water. Gypsum and $C_3A \cdot CaCl_2 \cdot H_{10}$ were the main products formed.

5.4 INTERFACE REACTIONS

5.4.1 Introduction

The contact between a cementitious plugging material and host rock has been postulated as being a critical area for the success of a seal. Inadequate performance is believed to occur most commonly in the annular region between the plug and the face of the borehole or shaft, or else in a disturbed zone in the rock. At least two mechanisms are apparent for developing a cementitious seal. One is mechanical and the other is chemical. The first is established once the matrix hardens. From that point, the grout or concrete must necessarily remain firmly in place against the host rock to prevent annular cracking. This mechanical feature can be enhanced by using expansive cement formulations, such as those already discussed. It is important for the plug to maintain contact with the wall rock from the initial set, at least until chemical bonding is established. (The exceptions occur in certain seal designs, where expansion of a swelling clay component, against concrete and rock, will provide the back-up seal).

Current research on pozzolanicity in concrete materials indicates that the reaction between a silicate rock and portland cement-based materials will most likely be very slow at room temperature, but the bond may be strong in the long term. The bonding between cement and rocks such as salt, dolostone and anhydrite

is believed to depend more upon reactions between the calcium aluminate hydrate-substituted AFt and AFm phases such as ettringite and Friedel's salt for its development. Since the quantity of aluminates in the cement is limited (<20 wt %) this controls the extent of such phase formation and consequent bonding. However, the substituted aluminate hydrates, particularly ettringite, are expansive, and especially in the interfacial region may be high in Cl^- , $\text{SO}_4^{=}$ and/or $\text{CO}_3^{=}$, these phases may swell with the addition of water, and seal any annular regions which are weak or would provide preferential pathways for water transport.

5.4.2 Interfacial Studies

In order to test these concepts, various interfacial studies have been carried out. One set was concerned with development of the chemical interface. Various mixtures were cast on silicate substrates, cured, and subsequently pulled apart, testing for strength and evidence of interfacial reaction by SEM examination. Some of these data have appeared elsewhere (Langton et al., 1980a; Roy et al., 1978). The studies confirmed the occurrence of a $\text{Ca}(\text{OH})_2$ -rich layer adjacent to the silicate substrate. Tabor (1981) has postulated that a bond involving $\text{Ca}(\text{OH})_2$ is not as strong as that involving C-S-H. Consequently, bonding should not be as strong as its potential until after the silicates in the rock react and combine with calcium hydroxide from the cement to form additional C-S-H. At elevated temperatures this happens relatively rapidly. Work by Grutzeck et al. (1981b) has shown that once established, massive $\text{Ca}(\text{OH})_2$ provides an effective barrier to diffusion of water, and fly ash glass spheres engulfed by $\text{Ca}(\text{OH})_2$ are retarded in their reaction. The existence of such calcium hydroxide layer surfaces on a plug surface in a repository shaft might prevent adequate bonding from taking place later. Experiments with lime-depleted cements are attempting to reduce such barriers to rapid build-up of bond strength between cement and wall rock.

In other studies, the evaluation of bond strength (in shear) and permeability of composite cylindrical samples of host rock filled with cementitious formulations has been made. Procedures for these tests are given in Langton et al. (1980b),

One study cast small simulated borehole plugs in cores of Castile formation anhydrite. The mixtures used were BCT-1FF (79-091) and PSU salt-free (79-080) discussed in section 3.1. Both permeability and bond strength measurements were made.

Permeabilities of these simulated borehole samples determined parallel to the cylinder axis, were commonly about 10^{-6} - 10^{-7} μm^2 (darcys) for samples cured 7 to 28 days at 35°C in a complex Mg brine (WIPP-A). Bond strength was measured by pushing out the plug. Although there are some limitations of the measurement method, the values were reasonably consistent, increasing with curing time to 28 days. Values at 7, 14 and 28 days were approximately 4.9, 7.1, and 14.2 MPa for the 79-091 mortar in anhydrite. Additional data are available in Gulick et al. (1980a).

Similar bond strength and permeability tests for mixtures 79-040 and 79-050 at 60° and 90°C were completed. Formulations for these mixtures are given in section 3.3. These mixtures were cast in quartzite and limestone cores, respectively. Again permeabilities were on the order of 10^{-6} to 10^{-7} darcys (μm^2) through 28 days for mixture 79-040 and 10^{-6} to 10^{-7} darcys (μm^2) for mixtures 79-050 through 14 days. However, at 28 days high flow rates were observed for mixture 79-050 cast in limestone. Bond strengths in shear for both mixtures are given in Table 5.4.1. The mixtures are relatively similar but their bond strengths and permeabilities are different, especially at 28 days.

What is apparent from such studies is the effect of the degree of expansion of the mixture and the composition of the host rock upon the final properties of the composite material. The BCT-1F and PSU salt-free formulations had low w/c ratios, were expansive, and moderately compatible with their host rock, and thus have comparatively low permeabilities and high bond strengths. In comparison, the formulations 79-040 and 79-050 had higher w/c ratios (the former 0.69, and the latter 1.28) and were not designed to be expansive. Consequently, the early stage properties are not as good, since bonding involves both physical and chemical components.

The sample in the quartzite cylinder (simulating sandstone or silicate strata) showed relatively good bonding and adequate mechanical properties. The reasons for the inferior properties in the limestone cylinder are not fully explained. Perhaps it is related to the very high w/c ratio.

Additional work in these areas is expected to give significant evidence in evaluating potential long term durability of key formulations. Physical expansion obviously provides a seal, and suitable chemical interaction, in the absence of physical expansion may also provide a seal.

Table 5.4.1. Shear bond strength of mixtures cast in rock cylinders (MPa).

formulation	time (days)	curing temperature, °C	
		60°	90°
79-040 in quartzite cores	14	6.27	5.32
	28	9.97	3.99
79-050 in limestone cores	14	5.25	7.56
	28	1.14	1.50

5.5 DIFFUSION STUDIES; KINETICS

Transport phenomena in a hardened cement paste are very important to its durability, potentially affecting phase and properties changes. Factors affecting permeability of water through hardened cement pastes have been discussed elsewhere (Goto and Roy, 1981; Parker and Roy, 1982).

The ionic diffusion in a given material is influenced by the interaction of many variables, including the chemical composition, porosity and pore structure of the hardened cement paste; as well as temperature, pressure and electrical potential.

Diffusion of Na^+ and Cl^- ions through thin hardened cement paste sections was determined as a function of water/cement ratio, curing time, curing temperature, and diffusion temperature (Goto and Roy, 1981). Diffusivities of Na^+ ions were found to be smaller than for Cl^- ions in the temperature range measured up to 60°C . Activation energies for diffusion were calculated, and contrasts were made with diffusion through a low porosity quartzite rock having minimal surface interaction with the diffusing species.

Diffusion coefficients for Na^+ in the range of 10^{-7} to $10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ have been measured in cement pastes in work in the laboratory (see Figure 5.5.1). Comparisons with the diffusion of divalent ions are of interest. Spinks, et al. (1952) determined the diffusion coefficient of Ca^{2+} in mortars to be $2.8 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$, while Forrester and Lawrence (1961) determined extremely low self-diffusion coefficients in calcium silicate hydrates, which ranged from 1.08 to $60.7 \times 10^{-23} \text{ cm}^2 \text{ sec}^{-1}$, following release of more rapidly exchangeable species. Recent research has demonstrated that very fine pore structures exist in certain hydrated cementitious materials of low free calcium hydroxide content (Parker and Roy, 1982). It will be important to determine if both fine pore structure and low calcium hydroxide contents can be correlated with lower diffusion rates.

5.6 PHASES STABLE WITH RESPECT TO LOS MEDANOS WATERS

The purpose of the thermodynamic calculations was to compare products of activities calculated from free energies with those calculated from groundwater compositions. If they match, the species is considered to be stable. The water compositions can thus be shown to be in equilibrium with their geologic formation, or to be undersaturated with respect to their formation or to contain ions from another source. By the same methods the stability of the seal material phases with respect to the groundwaters may be determined.

Figure 5.5.1. Diffusion coefficients for Na^+ and Cl^- in cement paste. Activation energies for diffusion are given.

As a first approximation activity coefficients were assumed to be equal to one; then activities from the mean salt method (Garrels and Christ, 1965) were included. The differences on the log activity scale were small except for the most concentrated brines in the Salado and Castile. No mean salt activities were found for Mg, so the activity coefficient of Mg continued to be assumed equal to one. Activities calculated from Debye-Hückel cannot be used beyond an ionic strength of 0.1; the ionic strength of these brines varies from 0.4-10.

The calculated activity ratios were then compared with activity diagrams. For reactions between phases for which activity diagrams were not available, relative stability was determined by calculating from known free energies of formation, the free energy of reaction, ΔG_r° :

$$\Delta G_r^\circ = -2.303 RT \log K_r$$

where R = gas constant
 T = absolute temperature
 K_r = activity product for reaction.

For instance for solution or precipitation of anhydrite:

At 25°C,

$$-2.303 RT = -1.364$$

$$\Delta G_r^\circ = -1.364 \log K_r$$

If the brine in question is stable with respect to the species of interest, the $\log K_r$ calculated from brine compositions will be the same as the $\log K_r$ from free energies, within the errors of the method. The latter may be considerable; an error in free energy of one kcal/mol makes an error of 0.7 in $\log K_r$, or a factor of five in solution composition. Errors in activity coefficient may cause up to an error of 2 in $\log K_r$.

Water analyses were from Powers et al. (1978). Na^+ , K^+ , Mg^{+2} , Ca^{+2} , HCO_3^- , SO_4^{-2} were given, Al is missing and Si is only known as a range (0-2 ppm). There were two samples each from the Magenta and Culebra dolomites, four from the Salado, two from the Castile and one from the Bell Canyon. A third analysis

from the Castile was not used because it was wildly aberrant ($\text{pH} = 1.6$). In the other samples activity ratios were consistent within each formation for each reaction considered.

Activity ratios for Na/H, K/H, Ca/H, and Mg/H are given in Table 5.5.1. Because silica concentration is only known as 0-2 ppm (maximum log silica molarity of -4.5), the activity ratios of the ions in water are not plotted on the diagrams, but are presented in Table 5.6.1.

The difference between the activity ratios for calcium and magnesium in the high-ionic-strength Salado waters, and in the other formation waters, may be an artifact of the error in activity coefficients. Particularly in the case of magnesium an error of two units in log K is to be expected. The stabilities of some mineral phases are shown in Table 5.6.2. Inaccuracies in activity coefficients mean that the method will not distinguish between anhydrite ($\log K_r = -4.1$) and gypsum ($\log K_r = -4.6$) in the most concentrated brines. In the case of the magnesium minerals, the activities found from groundwater concentrations are all near both the kaolinite-gibbsite-chlorite join and the chlorite-Mg-smectite-kaolinite join, so that either or both chlorite and Mg-smectite are predicted to be stable within the error of the method.

These results from the groundwater geochemistry support the interpretation in section 4.1 of the clay mineralogy of the Salado that the corrensite (chlorite-smectite mixed layer) found there is diagenetic in origin: the present-day brines are sufficiently high in magnesium to replace the potassium-bearing illite by magnesium-bearing chlorite. In the Dewey Lake red beds high above the salt formations, the clays are illite-smectites and presumably detrital.

The phases which are not stable throw light on the unusual mineralogy of salt formations. The calcium does not enter the clays or zeolites as in many silicate rocks, but is primarily concentrated in sulfates and carbonates. The magnesium on the other hand forms the clays and chlorite as well. Aluminum is present in very small amounts and occurs as illite and chlorite but not in smectites. Sodium is principally in halite, and potassium in polyhalite.

Table 5.6.3 shows the relative stability of Friedel's salt and ettringite in brines. Sarkar et al. (1980) discussed these compounds in an earlier report in this study. Friedel's salt is stable in these brines. Ettringite is stable with respect to C_3A in a typical brine, but hydrogarnet appears to be stable with respect to ettringite at these same water compositions.

What needs to be determined next is the relative stability of Friedel's salt, ettringite, and any intermediates.

Table 5.6.1. Molalities and activity ratios at 25°C in Los Medanos waters, calculated from compositions given by Powers et al. (1978). Activity coefficients are from the mean salt method except for magnesium for which activity coefficient is assumed = 1.

Sample Number	formation	pH	Na molality	$\log \frac{a_{Na}^{+}}{a_{H}^{+}}$	K molality	$\log \frac{a_{Na}^{+}}{a_{K}^{+}}$	Ca molality	$\log \frac{a_{Ca}^{+2}}{(a_{H}^{+})^2}$	Mg molality	$\log \frac{a_{Ca}^{+2}}{(a_{H}^{+})^2}$
22	Magenta	7.4	0.248	6.5	0.00179	4.5	0.0222	12.6	0.0111	12.8
24	Magenta	7.4	0.183	6.5	0.00256	4.6	0.0180	12.5	0.0078	12.7
23	Culebra	7.6	0.409	7.1	0.00485	5.1	0.0195	12.9	0.0115	13.3
25	Culebra	7.4	0.826	7.2	0.0155	5.3	0.0374	12.8	0.0296	13.3
3	Salado	5.5	1.196	5.9	0.0767	4.1	0.0160	9.7	2.28	11.4
4	Salado	5.4	1.931	7.0	0.774	5.0	0.0125	9.4	2.58	11.0
5	Salado	5.5	2.01	6.5	0.774	5.1	0.0130	9.6	2.55	11.2
16	Salado	5.8	2.13	6.6	1.34	5.8	0.0314	10.6	1.58	12.0
14	Castile	7.3	4.87	8.1	0.13	6.2	0.00324	12.1	0.0144	12.8
15	Castile	7.7	5.42	8.6	---	---	0.0137	13.5	0.0765	14.3
9	Bell Canyon	7.1	3.34	7.7	0.0435	5.6	0.689	13.8	0.250	13.6

Table 5.6.2. Stability of mineral phases in Los Medanos waters at 25°C. A phase is considered stable in the water under consideration if its activity produce calculated from groundwater composition is equal to that calculated from free energies within the calculated error.

Formation	Mineral				
	Halite	gypsum or anhydrite	dolomite	clays	feldspars
Magenta	no	gypsum	yes	Mg-smectite chlorite kaolinite	Na- feldspar
Culebra	no	gypsum	yes	Mg-smectite chlorite kaolinite	Na- feldspar
Salado	yes	either gypsum or anhydrite	yes	kaolinite probably Mg-smectite and chlorite	no
Castile	no	either gypsum or anhydrite	no	chlorite illite Mg-smectite kaolinite	Na- feldspar
Bell Canyon	no	gypsum*	no	chlorite Mg-smectite kaolinite	Na- feldspar

*Bell Canyon waters according to these 25°C calculations are only slightly undersaturated with respect to anhydrite; in fact temperatures in Bell Canyon formation are much greater than 25°C, therefore anhydrite is probably stable rather than gypsum.

Table 5.6.3. Stability of cement phases in brines;
brine composition from Powers et al. (1978).

"typical" brine composition	brine WIPP-A
$\text{Ca}^{+2} = 0.003\text{m}$	$\text{Ca}^{+2} = 0.0126$
$\text{CO}_3^{-2} = 0.011\text{m}$	
$\text{Cl}^{-} = 4.624\text{m}$	$\text{Cl}^{-} = 4.55$
Friedel's salt stable with respect to C_3A	Friedel's salt stable
Ettringite stable w/r C_3A	
Hydrogarnet stable w/r ettringite	

6 CONCLUSIONS AND RECOMMENDATIONS

The experimental program has demonstrated that seal materials can be designed that are suitable for rock types characteristic of a bedded salt repository environment. Cementitious materials can be tailored to take advantage of the chemistry of a particular strata, be it salt, anhydrite, dolomite or silicate. Emphasis now lies on long-term evaluation of stability of materials specific to the various horizons.

The studies carried out have led to the following conclusions:

1. It is possible to formulate cementitious seal materials which are essentially impermeable, are usually strong and which appear suitable for sealing various geologic formations existing in a bedded salt repository area.
2. Such seal materials can be designed with specific properties, to perform in a desired fashion which will take advantage of the chemistry of the host rocks.
3. Since the integrity of the seal is dependent upon the nature of the interfacial zone, combinations of physical, chemical and mechanical effects must be optimized. The chemical potential or chemical gradients should be minimized, the volume stability maintained, thermal properties matched insofar as feasible, and the bonding should be optimized as much as possible.
4. Intrinsic stability of cementitious materials may be generated by partial replacement of cement with pozzolanic materials such as silica fume and fly ash, combined with use of high-range water reducers to generate low porosity and permeability. Such materials generally are expected to have greater longevity than non-substituted counterparts.
5. Formulations which generate slight expansive stresses tend to promote initially stronger seals, since the seal is potentially both chemical and mechanical in nature. Under the correct circumstances, the expansive mechanism can be based upon Aft (ettringite) or even possibly AFm (Friedel's salt) phase formation. Other methods for generating slightly expansion, some conventional, some to be developed, may be needed for different chemical and physical environments.
6. Free Ca(OH)_2 should be reduced with pozzolans, and additional strength will usually be realized from the formation of additional amounts of the major cementing phase, C-S-H.

7. Magnesium-containing clay mineral varieties appear to be most nearly in equilibrium with the various brine environments. The selection of specific clay and zeolite-containing seal materials for best potential performance in different horizons will require additional research. Such materials will possess important properties complementary to those of cementitious materials.

8. Potential seal materials which are hybrid between cementitious materials and clays show promise, having intermediate type properties, and merit further study.

The following recommendations are in order when attempting to assure the durability of a seal in a silicate host rock: Development of a seal material-host rock bond which involves C-S-H rather than simply calcium hydroxide is important. This is likely to be achieved by using low calcium aluminate cements and reducing free lime content by reaction with suitable pozzolans. Under certain circumstances Class C fly ashes and/or granulated blast furnace slag will be desirable constituents.

Aluminate-derived hydrate phases appear to be more compatible with the host rock, when considering carbonate, sulfate or salt rocks, since such hydrated phases can accept the appropriate carbonate, sulfate or chloride ions into their structures to a larger extent than can the silicate phase, C-S-H. Silica fume should still be used to reduce free lime.

In all cases, once in place and hardened, the cementitious seal material should maintain its volumetric stability while in contact with the rock. Shrinkage should be avoided as a chemical bond develops. Most conventional portland cements in the course of hydration undergo slight shrinkage. This is minimized by keeping low water contents, and using a large proportion of aggregate. Formation of AFt or AFm phases at an early stage, increasing only slightly in amount with time should counterbalance the tendency to shrink, providing volume stability. A slight stress is advantageous in maintaining this stability. The possible changes incurred when different formulations exist in contact with various brines must be considered in greater depth for estimating long-term stability.

Results of studies of exploratory mixtures to convert the cements' aluminate phases more fully to AFm and AFt phases have appeared to be promising. Their longer term behaviors should be investigated. This should include the potential effects of reaction with major amounts of calcium sulfate or carbonate, either in initial mixtures or through simulated intrusion of brines.

Additional experiments should be carried out with clays and zeolites to determine possible trade-offs between best early stage properties, and alternate materials which may take full advantage of trends toward change through longer term reaction with the host rock environment.

Information from other sources including study of old and ancient cementitious materials, recovered field plugs, refined thermodynamic data, additional diffusion experiments, and further high temperature and pressure studies should be directed to providing insight regarding longevity of the above types of seal materials.

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APPENDICES

Appendix A contains chemical compositions of the various cements, reactive additives and admixtures used in formulating most of the cementitious formulations given in the text of the report. In some cases no such analyses were available since mixtures were of a very exploratory nature formulated early in the program.

Appendix B consists of microhardness data for most of the mixtures discussed in the text of the report. In general, it is assumed that satisfactory mechanical properties are possible for a mixture having microhardness $\geq 20 \text{ kg mm}^{-2}$. The magnitudes of microhardness, like Young's modulus and density are compositionally dependent, as well as dependent upon microstructures (as is the strength). Therefore, differences do not follow exactly the same patterns as the latter. A more full interpretation will be presented elsewhere.

Appendix A. Chemical Analysis.

Cements

Oxide	C-2 El Toro	C-5 El Toro	H-4	H-7	H-8	H-9
SiO ₂	21.2%	20.7%	23.1	22.3	22.27%	22.0%
Al ₂ O ₃	2.72	2.8	3.8	3.84	3.60	3.5
Fe ₂ O ₃	5.17	4.80	3.83	3.80	4.01	4.19
CaO	65.7	66.55	63.45	64.78	64.40	64.92
MgO	0.90	0.83	2.35	2.08	2.87	2.91
SO ₃	2.62	2.93	2.82	1.92	1.99	1.79
Na ₂ O	0.21	0.16	0.13	0.09	0.15	0.16
K ₂ O	0.18	0.10	0.59	0.49	0.57	0.50
TiO ₂	0.13	0.10	0.19	0.19	0.17	0.21
P ₂ O ₅	0.05	0.07	0.10	0.14	0.11	<0.10
MnO	0.22	0.05	0.02	0.015	0.02	0.020
BaO	--	--	--	0.03	--	0.024
SrO	0.09	0.09	0.07	0.07	0.06	0.051
LOI	0.76	0.87	0.47	0.43	--	0.46
Total	99.86	100.05	100.92	100.18	100.22	100.74
CO ₂	0.26	0.55	0.45	0.21	0.48	0.24

Reactive Additives, B Compounds

Oxide	B15	B17	B24	B25	B26	B27	B31	B44	B51
SiO ₂	40.6	87.47	97.2	50.2	33.2	96.0	94.3	37.8	92.6
Al ₂ O ₃	17.4	1.05	0.10	27.0	17.6	0.10	0.36	20.2	0.05
Fe ₂ O ₃	5.05	2.28	<0.1	13.8	6.03	<0.1	0.66	5.79	0.1
CaO	26.86	0.66	0.13	1.82	29.91	0.12	0.27	25.2	0.08
MgO	3.58	1.17	0.16	0.84	5.07	0.13	1.42	4.51	0.20
SO ₃	1.40	0.34	--	--	2.77	--	--	1.75	--
Na ₂ O	0.96	0.96	0.20	0.24	1.03	0.1	0.76	1.43	0.1
K ₂ O	0.72	1.83	0.42	2.45	0.41	0.45	1.11	0.56	0.47
TiO ₂	1.24	0.01	<0.1	1.40	1.55	<0.1	<0.1	1.44	<0.1
P ₂ O ₅	0.65	0.10	0.07	0.49	0.95	0.07	0.05	--	0.02
MnO	0.026	0.11	0.010	0.034	0.034	0.010	0.023	0.018	0.003
BaO	0.58	<0.01	--	--	0.84	--	--	--	--
SrO	0.23	0.02	--	--	0.37	--	--	--	--
LOI	0.47	4.06	--	--	0.44	--	--	0.74	--
Total	99.77	100.06	98.25	98.27	100.20	96.80	98.95	99.43	93.42
Other		carbon 1.84		Ba 1250 ppm Sr 900 ppm					
CO ₂	0.17	<0.05	--	--	0.22	--	--	0.07	--

No analysis available for B3, B5, B7, B8, B19, B23, B31.

Admixtures

	A3	A27	A28	A29	A31	A36	A41
loss at 105°C	54.5%	**	**	**	**	57.4%	**
LTA*	35.3					33.6	
S	11.2					11.0	
N	0.02					0.02	
C	46.3					46.6	
H	3.16					3.25	
LTA							
Ca	0.1					3.8	
Na	45.6					52.1	
Mg	0.01					0.01	

*Low temperature ash.

**No analysis available.

E01 = deionized water; E11 = freshly boiled deionized water.

Appendix B. Microhardness, Kg/mm².

specimen age (days)	cure temp (°C)	<u>Salt-containing and Derivative Mixtures</u>						
		mixture					wet 81-091	dry 81-091
		79-071	79-091	79-08	80-081	81-030		
3	27						49.09	32.51
	35							
	38				30.18			
	45						54.42	39.17
	60						56.74	44.81
	90						69.69	38.62
7	27			63.89		34.84	33.43	38.37
	35			74.35				
	38				23.44			
	45					43.55	44.12	47.80
	60			98.06		44.59	50.40	61.52
	90			74.89		45.42	49.67	51.73
14	27	30.99		56.48		44.76		
	35			65.66				
	38							
	45					49.64		
	60	31.96		83.60		50.91		
	90	46.03		57.11		52.38		
28	27	25.48		55.92		50.89	44.75	38.55
	35			67.62				
	38				40.12			
	45					56.54	52.73	49.29
	60	42.52		70.46		51.99	48.62	50.85
	90	43.31		63.28		54.89	48.40	50.16
56	27	52.70		49.66			49.74	49.59
	35			69.40				
	38				35.75			
	45						48.74	52.85
	60	52.54		76.26			46.06	58.07
	90	49.04		54.57			50.46	47.22
90	27	46.70		65.85			60.87	48.06
	35			71.44				
	38				38.27			
	45						48.83	61.40
	60	41.29		57.89			54.25	59.72
	90	50.21		56.34			61.79	50.39
180	27	63.43					51.73	56.57
	35							
	38				39.46			
	45						55.09	76.64
	60	43.42					56.41	67.17
	90	60.77					59.28	56.73
365	38				49.00			

Appendix B (continued)

specimen age (days)	cure temp (°C)	<u>Pozzolan-containing Mixtures</u>							
		mixture							
		81-010	79-010	79-020	79-030	79-060	80-010	79-050	79-040
7	27	54.60				45.45	46.33	36.73	59.56
	45	53.98				68.82	59.58	36.12	61.90
	60	53.78				48.53	66.70	33.57	62.76
	90	56.72				45.09	47.71	41.16	55.74
14	27	68.99			49.29	52.16	49.93	33.56	49.46
	45	72.77				50.07	43.58	29.46	52.57
	60	78.97			60.70	46.49	52.06	32.67	54.62
	90	84.82	29.41	34.26	44.96	49.96	58.14	35.27	64.75
28	27	70.34			50.80	32.74	46.21	25.68	50.91
	45	77.50				43.55	45.08	29.90	46.89
	60	75.09			62.02	44.17	41.68	29.69	50.71
	90	93.48	47.98	54.67	47.38	41.11	45.93	42.42	49.12
56	27				78.82				
	45								
	60				72.68				
	90		56.20	58.64	67.08				
90	27				51.12				
	45								
	60				62.41				
	90		31.00	39.40	32.01				
180	27				39.31				
	45								
	60				34.80				
	90		39.34	38.99	41.34				

Appendix B (continued)

specimen age (days)	cure temp (°C)	<u>Exploratory Mixtures</u>							
		mixture							
		81-141	81-101	80-020	80-030	80-040	80-050	81-121	81-111
3	27							36.95	33.09
	38	38.08	35.28						
	45							53.44	35.36
	60							56.47	32.85
	90							58.64	43.97
7	27			52.26	53.82	33.47	52.45	56.92	32.04
	38	48.10	42.57						
	45			61.45	55.21	39.16	52.95	55.62	40.09
	60			67.53	51.81	42.10	72.96	64.26	48.55
	90			65.79	58.05	50.38	56.07	59.64	60.24
14	27			55.51	52.66	44.28	53.41		31.46
	38		50.45						
	45			63.80	63.73	48.08	54.68		43.53
	60			61.27	62.13	48.97	56.96		43.29
	90			70.16	63.13	50.53	59.00		41.60
28	27			64.31	55.03	47.93	61.32	64.13	36.47
	38	53.47	48.35						
	45			65.83	58.06	51.63	53.45	64.18	46.97
	60			73.89	59.46	52.04	59.53	59.16	55.61
	90			79.05	63.26	60.80	53.47	59.30	55.63
56	27							67.78	54.55
	38	48.03	52.17						
	45							62.04	48.27
	60							75.21	53.18
	90							66.12	45.58
90	27								63.18
	38								
	45								61.77
	60								60.38
	90								57.92

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