WSRC-RP-2005-01733

SALTSTONE PHYSICAL AND MECHANICAL PROPERTIES

A Report to

E.I. duPont de Nemours and Company
Dupont-Savannah River Plant
Aiken, SC 29808

by

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Introduction

In support of the saltstone durability studies conducted at the Materials Research Laboratory of The Pennsylvania State University, the physical/mechanical properties of eight formulations containing salt waste solution have been determined. Formulations for the eight saltstones were provided by SRL and included their current reference formulation. It is felt that the observation of changes in the physical/mechanical properties may be interpreted to indicate durability of the materials and/or provide an indication of ensuing degradation mechanisms.

General

The composition of the formulations used in this study are shown in Table 1 along with their PSU/MRL designations. The following basic properties as a function of time were considered necessary for comparative evaluation of placement and performance of the saltstones:

1. Compressive strength
2. Dynamic modulus
3. Permeability
4. Porosity
5. Density
6. Dimensional change
7. Leach rate*
8. Diffusivity*

In addition to the above, slurry properties, i.e., flow table, flow cone and Vicat setting time, were determined for each formulation.

Mixing of the saltstone was carried out in accordance with ASTM procedure C305, using a simulated DWPF waste solution as the mixing fluid. Composition of this solution is given in Table 2. The other starting materials have been characterized and reported elsewhere (1).

After mixing, samples were cast into their appropriate mould configuration for the various tests being conducted. The samples were then cured/stored at 38°C and >95% RH until the tests were conducted.

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*The results of leaching and diffusion experiments are reported elsewhere (2,3).

Table 1. Compositions of Saltstone Formulations Tested at PSU for Durability.

	Cement				Fly Ash				Modifiers		
PSU Mix No.	Class H H-10 wt%	Type II II-06 wt%	Type I I-12 wt%	SRP Reference Blend Z-58 wt%	Class C B75 wt%	Class F** B74 B83 wt%	Class F ESP B73 wt%	Slag B63 wt%	Extender Attapulgite C86 wt%	Cs^+ Sorber Chabazite C84 wt%	DWPF Solution (32 wt%) salt) E34 wt%
84-40				62.5							37.5
84-41	12.0					38.0 (B74)					50.0
84-42	12.0						38.0 (B73)				50.0
84-43			15.0			45.0 (B83)					50.0
84-44		15.0				45.0 (B83)					40.0
84-45			7.5			45.0 (B83)		7.5			40.0
84-46			12.0		26.0				2.0		60.0
84-47				58.0						2.0	40.0

*Reference blend contained 20 wt% H cement and 80 wt% Class C fly ash.
**Material was supplied by SRL personnel in two different shipments and consequently received two different PSU numbers.

Table 2. Simulated DWPF Waste Solution Components.

component	wt.%
H_2O (deionized)	69.00
$NaNO_3$	17.05
$NaNO_2$	4.26
NaOH	4.60
$NAlO_2$	2.74
Na_2SO_4	2.08
NaCl	0.13
Na_3PO_4	0.14

Presentation of Data

Slurry Properties

Flow table data reflects the ability of a slurry to flow under sustained vibration; it may or may not reflect the workability of the mix. Flow cone data on the other hand better reflects the rheology of the mix under static conditions. Initial setting time is defined as the onset of rigidity, being distinct from hardening, which indicates the development of measureable strength.

Flow table, flow cone and Vicat initial setting time for the formulations tested are presented in Table 3.

Cured Properties

Physical properties of the saltstone formulations were measured as a function of time for an indication of the hydration reactions which occur after initial set. Data for compressive strength, modulus of elasticity, bulk density, porosity, dimensional change, and water permeability, as a function of time, for each of the formulations are shown in Tables 4 thru 11.

Compressive Strengths. Compressive strengths were determined on all samples in accordance with ASTM C 109. A composite of the data is shown in Fig. 1. The two formulations containing Class C fly ash (84-40 and 84-47) appear to be superior in performance over the time period of the test. Both developed reasonable early strength up to 180 days. Mix 84-40 showed the

Table 3. Slurry Properties--Savannah River Saltstone.

Test	84-40	84-41	84-42	84-43	84-44	84-45	84-46	84-47	Acceptable Values*
Flow Table (%) (ASTM C 124)	>150	>150	>150	>150	>150	>150	>150	>150	>50
Flow Cone (secs.) (ASTM CRD C 79-77)	26	83	17	26	15	16	10	17	15-90
Vicat Initial Setting Time (hrs) (ASTM CRD C 82-76)	48	90	96	48	72	72	>140	>110	4-120

*Provided by SRL.

Table 4. Physical Properties (84-40).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change $\Delta l/l$ (%)	Permeability (Darcy)
7	17.00/2465	1.61	1.54	39	40.0	0.016	$<10^{-8}$ $<10^{-8}$
28	26.60/3858	1.94	1.70	40	40.0	0.020	<10-8
56	32.99/4785	1.99	1.48	46	40.0	0.030	6.46×10^{-7}
90	33.60/4873	2.06	1.50	41	37.2	0.056	2.38×10^{-7} 5.15×10^{-5} 6.10×10^{-7}
180	38.80/5627	2.20	1.59	33	38.6	0.100	4.54×10^{-3} 1.26×10^{-6}
360	33.86/4910	2.21	1.53	40	35.5	0.140	4.11×10^{-3} 4.8×10^{-4}

Table 5. Physical Properties (84-41).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porostiy (%)	Length Change Δl/l (%)	Permeability (Darcy)
7	1.18/171	1.42	1.06	45	54.8	----	$>10^{-2}$ $>10^{-2}$
28	1.91/277	1.58	1.05	45	64.6	0.020	1.72×10^{-3} $>10^{-2}$
56	2.08/302	1.25	1.05	45	54.2	----	$>10^{-2}$ $>10^{-2}$
90	1.82/264	0.098	1.03	48	59.5	----	$>10^{-2}$ $>10^{-2}$
180	1.91/277	0.106	1.03	47	60.2	----	$>10^{-2}$ $>10^{-2}$
360	1.88/273	0.116	1.08	45	58.4	----	9.16×10^{-3} 8.69×10^{-3}

Table 6. Physical Properties (84-42).

Curing Time (days)	Compressive Strength MPa/PSI	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change Δl/l (%)	Permeability (Darcy)
7	0.60/87	--	--	--	--	----	----
28	0.97/146	--	--	--	--	----	----

Table 7. Physical Properties (84-43).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change Δl/l (%)	Permeability (Darcy)
7	1.77/257	—	1.56	50	50.5	----	$>10^{-2}$ 4.0×10^{-3}
28	5.45/790	—	1.30	43	50.1	----	2.52×10^{-3} $>10^{-2}$
56	6.62/960	—	1.30	44	46.0	----	9.23×10^{-4} 9.37×10^{-4}
90	11.50/1667	—	1.38	37	46.0	----	6.11×10^{-5} 7.31×10^{-3}
180	20.09*/2914	—	1.34	41	45.6	----	3.21×10^{-5} 3.25×10^{-5}
360	35.33/5124	—	1.27	46	40.9	----	5.03×10^{-6}

*Visible cracks on sample surface.

Table 8. Physical Properties (84-44).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change Δl/l (%)	Permeability (Darcy)
7	1.14/165	--	1.30	41	48.8	----	6.0×10^{-3} $>10^{-2}$
28	5.43/788	--	1.32	42	47.7	----	1.03×10^{-3} 5.89×10^{-4}
56	8.51/1234	--	1.34	41	45.6	----	2.65×10^{-4} 4.19×10^{-4}
90	18.55/2690	--	1.33	41	47.3	----	7.09×10^{-3} $>10^{-2}$
180	23.32/3382	--	1.31	43	42.6	----	3.14×10^{-4}
360	23.43/3398	--	1.30	45	42.5	----	$>10^{-2}$

Table 9. Physical Properties (84-45).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change $\Delta l/l$ (%)	Permeability (Darcy)
7	8.91/1292	1.07	1.33	40		0.000	2.46×10^{-3} 5.30×10^{-7}
28	18.30/2654	1.38	1.33	43	42.5	0.200	$<10^{-8}$
56	21.40/3104	1.36	1.41	34	45.4	0.230	$<10^{-8}$ 1.60×10^{-6}
90	22.82/3309	--	1.31	43	44.4	0.240	1.49×10^{-5}
180	24.12/3498	1.39	1.29	44	42.5	0.244	6.42×10^{-8} 3.28×10^{-6}
360	24.46/3547	1.22	1.30	45	43.7	0.250	2.4×10^{-5}

Table 10. Physical Properties (84-46).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change Δl/l (%)	Permeability (Darcy)
7	0.66/88	--	1.15	41	54.2	0.037	4.89×10^{-5}
28	0.90/131	--	1.12	43	54.9	0.045	2.21×10^{-5}
56	1.18/171	--	1.06	44	52.8	0.045	1.01×10^{-5}
90	1.28/186	--	1.04	46	58.9	0.045	9.87×10^{-4} 1.11×10^{-5}
180	1.21/175	--	1.03	50	59.3	0.045	1.42×10^{-5}
360	1.65/239	--	1.10	47	52.4	0.045	1.9×10^{-3}

Table 11. Physical Properties (84-47).

Curing Time (days)	Compressive Strength MPa/psi	Dynamic Modulus (10^6 psi)	Bulk Density (g/cc)	Bulk Porosity (%)	Hg Intrusion Porosity (%)	Length Change $\Delta l/l$ (%)	Permeability (Darcy)
7	14.92/2163	1.58	1.48	37	38.6	0.005	$<10^{-8}$ $<10^{-8}$
28	26.97/3912	--	1.44	41	40.2	0.009	$1.47x10^{-6}$ $1.78x10^{-7}$
56	27.5/3988	1.78	1.41	43	40.6	0.014	$<10^{-8}$
90	35.1/5090	1.79	1.43	44	39.4	0.028	$5.74x10^{-7}$
180	37.73/5472	--	1.43	44	37.8 35.4	0.110	$1.68x10^{-4}$ $4.86x10^{-4}$
360	35.43/5139	1.96	1.41	46	40.7	0.160	$7.78x10^{-5}$

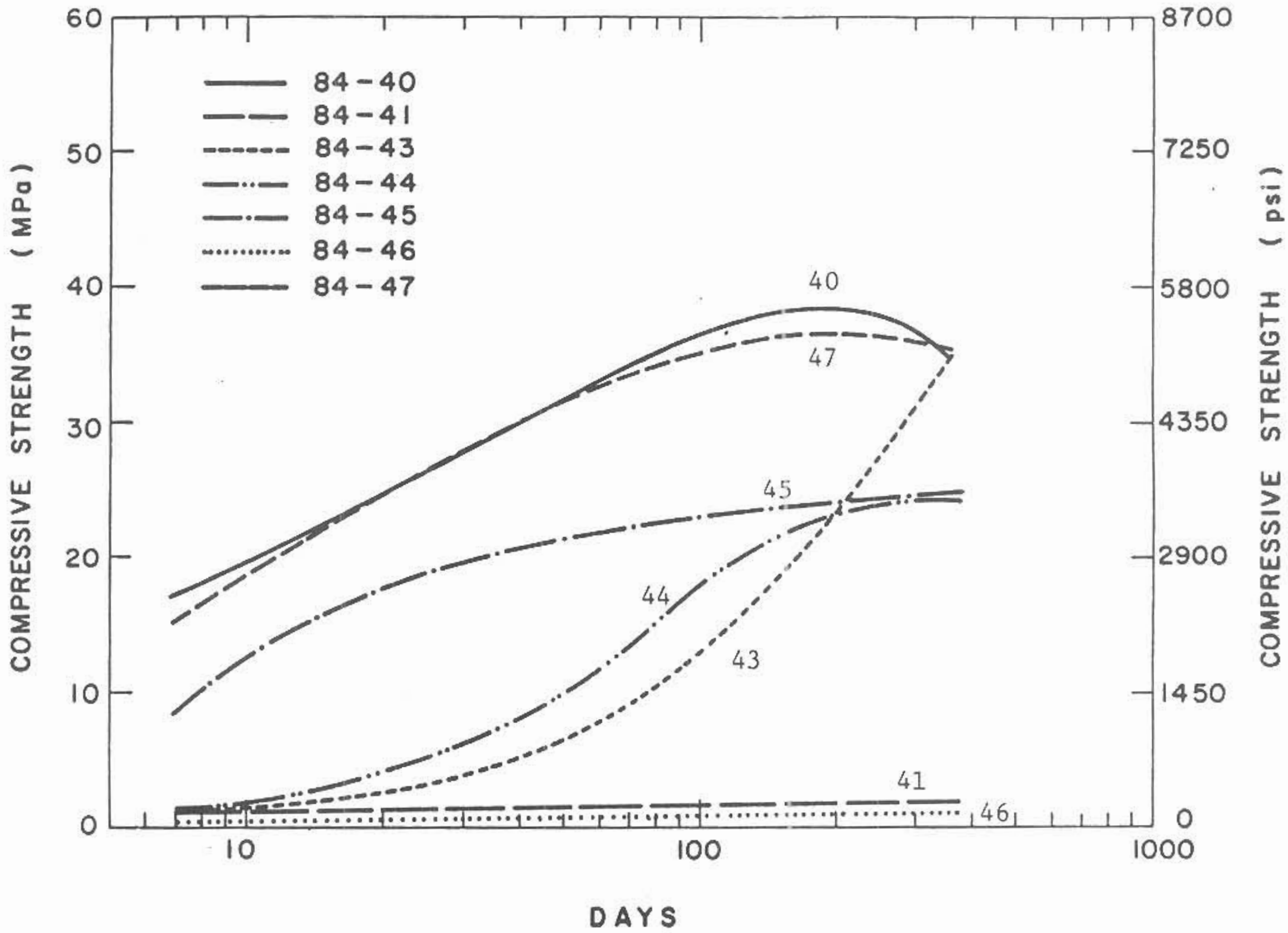

Fig. 1. Compressive Strength Trends (SRL *Saltstone*).

development of surface microcracks at this point with an accompanying small strength regression starting at 180 days. Mix 84-46, which also contained Class C fly ash, developed very little strength, possibly due to the presence of clay which in the early stages had taken up the water necessary for complete hydration.

Those formulations containing Class F fly ash (84-41, 84-42, 84-43, 84-44) did not gain the higher early strengths exhibited by the C fly ash containing mixes, an indication of the relative hydration activity of the two classes of ash (formulation 84-41 showed early deterioration which precluded meaningful compressive strength data). Furthermore, all of these formulations showed signs of early cracking possibly due to development of expansive phases (alkali silica).

Formulation 84-45 with a combined slag/cement base and Class F fly ash shows reasonable strength development with time. Minor surface microcracking appeared at approximately 360 days.

Dynamic Modulus. Dynamic modulus is used almost exclusively to track degradation in durability studies; for example studies relating to freeze-thaw action and those resulting from exposure to an aggressive environment. In general, no simple relationship exists between dynamic modulus and compressive strength for different formulations. Correlations do exist when changes in dynamic modulus are produced by internal deterioration and comparisons made of the same formulation as a function of time. On this basis it appears to be a good indicator of maturity and crack development for the SRL formulations. ASTM C 215 procedures were followed in the dynamic modulus (resonant frequency) tests with the resulting data shown in Fig. 2 for formulations 84-40, 84-41, 84-45 and 84-47.

Of those not shown (84-42, 84-43, 84-44, 84-46); formulation 84-42 had degraded prior to initial measurement; 84-43 developed early cracking; formulation 84-46, while it appeared to have an initial set point, did not harden, resulting in no discrete resonances after 9 months of curing and sample 84-44 was broken in sample preparation.

Of the samples measured 84-41 showed a rapid decrease in modulus after $\cong$30 days. Formulations 84-40, 84-45 and 84-47 showed progressive gains, an indication of viability of their internal structure.

Dimensional Change. Length change of unrestrained saltstone formulations were monitored as a function of curing time in accordance with ASTM standard C

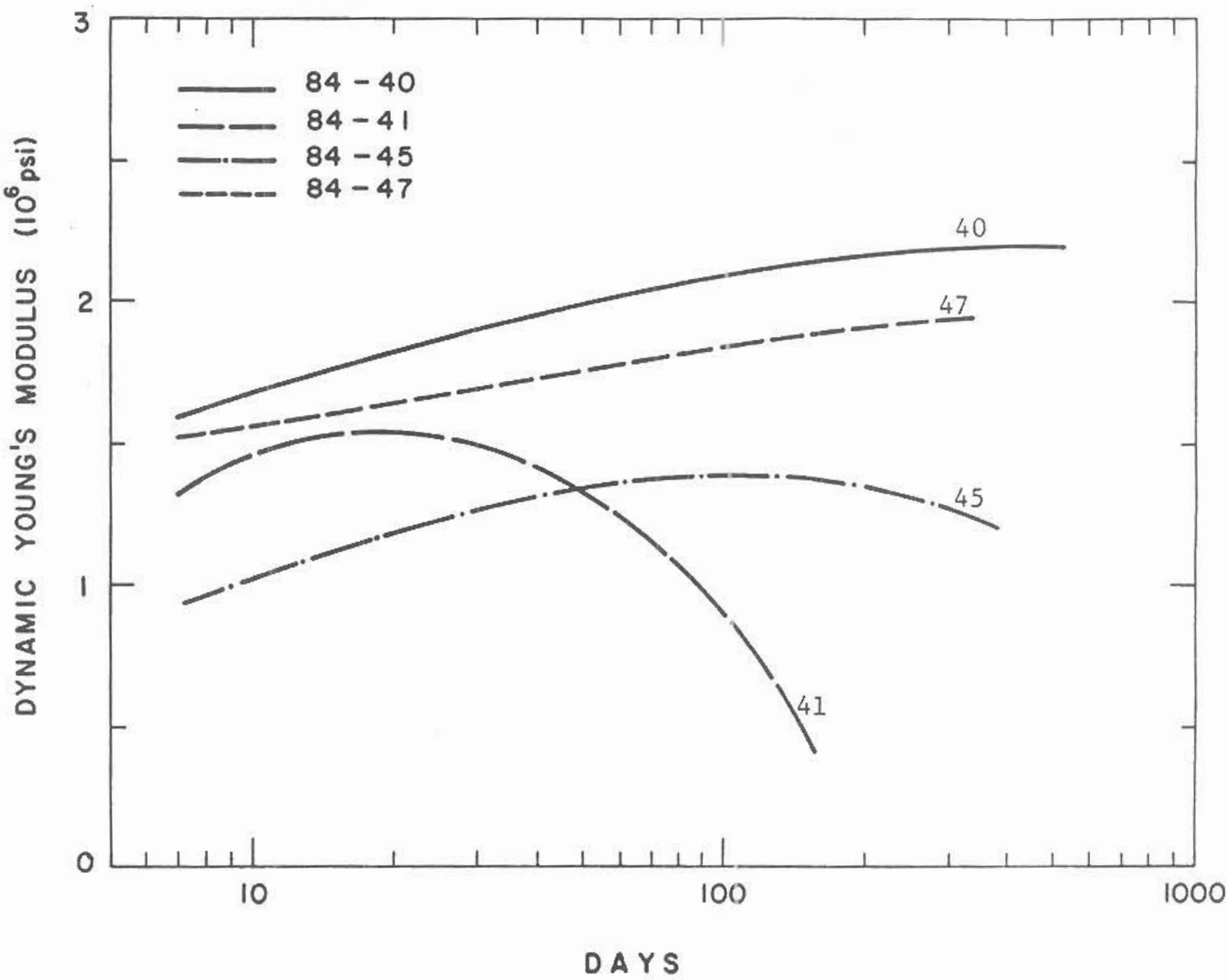

Fig. 2. Dynamic Modulus Trends (SRL Saltstone).

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All samples tested (84-40, 84-45, 84-46, 84-47) show an 'effective' positive expansion; those not tested, i.e., 84-41, 84-42, 84-43, 84-44, due to early failure, were largely victims of excessive tension cracking. Basically the same mechanism appears to be operative in all samples to one degree or other, e.g., alkali-silica reaction due to the presence of reactive silica, alkalis and water. Water in the mix, dosed with alkalis from the waste form, react with the silica producing a calcium alkali-silica gel which is hygroscopic, imbibes water and swells, giving way to micro/macro crack development, as a function of time. The time of occurrance and extent of the cracking, being a combined time function of reactivity and strength development within the sample.

Porosity. Porosity was determined by two different techniques. 1) ASTM 642 was used to determine effective porosity of the sample, i.e., that bulk porosity to water penetration at atmospheric pressure. 2) The mercury porosimeter was used to determine pore volume to mercury under pressure (1 atmosphere to 60,000 psi) with a sensitivity to pore diameters between 7.5 µm to 1.8 µm.

The ASTM method provides a bulk porosity for larger samples, integrating the effects of fractures/cracks which occur within the sample, along with their normally distributed porosity. The mercury porosimeter on the other, while using smaller samples (one to two grams) does have the ability to better reflect microfractures due to the pressure used.

No clear-cut pattern evolves for any given sample as a function of hydration time. Although the trend does appear to be toward lower porosities with age, variations in this trend may be due to the combined nature of the hydration products, the development of micro/macro fractures within the individual samples tested, regelation of micro fractures, etc. Of note, however, is the fact that a comparison of the 360 day values alone show formulation 84-40 to have a significantly lower porosity than the others tested.

Permeability. Water permeability of the formulations tested using samples one inch in diameter by approximately one-half inch in length, showed the following trends with time.

84-40 - Low initial permeability ($<10^{-8}$ Darcy) increasing significantly after 180 days.

84-41 - Constantly high permeability throughout the test period.

84-43 - Moderate to high permeability throughout the test period, with a general decrease in permeability with time.

84-44 - High permeabilities throughout the test period.

84-45 - Low permeability throughout the test period.

84-46 - Consistently moderate permeabilities throughout test period.

84-47 - Low initial permeability increasing with time.

While the terminology high, moderate and low is somewhat arbitrary it does reflect the relative changes of permeability within a given formulation as a function of time and makes comparisons between formulations.

A good OPC mortar/concrete formulation would normally show a continuous, dramatic decrease in permeability with hydration time assuming good consolidation, non-excessive segregation of the components and a reasonable w/c ratio.

The SRL formulations encompass a range of permeabilities and show some inconsistancies within replicate samples of the same formulation. This may be attributed to the development of micro cracks within some of the replicates.

Departure of permeability values, with time, for the same formulation from the decrease expected in a normal concrete/mortar would reflect those same parameters which influence porosity including the high water to cementitious solids ratio of the samples tested. The lowest permeabilities (10^{-7} - 10^{-8} Darcy) at any age were exhibited by formulations 84-40, 84-45 and 84-47.

Summary and Conclusions

The physical and mechanical properties of eight SRL formulations have been determined over a one-year period to provide input as to their potential viabilities over an extended period of time.

The basis of all formulations was either a Class F or Class C fly ash and portland cement in combination with DWPF mixing solution. In several instances slight amounts of modifiers, i.e., attapulgite, chabazite were added.

The low-calcium ash, 84-41, 84-42, 84-43, 84-44 formulations, although having the potential for better long-term sorptive powers towards radwaste ions showed inferior physical/mechanical properties, i.e., compressive strengths, dynamic modulus, permeability at an early age. The single exception to this was formulation 84-45 which had a 7.5% replacement of cement by slag which gave a marked improvement in properties, approaching those of the reference mix (84-40) containing Class C ash. Slag appears to compensate for the lack of hydraulic reactivity expressed by low calcium ash.

Of the other two formulations containing Class C ash, 84-46 failed to develop the required strength after one year curing, even though it showed moderate permeability throughout this time period. Formulation 84-47, comparable to formulation to 84-40 in composition, with the addition of 2% chabazite, showed high strength development and low permeabilities, again comparable to 84-40.

Permeability is stressed as one of the major indicators of long term durability in cementitious materials in that it plays an important role in the rate of entry of moisture into the monolith, particularly if it contains hygroscopic salts such as included in the DWPF solution.

A photograph of the samples tested, after approximately one year curing at 38°C and 95% RH, is shown in Fig. 3. Macroscopic examination of the samples shows the extensive deterioration of formulations 84-42, 84-43, 84-44, and minor surface microcrack development in formulations 84-40 and 84-47. While showing no surface cracking, formulation 84-46 developed little strength over this time period. Subsequent sample examination at approximately two years shows little or no change over that shown in Fig. 3. The observations confirm the early degeneration of physical properties observed in formulations 84-41, 84-42, 84-43, and 84-44.

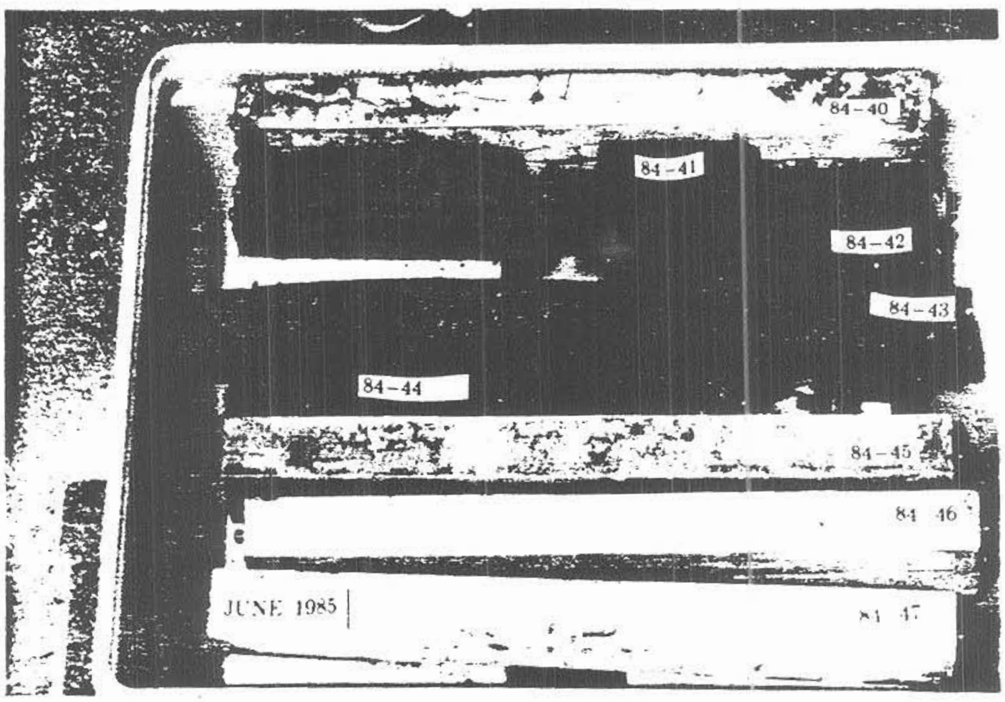

Fig. 3. Photograph of Samples After Approximately One Year.

References

1) CHARACTERIZATION Report

2) Kumars Report

3) M. Barnes Report -

Chris -
I don't know how you
designated these at ∞

MIXED - 02/11/83

84-48

	Compressive Strength (MPa) 38°	Static Modulus (MPa) 38°	Bulk Density (g/cc) 38°	Porosity 38°	Total Porosity % 38°	Absolute Density (g/cc) 38°	Permeability 38°
7d	11.01 ±0.13 3 SAMPLES	2327 ±101 2 SAMPLES	1.21	0.45			
28d	13.46 ±1.30 3	2570 — ALL OUT OF RANGE	1.20	0.47			
56d	14.99 ±0.10 3 SAMPLES	2461. ±100. 3	1.19	0.47			