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Report to

DEPARTMENT OF ENERGY
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DOE Contract No. EM-78-C-02-5011
PCA Contract No. CR-7582-4330

FINAL QUARTERLY TECHNICAL PROGRESS REPORT
PHASE I

Sulfate Specifications as a Constraint
To Gypsum Addition to Cement and
Possible Replacement of Gypsum
as an Additive

December 1979 - January/February 1980

Submitted by

D. L. Kantro

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April 1980

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Possible Replacement of Gypsum as an Additive
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March 1980

SUMMARY

The results obtained during this quarter indicate that, based on x-ray diffraction observations, rapid uptake of sulfate can be effected in low C_3A systems. This uptake is of sulfate accompanying alkali and is by the aluminoferrite phase.

Expansion studies indicate low expansions by low C_3A systems. Further reductions in expansion occur with the use of admixtures. The lowest expansions occur in high alkali sulfate containing systems. This result is consistent with the observation of rapid sulfate uptake in such systems.

Carbonate addition results indicate that increasing carbonate content decreases rate and extent of outside sulfate attack. With respect to compressive strength, there appears to be an optimum value for carbonate addition to a high alkali-high C_3A clinker. Addition of ground dolomite gives results similar to those for limestone. Use of a high-fineness limestone has a strength-enhancing effect and no adverse effect on flow.

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Task I - Alternate Methods for Controlling Set

The x-ray diffraction patterns of hydrated mixtures of C_6AF_2 or C_6A_2F with $Ca(OH)_2$ and various calcium and alkali sulfates indicate hydration characteristics similar to C_4AF . The preparations contained less excess lime than did those containing C_4AF ; this condition resulted in the formation of a substantial quantity of the cubic $C_3(A,F)H_6$ by 28 days. As in the C_4AF systems, the heat peak represents the exhaustion of the available sulfate but not the disappearance of ettringite. Ettringite is still present at the time of the heat peak.

In aluminoferrite systems containing K_2SO_4 , the heat peak occurs earlier the higher the A/F ratio. When K_2SO_4 is the only sulfate present, the heat peak for C_6AF_2 occurs at 34 hours, earlier than the heat peak for the C_3A -gypsum system at the same $\bar{S}/A$ ratio. Thus relatively rapid sulfate uptake occurs in high alkali sulfate systems even in the absence of C_3A .

Task II - Deterring Sulfate-Induced Expansion

Expansion observations have been continued with samples listed in the report for the period June-August 1979. The compositions of the mixes used are given in Table 1 (same as Table 5 of the June-August 1979 report). The expansion values for the various pastes from 61 days on are given in Table 2 (a modification of Table 7 of that earlier 1979 report).

Relative expansions at 90 days of high C_3A systems are shown in Table 3 (updated version of Table 7 in the June-August 1979 report). The reference system (arbitrarily) selected is blend No. 328, Mix D (Table 1) containing 10% C_3A and with 0.1%

sucrose added. The corresponding 180 day relative expansions, based on the appropriate value of the same reference system, are given in Table 4. The 180 day results are substantially the same as the 90 day results. Expansion control is affected by sucrose additions to gypsum- and anhydrite-containing systems. When a relatively large proportion of the total sulfate is present as anhydrite, a smaller amount of sucrose and a sugar derivative, L-ascorbic acid, also limit expansion. Expansion was held to the lowest levels by sucrose in the system in which a relatively large proportion of the sulfate was present as K_2SO_4 .

Tables 5 and 6 give the relative expansion results for low C_3A systems at 90 and 180 days. The reference system was the admixture-free paste, Mix A of blend No. 327 (Table 1) containing 23.8% C_4AF . While expansions for the low C_4AF systems are in general are relatively low, the admixture and sulfate effects are nevertheless evident from the data in the tables. These effects are similar to those for the high alumina cases. Some expansion control is effected also by conventional admixtures calcium lignosulfonate and corn syrup, relative to corresponding admixture-free systems. Again, the greatest effect occurred in the high K_2SO_4 system.

The heat peak data have indicated rapid uptake of sulfate in high K_2SO_4 systems. Perhaps with high alkali sulfate, even higher $\bar{S}/A$ ratios would be tolerated if the C_3A is kept low and an appropriate admixture is employed. What is now needed

is a program of research with clinkers of various compositions and a wide range of admixtures.

Task III - Carbonate Substitution for Sulfate in Cement

The C191 Vicat setting times have been obtained on the higher carbonate content mortars using cement LTS-11. The results in Table 7 include those previously reported (March-May 1979, Quarterly Report, Table 6), and also the percentage compositions of the various cements used for these mortars. The Wolochow expansion tests have been started with Mixes I through P. Results are summarized in Table 8. Expansion values are given for the various mixes at selected times. The time in weeks at which expansion exceeded 0.10% is given in the last column. Previously, results for A through H had been reported. They are repeated here in this form for ready comparison.

Tests have been initiated with another clinker, MCC-292. The analysis and composition of this clinker were reported in the Sept-Nov. 1979 report, Table 1, and the microscopic examination results are given in the June-Aug. 1979 report, Table 1. Clinker MCC-292 is a high C_3A , high alkali sulfate product. At the present time, compressive strength results have been obtained at ages up to 7 days for mixes containing limestone with two different finenesses and ground dolomite. The results are given in Table 9. These data indicate that for the 5000 cm^2/g fineness limestone, there is a suggestion of an optimum with regard to compressive strength with a 3 to 5% addition. This is in accord with the LTS-11 results (March-May 1979 report, Table 5). The results with dolomite ground to

5000 cm²/g do not suggest an optimum, but like the limestone case, there is no adverse effect due to the addition. The addition of 5% of a high-fineness (12000 cm²/g) limestone resulted in a distinct increase in strength. There was also no appreciable influence on the flow due to any of the additions. Work in this area is continuing with other clinkers and with time of set, drying shrinkage, and Wolochow expansion tests on the cements described in Table 9.

TABLE 1

Compositions Used for Expansion Studies

Blend Compositions							
Sample No.	% C ₃ A	% C ₄ AF	% Gypsum	% Plaster	% Anhydrite	% C ₃ S	% C ₂ S
326	13.25		7.59			60.00	19.16
327		23.83	7.59			60.00	8.58
328	10.00	5.86	7.59			60.00	16.55
329	2.00	20.26	7.59			60.00	10.15
334	10.00	5.86	6.00	1.34		60.00	16.80
335	2.00	20.26	6.00	1.34		60.00	10.40
336	10.00	5.86	2.00	4.71		60.00	17.43
337	2.00	20.26	2.00	4.71		60.00	11.03
346	10.00	5.86	6.00		1.26	60.00	16.88
347	2.00	20.26	6.00		1.26	60.00	10.48
348	10.00	5.86	2.00		4.42	60.00	17.72
349	2.00	20.26	2.00		4.42	60.00	11.32
362	10.00	5.86	0	6.56	(Calcium Langbeinite)	60.00	17.58
363	2.00	20.26	0	6.56	(Calcium Langbeinite)	60.00	11.18
364	10.00	5.86	6.00	1.61	(K ₂ SO ₄)	60.00	16.53
365	2.00	20.26	6.00	1.61	(K ₂ SO ₄)	60.00	10.13
366	10.00	5.86	2.00	5.66	(K ₂ SO ₄)	60.00	16.48
367	2.00	20.26	2.00	5.66	(K ₂ SO ₄)	60.00	10.08

Admixture Identity and Amount

A	No Admixture
B	Calcium Lignosulfonate, 0.25%
C	Corn Syrup, 0.20%
D	Sucrose, 0.10%
E	Sodium Gluconate, 0.10%
F	Sucrose, 0.05%
G	Sucrose, 0.10% + Triethanolamine, 0.10%
H	Triethanolamine, 0.10%
I	L-Ascorbic Acid, 0.10%
J	Mannitol, 0.10%

TABLE 2

Expansion Results

(D indicates discontinued series)

% Expansion at:

Mix	61d	90d	120d	150d	180d	210d	240d	300d	360d
326-D	0.323	0.332	0.334	0.336	0.391	0.385	0.384	0.389	0.392
G	0.415	0.422	0.424	0.414	0.417	0.414 (D)			
I	0.957	0.956	0.960	0.950	0.957 (D)				
327-A	0.095	0.075	0.074	0.083	0.083	0.085	0.078	0.075	0.076
B	0.028	0.034	0.040	0.044	0.043	0.043	0.034	0.034	0.033
C	0.056	0.052	0.053	0.054	0.058	0.044	0.043	0.043	0.042
D	0.039	0.042	0.41	0.043	0.039	0.034	0.030	0.032	0.032
328-C	0.526	0.528	0.529	0.531	0.530	0.531	0.532	0.530	0.525
D	0.129	0.142	0.138	0.142	0.142	0.135	0.134	0.135	0.137
329-A	0.196	0.206	0.211	0.225	0.215	0.222	0.213	0.209	0.212
B	0.115	0.110	0.120	0.123	0.124	0.123	0.117	0.115	0.116
C	0.081	0.097	0.090	0.092	0.100	0.090	0.078	0.084	0.085
D	0.073	0.100	0.098	0.101	0.097	0.090	0.091	0.097	0.099
334-C	0.462	0.464	0.455	0.473	0.463	0.467	0.472	0.475	
D	0.287	0.293	0.309	0.292	0.292	0.291	0.291	0.290	
I	0.767	0.769	0.774	0.775	0.774 (D)				
335-A	0.184	0.198	0.212	0.210	0.205	0.204	0.202 (D)		
B	0.125	0.147	0.157	0.160	0.170	0.164	0.161 (D)		
C	0.140	0.150	0.156	0.163	0.157	0.140	0.137	0.137	
D	0.077	0.078	0.079	0.071	0.070	0.071	0.071	0.070	
J	0.178	0.192	0.185	0.185 (D)					

TABLE 2 (continued)

% Expansion at:									
Mix	61d	90d	120d	150d	180d	210d	240d	300d	360d
336-D	0.664	0.662	0.668	0.657	0.655	0.656	0.657	0.655	
337-A	0.129	0.157	0.162	0.167	0.158	0.161	0.161 (D)		
B	0.114	0.130	0.138	0.138	0.145	0.137	0.135 (D)		
C	0.121	0.129	0.111	0.117	0.117	0.125	0.130	0.176	
D	0.089	0.094	0.097	0.091	0.088	0.089	0.087	0.086	
346-D	0.297	0.305	0.308	0.296	0.296	0.296 (D)			
F	0.681	0.686	0.688	0.684	0.686	0.687	0.690	0.691	
I	0.842	0.856	0.846	0.842	0.841 (D)				
347-A	0.172	0.185	0.186	0.183	0.184	0.182 (D)			
D	0.108	0.114	0.125	0.107	0.110	0.108 (D)			
F	0.152	0.166	0.167	0.167	0.168	0.170	0.174	0.173	
348-D	0.137	0.137	0.162	0.148	0.150	0.148 (D)			
F	0.080	0.083	0.087	0.086	0.086	0.089	0.093	0.089	
I	0.094	0.096	0.101	0.099	0.099 (D)				
349-A	0.203	0.229	0.229	0.220	0.222	0.222 (D)			
D	0.126	0.143	0.158	0.154	0.158	0.160 (D)			
F	0.090	0.091	0.94	0.095	0.095	0.102	0.107	0.110	
363-A	0.115	0.129	0.147 (D)						
D	0.068	0.086	0.081	0.080	0.079	0.079			
365-A	0.203	0.239	0.266 (D)						
D	0.087	0.100	0.098	0.097	0.097	0.097			
366-D	0.051	0.058	0.057	0.056	0.055	0.54			
367-A	0.094	0.103	0.125 (D)						
D	0.041	0.044	0.041	0.040	0.041	0.042			

TABLE 3

Relative Expansions at 90 Days, High C₃A Blends

Blend	Mix	A	B	C	D	F	G	I	J
326		*	*	9.1	2.3	*	3.0	6.8	*
328		*	*	3.7	1.0	*	*	11.1	*
334		*	*	3.3	2.1	*	*	5.4	*
336		*	*	*	4.7	*	*	*	
346		*			2.1	4.8		6.0	
348		*			1.0	0.6		0.7	
362		*			*				
364		*			*				
366		*			0.4				

* Samples expanded excessively.

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TABLE 4

Relative Expansions at 180 Days, High C₃A Blends

Blend	Mix	A	B	C	D	F	G	I	J
326		*	*	*	2.8	*	2.9	6.7	*
328		*	*	3.7	1.0	*	*	*	*
334		*	*	3.3	2.1	*	*	5.5	*
336		*	*	*	4.6	*	*	*	
346		*			2.1	4.8	5.9		
348		*			1.1	0.6	0.7		
362		*			*				
364		*			*				
366		*			0.4				

* Samples expanded excessively.

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TABLE 5

Relative Expansions at 90 Days, High C₄AF Blends

Blend	Mix	A	B	C	D	F	J
327		1.00	0.45	0.69	0.56		
329		2.75	1.47	1.29	1.33		
335		2.64	1.96	2.00	1.04		
337		2.09	1.73	1.72	1.25		2.56
347		2.47			1.52	2.24	
349		3.05			1.91	1.21	
363		1.72			1.15		
365		3.19			1.33		
367		1.37			0.59		

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TABLE 6

Relative Expansions at 180 Days, High C₄AF Blends

Blend	Mix	A	B	C	D	F
327		1.00	0.52	0.70	0.47	
329		2.59	1.49	1.20	1.17	
335		2.47	2.05	1.89	0.84	
337		1.90	1.75	1.41	1.06	
347		2.22			1.33	2.02
349		2.67	1.90			1.14
363					0.95	
365					1.17	
367					0.49	

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TABLE 7

Cement Compositions and C191 Vicat Setting Times

	<u>LTS-11</u>	<u>Gypsum</u>	<u>Limestone</u>	<u>Time of Set, hr:min</u>	
				<u>Initial</u>	<u>Final</u>
A	100	0	0	2:13	3:50
B	99.0	1.0	0	2:12	2:30
C	97.5	2.5	0	2:13	2:45
D	96.25	3.75	0	2:26	2:45
E	97.2	0	2.8	2:08	2:30
F	96.2	1.0	2.8	2:20	2:45
G	94.8	2.4	2.8	2:22	2:45
H	93.7	3.6	2.7	2:17	3:00
I	95.0	0	5.0	2:26	2:45
J	94.0	1.0	5.0	2:10	2:45
K	92.6	2.4	5.0	2:27	3:15
L	91.5	3.5	5.0	2:11	2:45
M	90.0	0	10.0	2:28	2:45
N	89.1	0.9	10.0	2:18	2:45
O	87.8	2.2	10.0	2:17	2:45
P	86.7	3.3	10.0	2:13	2:45

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TABLE 8

Expansions in 5% Na₂SO₄ Solution

Wolochow Test

Cement LTS-11

<u>Blend</u>	<u>% Expansion</u>						<u>Over</u>
	<u>2 wks</u>	<u>4 wks</u>	<u>8 wks</u>	<u>12 wks</u>	<u>15 wks</u>	<u>20 wks</u>	<u>0.10%</u>
A	.015	.026					7 wk
B	.021	.036					6 wk
C	.018	.031	.100				9 wk
D	.021	.034	.078				10 wk
E	.018	.029	.083				9 wk
F	.016	.026	.050				12 wk
G	.016	.023	.037	.052	.069		20 wk
H	.018	.028	.042	.060	.075	.099	
I	.008	.011					
J	.008	.011					
K	.007	.010					
L	.009	.013					
M	.008	.013					
N	.010	.014					
O	.008	.012					
P	.011	.015					

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TABLE 9

Carbonate Contents and Types, Cl09 Mortar Results, Clinker MCC-292

<u>Mix</u>	<u>% Gypsum</u>	<u>% Carbonate</u>	<u>Type</u>	<u>Carbonate Fineness cm²/g</u>	<u>Mortar Flow</u>	<u>Compressive Strength, psi</u>			
						<u>1d</u>	<u>3d</u>	<u>7d</u>	<u>28d</u>
A	2.28	0			103	1950	3020	3780	
B	2.22	3	Limestone	5000	100	2070	3120	3970	
C	2.18	4	"		98	1930	3180	3910	
D	2.06	10	"		103	1730	2790	3680	
E	2.22	3	Dolomite	5000	102	1980	2980	3820	
F	2.18	5	"		106	1840	2880	3720	
G	2.18	5	Limestone	12000	100	2180	3290	4210	