REDUCING THE PERMEABILITY OF CEMENT BY THE USE OF COMMERCIALLY AVAILABLE ADDITIVES

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INTRODUCTION

During the past several years there has been an increased interest in the determination of leachability characteristics of solidified radioactive wastes. Several studies by Neilson and Colombo[1,2,3] at the Brookhaven National Laboratory, along with individual studies[4,5,6] performed on simulated waste forms, have shown moderate degrees of leachability.

The American Nuclear Society, in anticipation of Federal regulations in the area of waste leachability, formed the ANS 16.1 Working Group to develop a standardized leachability test method. In response to these trends Hittman Nuclear & Development Corporation (HITTMAN) has undertaken a substantial Research and Development program for the evaluation and possible improvement in the quality of cement solidified low-level nuclear power plant wastes. Starting with a series of leach tests, the results of which are in general agreement with previously referenced works, we embarked on a program to test and evaluate various commercially available additives designed to reduce the permeability of cement. This report discusses why permeability was considered an important factor, the materials tested, the method of testing and their results.

DISCUSSION - WHY PERMEABILITY?

Leaching refers to the extraction of a soluble substance from a material caused by water flowing through the material. In shallow land burial sites this process occurs when groundwater contacts with the waste buried in the trench. There are, then, several ways to prevent this process from occurring. First, trench design can include engineered barriers which prevent water from entering the trench. Secondly, the waste can be buried in containers designed to isolate the waste from any intruding groundwater. Such containers have recently been introduced, including the HITTMAN RADLOK™ high integrity container. Thirdly, the waste itself can be of such a matrix as to keep the water out of the matrix once contact occurs. This property of the waste is referred to as its permeability. In the context of this report a low value shows a high resistance to permeability.

The waste form selected for these tests was bead ion exchange resin, chosen due to its porous nature and tendency to dry out during solidification and curing. This results in an increased capacity to absorb moisture, and through bead to bead contact, results in a migration pathway for moisture through the solidified waste when subsequently contacted with water. Since bead resin is the only porous low-level radwaste form it provides a worse case base for this study.

MATERIALS TESTED

Through discussions with various companies which manufacture additives for commercial cement and concrete work, and with Michael D. Dukes of Savannah River Laboratory, the following materials were identified as candidates for study.

Table I - Materials Tested

Supplier	Material	Significant Property
Dow Chemical Company	Latex DPSA	Sealer
	Saran Cement Modifier	Sealer
Master Builders	Masterseal	Curing and Sealing Compound
	Pozzolith 344N	Water reducer
	Stearox	Water repeller
	Pozzolith 344N plus Stearox	Water reducer and repeller
	Pozzolith 322N	Water reducer

	Pozzolith 100XR MB-VR	Water reducer Air extrainer
American Admixtures & Chemical Corporation	Melmont AMEX-210	Water reducer Air extrainer
Xyper Corporation	Xyper Xyper, modified	Water proofer Water proofer
Sika Corporation	Sikament Plastocrete	Water reducer Water reducer
Swindell-Rust Company	SWRI-110	Silicic Acid Polymer
	SWRI-120	Silicic Acid Polymer
American Fly Ash Co.	Fly Ash	Increased Density
Waylite Company	Slag	Increased Density

TEST METHOD

To test each material, samples were made using the manufacturers recommended proportions for the materials intended use. For materials such as fly ash and slag, where such recommended proportions do not exist, typical concentrations of other generally used additives were used. This permitted comparisons to be made on a common basis. Each sample was cast in a three inch diameter by six inch high mold using the following quantities of material:

Table II - Sample Parameters

Dewatered Ion Exchange Resin	450 grams
Portland Type I Cement	580 grams
Water	189 grams
Anhydrous Sodium Metasilicate	58 grams
Additives	Various

For each material tested a total of six samples were prepared. Half of these used the anhydrous sodium metasilicate and half did not. Each sample was mixed separately and poured into the mold. After 24 hours the samples were unmolded and allowed to cure an additional 48 hours. One sample of each mix underwent compression testing to determine the compressive strength of the monoliths. The other two samples were then set upright in one-quarter inch of water and allowed to stand for 24 hours. The weight gain and absorption height of water in each sample was measured one hour and 24 hours after setting in water. Values obtained were compared to control samples which contained no admixtures.

RESULTS

Tables III and IV present summaries of the data, including averages for the two samples of each admixture. After testing several admixtures, it became apparent that the absorption of water in the samples made without anhydrous sodium metasilicate was usually greater than in those made without this additive. It was therefore decided not to make up samples of Xyper; Xyper, Modified; Sikament; Plastocrete; Fly Ash; or Slag without the anhydrous sodium metasilicate. The samples made with the SWRI-110 and SWRI-120 are shown in Table IV since this material was tested as a replacement for the Portland cement rather than as an admixture to the cement.

Based on these initial results it was decided to test six of the admixtures at high concentrations and also to test some of the materials in combinations with others. The results of these tests are shown in Table V. Upon completion of these tests the following conclusions were drawn: (1) the anhydrous sodium metasilicate is a necessary ingredient to obtain low permeability; (2) while the latex is good, using it as a replacement for the water is not a realistic alternative; (3) higher concentrations of the Pozzolith 322N do not reduce the permeability of the matrix; and (4) combinations of fly ash and slag with the Masterseal are not as good as the Masterseal by itself. Table VI presents this same data after the 24 hour soak as percentage of the control sample. As seen from Table 6 increased concentrations of Masterseal continued to result in decreased permeability. To determine whether or not

Table III. Sample Made with Anhydrous Sodium Metasilicate.

Admixture	Quantity Added, ml	Weight Absorption, gm		Avg. Water Height, mm		Compressive Strength, psi	
		1 Hour	24 Hours	1 Hour	24 Hours	Initial	After Soak
Control	--	13.3	47.1	44.5	102	352	621
Latex	163*	9.8	19.4	11.9	30.9	657	728
Stearox	2	14.5	31.2	39.7	63.3	700	593
Masterseal	9	7.9	18.1	21.5	46.1	571	650
Saran	210*	15.1	71.0	26.6	119.5	357	329
Pozzolith 344N	2	14.0	34.0	35.2	71.3	600	614
Pozzolith 344N plus Stearox	2 2	12.6	26.4	33.4	57.3	614	543
Pozzolith 322N	1.8	9.6	25.9	34.7	70.7	714	950
Pozzolith 100XR	1.5	5.8	21.6	24.8	67.8	557	779
MB-VR	0.75-1.0	9.8	30.7	31.1	85.1	486	857
Melment**	15	7.1	22.7	26.7	50.8	--	729
Amex 210	0.2	4.9	15.2	26.2	40.9	--	629
Cunningham Concrete	24	7.9	24.1	25.5	48.7	--	356
Xyper	41	8.9	29.5	31.3	95.0	700	971
Xyper, Modified	41	9.4	29.5	32.2	99.0	543	807
Sikament	14.5	7.0	24.5	29.1	73.3	543	807
Plastocrete	1.9	10.4	23.5	34.8	56.1	514	800
SWRI-110 SWRI-120	Not tested due to failure of samples without sodium metasilicate						
Fly Ash	116	17.8	65.0	44.8	139.2	429	586
Slag	116	15.1	50.8	39.1	119.8	429	586

* Quantity of water used adjusted to compensate for water in admixture
**Only one sample made

Table IV. Sample Made Without Anhydrous Sodium Metasilicate.

Admixture	Quantity Added, ml	Weight Absorption, gm		Avg. Water Height, mm		Compressive Strength, psi	
		1 Hour	24 Hours	1 Hour	24 Hours	Initial	After Soak
Control	--	14.5	63.8	23.0	69.8	571	828
Latex*	163	3.7	41.9	6.4	52.4	614	857
Stearox	2	12.5	43.3	19.1	28.6	929	914
Masterseal	9	8.0	35.4	13.5	42.9	600	714
Saran*	210	16.7	103.9	25.4	109.5	386	650
Pozzolith 344N	2	11.8	57.5	19.1	29.0	857	1071
Pozzolith 344N plus Stearox	2 2	10.8	43.0	17.2	39.7	771	928
Pozzolith 322N	1.8	53.7	170.3	61.9	156.5	828	479
Pozzolith 100XR	1.5	44.6	160.6	59.0	155.5	814	571
MB-VR	0.75-1.0	37.3	153	48.1	155	871	521
Melment	15	42.0	158.8	50.4	152	529	407**
Amex 210	0.2	10.8	138	32	152	729	464
Cunningham Concrete	24	23.6***	164	37.3	149	171	343
SWRI-110	580+	Did not set - samples discarded					
SWRI-120	580+						

* Quantity of water used adjusted to compensate for water in admixture
** One edge of one sample broke off prior to compression test
***Actual samples were 40.0 gm and 7.2 gm
\+ Used in place of the Portland Cement

Table V. Admixtures Test Results.

Admixture	Quantity Added, ml	Weight Absorption, gm		Avg. Water Height, mm		Compressive Strength, psi	
		1 Hour	24 Hours	1 Hour	24 Hours	Initial	After Soak
Control	--	13.3	47.1	44.5	102	352	621
Masterseal	13.5 [1]	4.8	14.9	21.1	48.5	557	657
Masterseal	13.5	16.7	134.3	28.4	153	800	477
Masterseal	18.0 [1]	3.6	10.3	18.5	37.6	571	721
Masterseal	18.0	10.2	125.9	22.9	153	771	464
Latex	249 [1,2]	1.6	6.6	9.5	25.3	857	971
Latex	249 [2]	3.0	17.5	7.9	30.4	700	863
Amex 210	9	14.9	22.0	39.7	81.5	343	--
Pozzolith 322N	9	10.2	23.9	33.5	64.0	657	--
Pozzolith 322N	18	11.2	23.4	34.0	65.4	657	
Pozzolith 322N	27	Samples Cracked				Test discontinued	
Pozzolith 100XR	9	14.9	40.2	38.6	97.5	486	--
Plastocrete 161	9	12.5	29.7	36.7	73.5	543	--
Fly Ash and Masterseal	116gm [3] 72ml	4.8	11.8	21.0	47.5	Test discontinued	
Fly Ash, Slag, and Masterseal	58gm [3] 58gm 72ml	22.1	75.6	54.0	162	Test discontinued	

[1] Samples made with Anhydrous Sodium Metasilicate

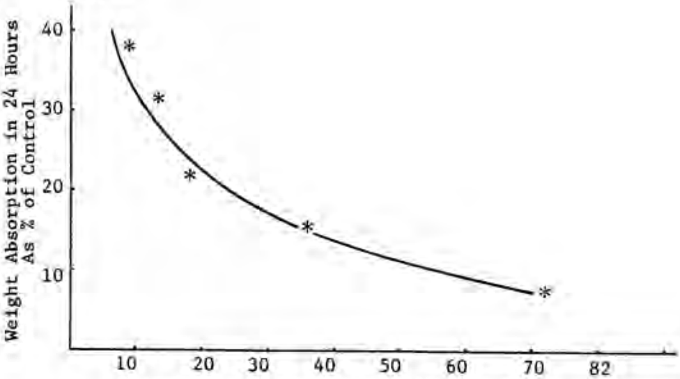
[2] Water added decreased to compensate for water in admixture

[3] Cement reduced to 464 grams

Table VI. Admixture Test Results As Percentage of Control Sample.

Admixture	Quantity Added, ml	Absorption at 24 Hours	
		Weight, gm	Height, mm
Control	--	47.1	102
Masterseal	13.5	31.6	47.5
Masterseal	13.5	285	150
Masterseal	18.0	21.9	36.9
Masterseal	18.0	267	150
Latex	249	14.0	24.8
Latex	249	37.1	29.8
Amex 210	9	46.7	79.9
Pozzolith 322N	9	50.7	62.7
Pozzolith 322N	18	49.7	64.1
Pozzolith 322N	27	Samples cracked	
Pozzolith 100XR	9	85.3	95.6
Plastocrete 161	9	63.1	72.1
Fly Ash and Masterseal	58gm 72ml	25.0	46.6
Flyash, Slag and Masterseal	58gm 58gm 72ml	46.9	159

additional reductions could be realized, a series of samples were made (with the anhydrous sodium metasilicate) using 36 ml and 72 ml of Masterseal. Table VII shows these results along with a tabulation of the previous Masterseal data, including compressive strengths of the samples. A plot of the absorption by weight at 24 hours, as a function of quantity added to the samples, is shown below.



CONCLUSIONS

Several conclusions which guided the latter portion of the test program have already been discussed. With completion of the last tests using 72 ml of the Masterseal it is evident that, of the materials tested, Masterseal offers the best reduction in the permeability of the solidified matrix. Additional quantities would not be justified since a point of diminishing return has already been reached at 72 ml. Although the data for latex was promising, it would only be applicable to a limited scope of waste materials containing very small quantities of water, such as dewatered resins as compared to evaporator bottoms.

Table VII. Results with Masterseal.

Quantity Added, ml	Absorption at 1 Hour: Weight, gm	Absorption at 1 Hour: Weight, % of Control	Absorption at 1 Hour: Height, mm	Absorption at 1 Hour: Height, % of Control	Absorption at 24 Hours: Weight, gm	Absorption at 24 Hours: Weight, % of Control	Absorption at 24 Hours: Height, mm	Absorption at 24 Hours: Height, % of Control	Compressive Strength, psi: Initial	Compressive Strength, psi: After Soak
Control	13.3	100	44.5	100	47.1	100	102	100	352	621
9	7.9	59.4	21.5	48.3	18.1	38.4	46.1	45.2	571	650
13.5	4.8	36.1	21.1	47.4	14.9	31.6	48.5	47.5	557	657
18	3.6	27.1	18.5	41.6	10.3	21.9	37.6	36.9	571	721
36	2.7	20.3	13.1	29.4	7.3	15.5	27.8	27.3	586	707
72	1.5	11.3	8.6	18.3	3.6	8.1	20.4	20.0	485	578

The next step, to determine how this decreased permeability translates into leachability, is to conduct a series of leach tests and compare the data to a set of control samples. Initial leach tests, using the ANS 16.1 leachability test, are currently being performed.

References

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