

CONCRETE VARIABLES AND CORROSION TESTING

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We partially submerged 710 reinforced concrete blocks in a saturated sodium chloride solution. Based on the test criterion that a sufficient quantity of chloride-absorbed concrete causes the steel to change from a passive to an active or corroding half-cell potential, the test results showed that increasing the cement factor and increasing the length of water curing increased the time to an active half-cell potential. Steam curing of the concrete resulted in a reduction of the time to an active half-cell potential as well as a reduction in absorption as compared to just water curing. The test procedure used verified capillary action as the primary mechanism of water absorption. The chloride content of the concrete was determined. Of the three tested admixtures and corrosion inhibitors, only pozzolan appeared to result in a significant benefit even though this concrete had the greatest absorption and also the greatest drying shrinkage.

•THE California Division of Highways reported in 1957 the causes of corrosion of steel in concrete (1). In 1963, an empirical equation was developed from field and laboratory data for estimating the time to corrosion of embedded steel (2). These works indicated that additional data were required regarding the influence of curing, admixtures, and other concrete design variables when a structure is designed for a specific maintenance-free life (2).

Based on a literature survey, it was found that at least 15 different methods have been used for testing the corrosion of steel in concrete (3). In general, some of the methods are as follows:

1. Exposure to tidal water (4, 5),
2. Normal outdoors (5, 6, 7, 8, 9, 10),
3. Laboratory, high humidity (6, 8, 11, 12),
4. Laboratory, low humidity (6, 13),
5. Alternate immersion (6, 12),
6. Alternate but partial immersion (14, 15),
7. Variable salt, moisture, temperature (16),
8. Salt spray cabinet (17),
9. Partial covering with a wet towel (13),
10. Flow of water vapor (18),
11. Periodic spraying with salt water (18),
12. Immersion in water (12),
13. Partial immersion (9),
14. Dry cellar (19), and
15. Impressed voltages (1).

In effect, a test method for obtaining precisely reproducible results even by the same investigator (20, 21) has not been clearly established.

In the selected partial-immersion corrosion test of the reinforced concrete blocks, there are two ways to measure the corrosion phenomenon: One is to measure the half-

cell potential of the steel, and the other is to visually inspect the concrete for cracks that result from the rusting of the steel.

In a previous study (21), it was found that one could electrically measure a change from a noncorroding passive half-cell potential (no salt at the steel-concrete interface) to an active half-cell potential, which occurs when there are sufficient chlorides present to cause corrosion of the steel. With proper instrumentation, it is less costly to measure the half-cell potential of the steel than to make periodic visual inspections for corrosion-caused concrete cracking; therefore, electrical measurements were used in this study as the sole criterion for the determination of the time to corrosion.

This study is a report on observations of the effects of curing method, curing time, cement factor, admixtures, and corrosion inhibitors and the test method used to determine the influence of these variables on the time to corrosion when the concrete was partially immersed in a saturated sodium chloride solution.

FABRICATION AND TESTING OF BLOCKS

The variables of concrete manufacture as used in this series of tests are given in Table 1. The river run aggregate was $\frac{3}{4}$ in. maximum, and the gradation complied with the 1964 Standard Specifications of the California Division of Highways. The cement used was type 2 modified, low-alkali, which also complied with the California specifications.

The reinforced concrete specimens were $4\frac{1}{2}$ in. wide, $2\frac{1}{2}$ in. thick, and 15 in. long. The No. 4 reinforcing steel was sandblasted and cast in the concrete to provide a minimum of $\frac{7}{8}$ -in. concrete cover at any point. Figure 1 shows a typical test specimen.

Ten corrosion test specimens, four 6- \times 6-in. cylinders and six 3- \times 3- \times 11 $\frac{1}{4}$ -in. shrinkage bars, were cast from a single batch. Except for the test variations in batching, all concrete was batched in 1 day for each test variable. The 10 corrosion specimens were then either water-cured or steam- plus water-cured. Water curing was the complete submersion of the block in water at a temperature of approximately 72 F.

Specimens to be steam-cured were subjected to approximately 16 hours of steam curing at 138 ± 5 F and then water-cured for the length of time that related to that test variable of curing time. All steam-cured specimens were allowed to stand in their casting mold for a minimum of 4 hours. In all cases, the specimens were steam-cured on the day they were cast.

In all cases, the concrete slump was maintained at approximately $3\frac{1}{4} \pm \frac{1}{4}$ in. by adjusting the amount of mixing water. The vibration of the concrete was accomplished by placing the steel molds on a Packer type of vibrating table.

After casting, the blocks were subjected to curing variables. In all cases, after the appropriate time of submerged water curing, the blocks were immediately transferred to the partial-immersion tanks. Figure 2 shows the blocks in place in the tanks. The blocks were partially immersed at an empirically selected depth of $3\frac{1}{2}$ in. on the 15-in. dimension in a saturated sodium chloride solution, the steel reinforcement rod being in a vertical position. A data acquisition system automatically obtained the half-cell potentials of the steel and also printed the results on tape.

The absorption tests were made in accordance with Test Method Calif. 538-A. Essentially, this test method first requires oven drying at 230 ± 9 F for a minimum of 3 days and a continuation of drying until the concrete water loss is less than 0.05 percent by weight. Prior to soaking, the concrete is stored overnight at room temperature. For the 6- \times 6-in. absorption cylinders used in this test program, the approximate drying time was 14 days. In soaking, the concrete is required to be submerged at least 1 in. below the surface of the water. The weight gain is recorded at approximately 1, 3, 5, 7, and 24 hours and 2, 3, 8, 16, and 28 days. The weight gain versus time data are then plotted on log-log paper, and the best fit of the weight gain curve at 28 days is either visually obtained or calculated by a regression analysis. The weight gain is then computed and reported as percentage of concrete by volume.

RESULTS

Absorption and Cure Method

The absorption values given in Table 2 were obtained by means of Test Method Calif. 538-A dated April 6, 1970. The values were obtained after 28 days of soaking of the initially oven-dried 6- x 6-in. cylinders. (The specimens contained 6 sacks of cement per cubic yard.) The results for three repetitive tests are also given in the table. Table 3 gives the statistical significance of the data in Table 2. In Table 4, the absorption values given are the average for three cycles of concrete absorption. The statistical significance of these data are given in Table 5.

Figure 3 shows the average values for three cycles of absorption testing for each batch of concrete of the various cement factors. All concrete had 28 days of water curing prior to absorption testing. When the data shown in Figure 3 were analyzed by the method of least squares, the following relationship was obtained:

$$A_s = 1.01 A_w - 0.422 \quad (1)$$

where

A_s = absorption of steam-cured and 28-day water-cured concrete, in percentage of concrete by volume, and

A_w = absorption of 28-day water-cured concrete, in percentage of concrete volume.

For this relationship of 20 pairs of values, the correlation coefficient was 0.9175 and the standard error of estimate was found to be 0.33 percent.

As indicated by the results for plain non-air-entrained concrete containing five through nine sacks of cement per cubic yard, the process of steam plus water curing reduces the 28-day concrete absorption value roughly by 0.3 percent by volume. However, as given in Table 3, in the case of pozzolan, steam curing did not result in a significant reduction in absorption.

Concrete Sorption

As a preliminary confirmation of the means whereby water is absorbed into concrete, 12 concrete blocks of 3 x 3 x 11¹/₄ in. were cast of ³/₄-in. maximum size aggregate. Originally, the blocks were moist-cured for 7 days and measured for drying shrinkage. These blocks had been on hand for a few years and, for the purpose of confirmation, were reused in this test. However, all were subjected to Test Method Calif. 538-A. After oven drying at 230 F, six of the room-temperature, oven-dried blocks were placed in a closed container so that the blocks were partially but horizontally immersed in water for ¹/₄ in. of length. The other six blocks were also placed in the same container but were elevated above the water's surface so that they were only exposed to approximately 100 percent relative humidity. The results of this test are shown in Figure 4. As indicated by this figure, gain in weight by the initially oven-dried concrete is contingent neither on complete immersion nor on being in direct contact with water.

These results seem to confirm previous work (2) indicating that the major control on the movement of water into saturated concrete that results in a buildup in the concentration of chloride is the continued evaporation of the water from some part of the concrete surface. Also, this reaffirms work (2, 22) that demonstrated that the major mechanism controlling the passage of water into good-quality concrete is capillarity and evaporation and not hydrostatic pressure as related to permeability measurements.

Half-Cell Potentials

The half-cell potential of the steel was referenced to a saturated calomel electrode and was normally measured thrice weekly with a data acquisition system of 10 megohms of input impedance.

The normal trend of the half-cell potential behavior in this test is shown in Figure 5. As determined in a previous study (21), the half-cell potential of the steel abruptly

Table 1. Concrete mix variables.

Admixture	Cement Factor	Slump (in.)	Air (percent)	Unit Weight (lb/cu ft)	Mixing Water (lb/cu yd)	
					Gross	Net
None	6.00	3 1/4	1.9	153.1	329	286
Pozzolan, 15 lb/sack	5.99	3 1/4	1.7	152.1	339	298
Pozzolan, 30 lb/sack	5.99	3 1/4	1.7	150.4	363	325
2 percent hydrated lime, 1.89 lb/sack	6.00	3 1/6	1.8	153.3	324	282
4 percent hydrated lime, 3.76 lb/sack	5.98	3	1.8	153.1	326	283
1 percent sodium benzoate, 0.94 lb/sack	5.96	3 1/4	4.9	149.4	301	269
2 percent sodium benzoate, 1.88 lb/sack	6.04	3 1/2	4.9	149.1	302	260
None	5.02	3	2.3	151.5	333	289
None	7.51	3 1/4	1.7	154.4	322	282
None	9.01	3	1.6	154.7	334	297

Figure 1. Corrosion test specimen.



Figure 2. Test specimens placed in partial-immersion tanks.

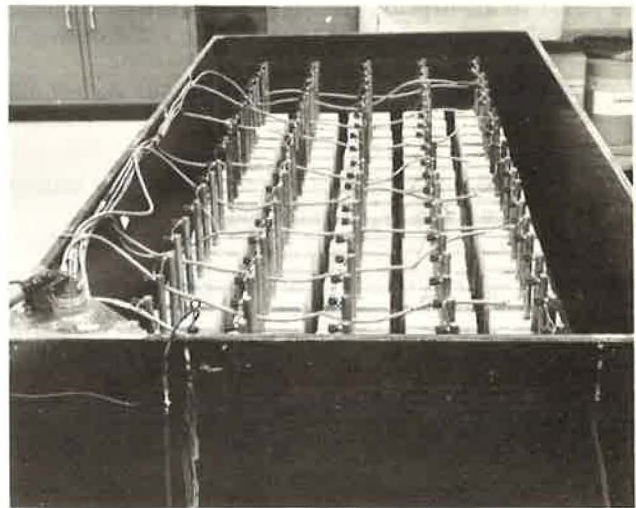


Table 2. Percentage of concrete absorption.

Batch	Cycle	5 Sacks/Cu Yd		6 Sacks/Cu Yd		7 1/2 Sacks/Cu Yd		9 Sacks/Cu Yd	
		WC ^a	SWC ^a	WC	SWC	WC	SWC	WC	SWC
1	1	14.63	14.20	13.66	13.53	12.79	12.41	13.13	12.87
	2	14.74	12.34	13.79	13.66	12.80	12.57	12.95	12.92
	3	14.82	14.36	13.68	13.70	12.79	12.56	13.01	12.94
2	1	14.69	14.71	13.95	13.24	12.94	12.29	12.84	12.51
	2	14.84	14.86	14.12	13.48	13.09	12.52	12.84	12.68
	3	14.89	14.99	14.09	13.42	13.13	12.62	12.85	12.71
3	1	14.19	14.41	13.58	13.49	13.17	12.70	13.10	12.65
	2	14.31	14.53	13.68	13.63	13.11	12.81	13.08	12.73
	3	14.37	14.70	13.60	13.67	13.22	12.92	13.03	12.85
4	1	14.87	14.97	14.18	13.55	13.13	12.87	13.15	12.64
	2	14.77	14.81	14.15	13.55	12.98	12.84	12.95	12.66
	3	14.94	15.01	14.22	13.57	13.02	12.94	12.96	13.06
5	1	14.81	14.50	13.89	13.63	13.48	12.48	13.01	12.61
	2	14.81	14.67	13.93	13.76	13.38	12.68	12.89	12.80
	3	14.81	14.75	13.89	13.72	13.35	12.72	12.89	12.83

^aWC = water-cured concrete; SWC = steam- plus water-cured concrete.

Table 3. Statistical significance of data given in Table 2.

Sacks/Cu Yd	Mean		Standard Deviation		Coefficient of Variation	
	WC	SWC	WC	SWC	WC	SWC
5	14.700	14.654	0.228	0.255	1.55	1.74
6	13.894	13.573	0.222	0.133	1.60	0.98
7 1/2	13.092	12.662	0.213	0.193	1.63	1.52
9	12.979	12.764	0.103	0.148	0.79	1.16

Table 4. Percentage of concrete absorption of admixtures and inhibitors.

Batch	Pozzolan				Sodium Benzoate				Hydrated Lime			
	15 Lb/Sack		30 Lb/Sack		1 Percent/Sack		2 Percent/Sack		2 Percent/Sack		4 Percent/Sack	
	WC	SWC	WC	SWC	WC	SWC	WC	SWC	WC	SWC	WC	SWC
1	14.97	14.94	16.86	16.97	12.66	12.56	13.05	13.23	13.77	13.33	13.97	13.77
2	15.40	15.14	17.25	17.15	13.09	12.37	13.36	12.61	14.07	13.88	14.13	13.69
3	14.99	15.11	17.11	17.60	12.59	12.18	12.74	12.47	13.73	13.64	13.90	13.51
4	14.94	15.03	17.14	17.10	13.39	13.06	12.39	12.01	13.68	13.75	14.23	13.87
5	15.11	14.95	17.08	17.13	12.46	11.81	13.47	12.87	13.75	13.79	13.95	14.20

Table 5. Statistical significance of data given in Table 4.

Admixture-Inhibitor	Mean		Standard Deviation		Coefficient of Variation	
	WC	SWC	WC	SWC	WC	SWC
Pozzolan						
15 lb/sack	15.08	15.03	0.189	0.091	1.25	0.60
30 lb/sack	17.09	17.19	0.143	0.240	0.84	1.39
Sodium benzoate						
1 percent/sack	12.84	12.40	0.389	0.463	3.03	3.74
2 percent/sack	13.00	12.64	0.445	0.455	3.42	3.60
Hydrated lime						
2 percent/sack	13.79	13.68	0.166	0.213	1.20	1.56
4 percent/sack	14.04	13.81	0.138	0.256	0.99	1.85

Figure 3. 28-day absorption of steam- and water-cured concrete.

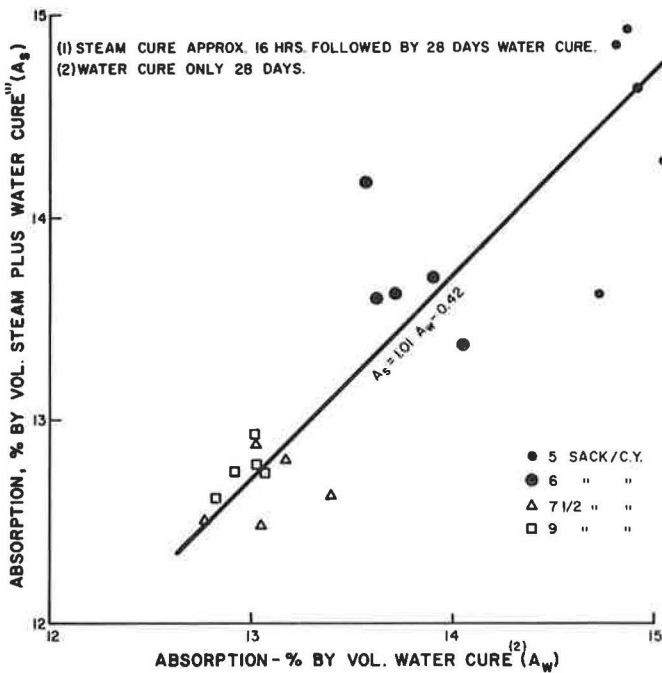


Figure 4. Weight gain of partially immersed specimens.

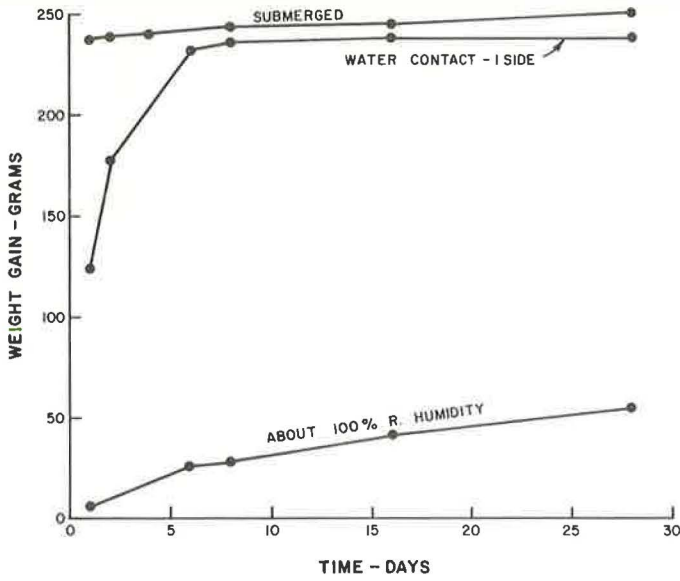
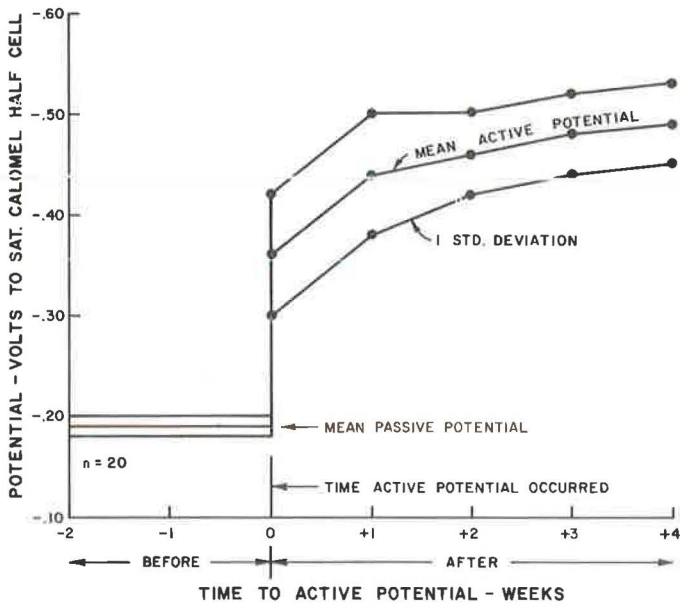


Figure 5. Typical half-cell potential of steel in concrete.



changes from passive to active when sufficient chlorides come in contact with the steel to cause corrosion. This change in potential has been measured to have a rate of change of about 0.15 volt in 3 hours; however, this rate is not known to be an average rate of change.

As indicated in Figure 5, the passive or noncorroding potential of the steel has a mean value of about -0.19 volt as referenced to the saturated calomel half-cell. In a previous study (21), the mean passive potential of 200 specimens was found to be approximately -0.11 volt, so these fall into a normal statistical distribution about the mean.

As shown in Figure 5, the mean change in potential at the time when it was observed was from -0.19 to -0.36 volt to the calomel cell. With increasing time, the mean active potential continues to increase to an average value of about -0.49 volt.

The observed value of an active potential of -0.36 volt seems to compare fairly well with the previously observed value of -0.33 volt (21). However, in this study as well as in another, it was observed that the steel in about 5 percent of the test blocks would have an abrupt change from a passive potential of about -0.19 volt to an active potential of about -0.36 volt and then drop back down to a passive potential. This phenomenon of shifting from passive to active for a small percentage of blocks is cyclic and has been observed in this and a previous study (21).

In a previous study (21), we showed that the time to the active potential of steel in concrete that is partially immersed in a saturated sodium chloride solution is mathematically related to the time to concrete cracking due to corrosion. Therefore, we did not include the test parameter of observing the surface of the concrete for cracks or rust stains. Visual observations not only are of questionable accuracy depending on the observer but also are a more time-consuming and expensive procedure than is the measuring of half-cell potentials.

Batch Variations

An attempt was made to determine the influence, if any, of batching procedures on the corrosion test results. In this test series, as given in Tables 6 and 7, the six-sack concrete was batched as follows:

1. Series 1 concrete was batched at a rate of one batch per week, and
2. Series 2 concrete was all batched in 1 day.

Each batch contained 10 blocks, of which one-half were water-cured for 28 days and the other steam- plus water-cured.

By an analysis of variance (25), it was determined that, for the steam-cured concrete, there was an F-ratio (for N = 50) of 0.0671, which does not indicate there was any significance between the test results for the different batching procedures.

For the moist-cured concrete, the analysis of variance was calculated to have an F-ratio of 10.01 (for N = 50), which is considered to represent a significant difference at the 95 percent confidence level as a result of the methods of batching.

In effect, the data show that batching methods both do and do not affect the results.

Effect of Cement Factor

To determine the influence of cement content on the time to corrosion of the steel, we cast concrete blocks containing 5, 6, 7½, and 9 sacks of cement per cubic yard. The test specimens were either water-cured or steam- plus water-cured for 28 days. Table 6 gives the days to an active half-cell potential for the cement variables (Fig. 6). The statistical significance of the results is given in Table 7. As shown in Figure 6, time to an active half-cell potential depends on the cement content of the concrete.

By the method of least squares, a regression analysis indicated the following relationship between cement factor and time to an active potential for the steam- plus water-cured concrete:

$$P_s = 0.157(C)^{3.34} \quad (2)$$

Table 6. Days to active half-cell potential with various cement contents.

Batch	5 Sacks/Cu Yd		6 Sacks/Cu Yd ^a				7½ Sacks/Cu Yd		9 Sacks/Cu Yd	
			Series 1		Series 2					
	WC ^b	SWC ^b	WC	SWC	WC	SWC	WC	SWC	WC	SWC
1	49	42	104	56	107	82	287	158	394	151
	71	41	78	71	118	77	287	326	406	393
	39	29	32	71	98	61	369	139	362	270
	34	48	18	64	100	91	317	174	518	286
	56	28	67	61	77	103	53	146	394	403
2	38	44	55	73	63	68	132	174	416	237
	64	20	70	62	135	49	251	129	367	181
	62	34	80	45	152	55	276	70	388	185
	45	31	111	50	128	61	223	120	351	185
	35	24	146	64	128	44	199	118	388	185
3	56	29	62	37	93	55	201	145	553	390
	34	33	79	44	89	61	177	166	322	210
	41	33	62	72	40	61	177	124	488	56
	40	40	56	58	70	68	177	135	504	194
	56	26	79	72	55	48	208	112	399	320
4	54	25	54	104	114	57	316	207	316	270
	54	54	48	64	98	70	316	124	396	253
	26	43	48	71	131	55	176	162	512	165
	57	33	35	39	121	55	109	188	405	272
	54	32	61	71	61	63	232	125	316	272
5	29		118		110	77	213		307	
	35		85		75	77	204		385	
	35		84		30	44	206		276	
	27		77		112	77	171		449	
	31		97		91	77	66		68	

Note: Batch 6, cast in 1 day, was done at 6 sacks/cu yd. For water-cured concrete, the results were 137, 110, 96, 77, and 103 days to active potential; and, for steam-plus water-cured concrete, the results were 34, 72, 48, 51 and 65 days to active potential.

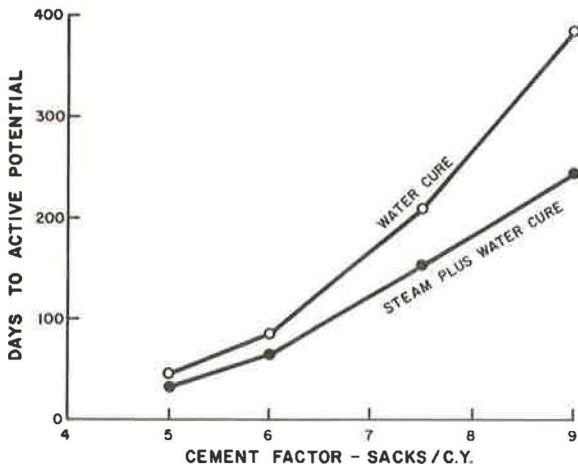
^aSeries 1 samples were cast at one batch per week, and series 2 were all cast in 1 day.

^bWC = water-cured concrete; SWC = steam-plus water-cured concrete.

Table 7. Statistical significance of data given in Table 6.

Variable	5 Sacks/Cu Yd		6 Sacks/Cu Yd				7½ Sacks/Cu Yd		9 Sacks/Cu Yd	
			Series 1		Series 2					
	WC	SWC	WC	SWC	WC	SWC	WC	SWC	WC	SWC
Mean	44.9	62.5	72.2	62.5	97.3	63.5	213.7	152.1	387.2	243.9
Standard deviation	12.7	15.2	28.5	15.2	29.5	15.0	77.8	51.2	97.3	88.2
Coefficient of variation	28.4	24.3	39.5	24.3	30.3	23.7	36.4	33.6	25.1	36.1

Figure 6. Effect of cement factor on time to active potential.



where

P_s = days to an active potential, steam plus 28 days of water curing of concrete, and
 C = cement factor, in sacks per cubic yard.

For this relationship, the correlation coefficient was 0.910 and the standard error of estimate was $0.1306 \log_{10}$ for the 110 pairs of data.

When we analyzed the data for the 28-day water-cured concrete, a regression analysis indicated the following relationship:

$$P_w = 0.104(C)^{3.72} \quad (3)$$

where P_w = days to an active potential, water-cured concrete, and C is as described above. For this relationship, the correlation coefficient was 0.8797 and the standard error of estimate was $0.1765 \log_{10}$ for the 130 pairs of data.

To determine the average fit between the water- and steam- plus water-cured concrete, we combined the data by mathematically equating the water- to the steam-cured concrete (Eq. 8). The result of this analysis was

$$P_{ws} = 0.125(C)^{3.42} \quad (4)$$

where P_{ws} = days to active potential of mathematically combined water- and steam-plus water-cured concrete. For this relationship, the correlation coefficient was 0.8915, and the standard error of the estimate was $0.1504 \log_{10}$ for the 240 pairs of data.

Concrete Curing Time

To study the effect of the length of curing on the time to an active potential of the embedded steel, we water-cured concrete for 2, 4, 8, 16, and 32 days. As given in Tables 8 and 9, and also Figure 7, the length of water curing has a definite influence on the time to corrosion. The longer the curing time is, the longer the time to an active potential is.

By the method of least squares, a regression analysis was made to determine the effect of water curing time on the time to an active potential. For the steam- plus water-cured concrete, results of the analysis were

$$P_s = 6.23(D)^{0.66} \quad (5)$$

where

P_s = days to an active potential, steam- plus water-cured concrete, and
 D = days of post-underwater curing.

For this relationship, the correlation coefficient was 0.8165, and the standard error of estimate was $0.2014 \log_{10}$ for the 100 pairs of data.

The regression analysis of the effect of water curing time of water-cured concrete on the time to an active potential of the steel produced the following equation:

$$P_w = 6.0(D)^{0.90} \quad (6)$$

where P_w = days to active potential, water-cured concrete. For this relationship, the coefficient was 0.826, and the standard error of estimate was $0.2651 \log_{10}$ for the 100 pairs of data.

To combine the effect of the two curing methods, we corrected the time to an active potential of the water-cured concrete to that of the steam- plus water-cured concrete by use of Eq. 8. The results of this analysis indicate the following influence of water time on the time to an active potential:

$$P_{ws} = 6.1(D)^{0.78} \quad (7)$$

Table 8. Days to active half-cell potential at various underwater curing times.

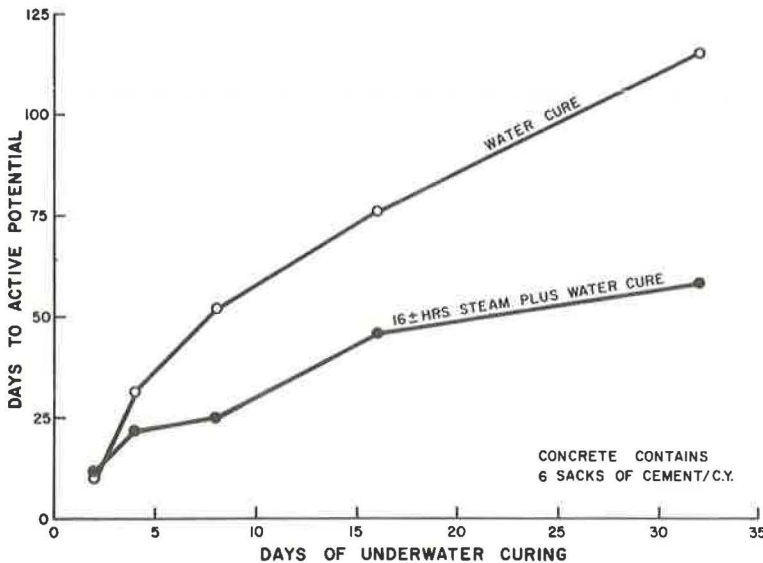
Batch	Days of Underwater Curing of WC ^a					Days of Underwater Curing of SWC ^a				
	2	4	8	16	32	2	4	8	16	32
1	9	21	29	58	115	23	56	23	55	94
	5	18	47	63	60	9	6	8	34	49
	23	41	83	47	129	6	10	28	22	53
	12	19	68	84	117	23	19	37	30	49
	8	24	50	72	103	7	4	12	29	56
2	5	3	26	47	101	13	10	29	61	53
	21	38	76	61	129	19	27	19	54	62
	12	31	48	63	138	12	21	33	28	72
	6	21	65	84	183	8	38	37	26	80
	26	24	65	69	80	8	14	33	23	89
3	5	59	42	86	117	5	18	20	40	70
	2	63	44	112	140	13	17	20	35	70
	22	74	48	55	154	9	11	28	33	63
	5	59	49	75	143	5	12	16	47	61
	55	59	48	91	109	5	35	28	34	59
4	19	40	38	44	122	19	10	21	51	52
	2	63	44	86	119	26	7	34	36	75
	5	38	55	91	61	13	7	16	55	59
	2	38	52	149	75	5	31	34	68	101
	5	27	52	84	109	13	19	29	55	52

Note: All specimens composed of six sacks of cement per cubic yard.
^aWC = water-cured concrete; SWC = steam- plus water-cured concrete.

Table 9. Statistical significance of data given in Table 8.

Days of Underwater Curing	Mean		Standard Deviation		Coefficient of Variation	
	WC	SWC	WC	SWC	WC	SWC
2	10.0	12	7.8	6.7	78.8	55.4
4	38	19	19.2	13.1	50.5	70.5
8	51.5	25	14.2	8.5	27.7	33.5
16	76.1	41	24.7	13.7	32.4	15.3
32	115.2	66	30.5	15.3	26.5	23.2

Figure 7. Effect of curing time on time to active potential.



where $P_{w,s}$ = days to active potential, water-cured and steam- plus water-cured concrete. For this relationship, the correlation coefficient was 0.7894, and the standard error of estimate was 0.2603 \log_{10} for the 200 pairs of data.

Curing Method and Time to Active Potentials

The average time in days to an active potential for the two curing methods is shown in Figure 8. By the method of least squares, a regression analysis indicated the following relationship between water and steam plus water curing to the time to an active potential of the steel:

$$P_s = 0.595 P_w + 4.21 \quad (8)$$

where

P_s = days to active potential, steam- plus water-cured concrete, and
 P_w = days to active potential, water-cured concrete.

For this relationship, the correlation coefficient was 0.9680, and the standard error of estimate was 18.1 days for the 40 pairs of averaged data points.

Admixture-Inhibitor Study

In a preliminary evaluation of using admixtures in concrete to forestall the time to corrosion of steel in concrete, three were selected. Hydrated lime was added to the concrete mix at the rate of 2 and 4 percent by weight of the cement. Sodium benzoate, a reported corrosion inhibitor for steel in concrete (23), was added to the concrete mix at a rate of 1 and 2 percent by weight of the cement, and pozzolan, a material that is reported to enhance some properties of concrete (24), was added at a rate of 15 and 30 pounds per sack of cement.

The pozzolan was a calcined volcanic tuff tested under ASTM C 618. All concrete used in the admixture-inhibitor study contained 6 sacks of cement per cubic yard and had a total underwater curing time of 28 days before corrosion testing. The results are given in Table 10, and are shown in Figure 9. The statistical significance of the data are given in Table 11.

Concrete Shrinkage

At the time the concrete corrosion specimens were batched, three 3- x 3- x 11 $\frac{1}{4}$ -in. bars were cast to measure the 14-day drying shrinkage at 50 percent relative humidity and 73 F. As given in Table 12, without altering the ratio of coarse and fine aggregate, we found that shrinkage of the concrete increased with increasing cement factor apparently because of the increase in mixing water. Also, when pozzolan was added to the mix, there was an increase in drying shrinkage associated with an increase in mixing water needed to maintain constant slump. When hydrated lime was added to the concrete mix, the mixing water and shrinkage were not significantly changed.

The addition of the corrosion inhibitor (23) sodium benzoate did not result in a highly significant change in shrinkage. However, it is of interest that, even with reduction in mixing water, the concrete containing sodium benzoate did not show any significant reduction in its drying shrinkage over the concrete without admixture. During the mixing of the concrete containing sodium benzoate, the mix was observed to have a frothy or bubbly appearance.

Chloride in Concrete

As an indication of the quantity of salt that could be absorbed by the concrete at the steel-concrete interface, 40 six-sack, 2-day water-cured blocks were analyzed. Half of these blocks were water-cured for 2 days, and the other half were first steam-cured for about 16 hours and then water-cured for 2 days.

Fourteen days after the reinforcing steel had a measured active half-cell potential, the blocks were mechanically split to expose the concrete mortar interface with the

Figure 8. Water curing versus steam plus water curing.

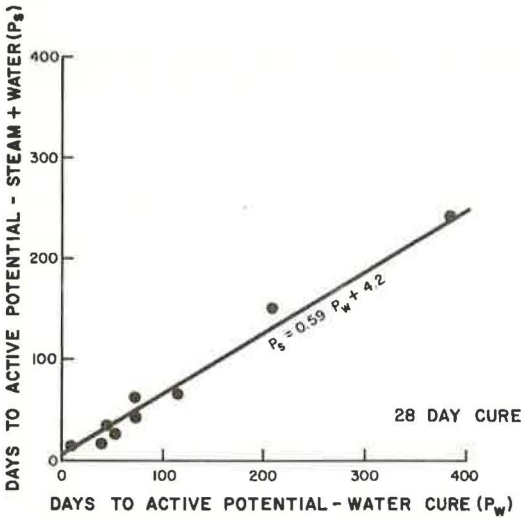


Table 10. Days to potential half-cell with various admixtures and inhibitors.

Batch	15 Lb Pozzolan		30 Lb Pozzolan		2 Percent Lime		4 Percent Lime		1 Percent Sodium Benzoate		2 Percent Sodium Benzoate	
	WC ^a	SWC ^a	WC	SWC	WC	SWC	WC	SWC	WC	SWC	WC	SWC
1	387	281	67	566	90	49	120	54	193	95	174	88
	130	211	137	515	106	48	137	47	169	88	197	60
	485	172	139	517	82	50	69	71	151	75	172	75
	134	176	64	268	82	60	116	64	69	88	75	104
	61	274	67	71	67	69	75	54	71	137	145	67
2	55	195	62	265	143	55	87	55	141	101	185	70
	62	181	62	36	66	66	106	37	146	62	162	73
	66	164	561	220	77	64	70	55	188	101	181	35
	146	159	62	468	99	59	104	48	136	55	118	70
	174	97	62	48	77	50	62	64	176	64	92	66
3	54	177	62	516	89	51	119	84	147	89	168	96
	63	138	54	376	93	62	107	160	151	98	177	124
	58	170	53	247	56	75	62	58	177	126	257	107
	62	56	441	448	110	33	100	62	128	51	226	98
	62	247	54	322	98	58	86	62	161	54	243	151
4	46	26	477	316	148	55	85	39	109	179	237	190
	50	165	477	431	120	85	95	61	307	181	179	139
	46	190	48	272	129	64	29	57	151	151	218	176
	46	90	54	517	61	61	109	50	158	151	270	124
	319	218	57	57	134	43	124	61	57	83	61	134
5	475		69		69		106		120		188	
	349		43		104		90		125		106	
	225		69		84		111		141		120	
	80		69		86		78		132		183	
	69		77		106		69		55		84	

Note: Specimens composed of six sacks of cement per cubic yard.

^aWC = water-cured concrete; SWC = steam- plus water-cured concrete.

Table 11. Statistical significance of data given in Table 10.

Admixture-Inhibitor	Mean		Standard Deviation		Coefficient of Variation	
	WC	SWC	WC	SWC	WC	SWC
15 lb pozzolan	148	169	141	65.3	95	38.5
30 lb pozzolan	135	324	160	174	118	53.8
2 percent lime	95	58	25.2	11.5	26.5	19.9
4 percent lime	92.6	62	24.6	25.3	26.6	40.7
1 percent sodium benzoate	142	101	51.4	40.2	36.1	40.8
2 percent sodium benzoate	169	102	57.3	40.8	34.0	39.9

Figure 9. Effect of admixtures-inhibitors on time to active half-cell potential.

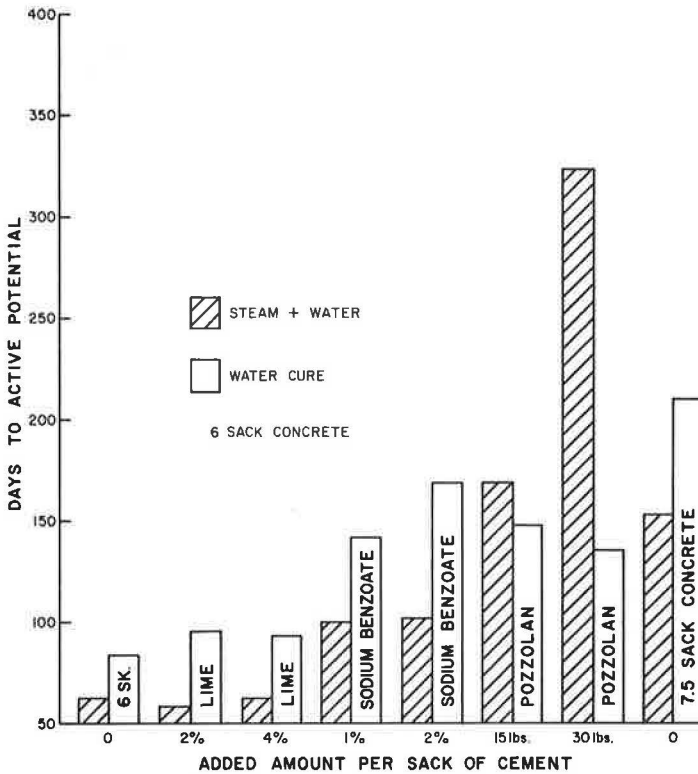


Table 12. 14-day drying shrinkage of concrete.

Cement Factor	Admixture	Percentage of Shrinkage ^a	Percentage of Control ^b
6.00	None	0.023	100
5.99	Pozzolan, 15 lb/sack	0.033	143
5.99	Pozzolan, 30 lb/sack	0.047	205
6.00	2 percent hydrated lime, 1.89 lb/sack	0.025	109
5.98	4 percent hydrated lime, 3.76 lb/sack	0.025	109
5.96	1 percent sodium benzoate, 0.94 lb/sack	0.027	117
6.04	2 percent sodium benzoate, 1.88 lb/sack	0.021	92
5.02	None	0.021	92
7.51	None	0.025	109
9.01	None	0.030	130

^a3- x 3- x 11½-in. bars

^bAverage of three bars.

steel. Then the mortar, for a depth of about $\frac{1}{16}$ in., was mechanically removed for about 3 in. This section of mortar would have been in that part of the concrete block that was immersed in the sodium chloride solution.

The concrete mortar was then chemically analyzed for chloride content, and it was estimated that the sand-cement mortar portion of concrete would weigh 2,040 lb/cu yd.

For the 20 water-cured blocks, the absorbed chloride in the concrete at the mortar-steel interface had a calculated mean value of 17.9 lb/cu yd, with a standard deviation of 2.38 lb/cu yd for the 20 data points. In the case of the steam plus 2 days of water curing, the mean chloride content at the mortar-steel interface was 21.7 lb/cu yd, and the standard deviation was 3.82 lb/cu yd for the 20 data points.

The computed chloride content of the concrete in this test is less than that found in bridge piles that were continuously submerged for about 40 years in seawater (28).

DISCUSSION OF RESULTS

Corrosion Testing

Although 15 different test methods have been identified, it might be well to discuss the differences that have been obtained in three separate tests with approximately the same six-sack concrete mix and test method by the same laboratory (20, 21).

In study 1 (20), the six-sack, non-air-entrained concrete blocks were fog-cured for 14 days and then air-dried by laboratory storage for 60 days, prior to being partially immersed in a saturated salt solution. The average time to corrosion-caused cracking of these concrete blocks was 22 days.

In study 2 (21), the six-sack concrete blocks were moist-cured in a fog room for 7 days and stored in the laboratory under controlled conditions of about 72 F and 50 percent relative humidity for 10.5 months. These blocks were then subjected to varying depths of partial immersion in fresh water for about 5½ months before being partially immersed in the saturated salt solution.

In study 1 concrete cracking was observed after 22 days, whereas in study 2 the time was 309 days, a time ratio of 14 to 1 for about the same quality of concrete.

In comparing results from the two previous tests, it is apparent that the moisture content of the concrete immediately prior to partial immersion of the blocks in the salt solution was of great significance. In test 1, the concrete had air-dried for 60 days, and, in test 2, the blocks were saturated with fresh water immediately prior to partial immersion. It is obvious that the partially air-dried blocks could almost immediately absorb the salt solution, whereas the blocks saturated in fresh water in test 2 had to transpire some of the absorbed water before the salt water could enter the concrete. Also, as shown by this study, the influence of concrete curing time prior to testing was also probably significant.

In this latest, or third test series, even though the concrete was saturated with fresh water immediately prior to saltwater exposure, the days to an active potential of the steel of the six-sack, water-cured concrete varied from an average of 10 to 115 days, depending on the length of water curing.

In addition to the variables of curing time and initial moisture content of the concrete, in study 1 it was observed that, when the atmosphere was about 54 percent relative humidity, the length of time to corrosion-caused cracking of a seven-sack concrete increased by approximately 50 percent when the relative humidity of the atmosphere was increased to 95 to 97 percent. Therefore, it is apparent that corrosion testing of steel in concrete can revolve about two basic concrete parameters: absorption by a dry concrete and combination of desorption by evaporation and absorption by capillary action of the aggressive water. Also, when considering desorption as a test parameter, it is obvious that the relative humidity of the atmosphere should be of significance.

Variation in Results

In study 2, and even in this third study, the coefficient of variation of the time to corrosion is roughly 30 to 35 percent. A coefficient of variation of this magnitude has a great bearing on the number of samples that must be tested to determine whether the

test results are real or accidental. For example, at the 95 percent confidence level and a coefficient of variation of 35 percent, it could be expected that the average test value for two blocks could have a maximum mean error of about 55 percent. Therefore, if two samples were used for testing a variable, a difference of 50 percent in the average test time would look good on a chart, but it could just as well be an accident.

Chloride Accumulation

It is acknowledged that, when the chloride ion is either mixed with (1, 11, 18) or absorbed by the concrete (2, 16, 17, 20, 27), this ion is primarily responsible for the overwhelming majority of the reported cases of corrosion of steel. Although this study has directed a maximum amount of attention toward the influence of concrete variables on the time to corrosion of steel, only a minor amount of attention was directed toward the actual mechanism of chloride accumulation by absorption or desorption of water in the concrete.

For example, this study shows that concrete absorption is not the single controlling mechanism for the time to corrosion. However, absorption seems to relate to concrete cement factor in this test, which does relate to the time to corrosion. In a previous study (2), it was empirically determined that the quantity of water that evaporated out of concrete could be related not only to concrete composition but also to the time to corrosion of the steel. It was assumed that chlorides that accumulated in the concrete by the process of water evaporation would leave a residual of salts.

In this regard, it was reported (28) that the computed concentration of chloride in concrete piling that was continually submerged for approximately 40 years was greater than that found in the seawater. Therefore, it is inferred that chlorides are transferred into the concrete by capillary action and concentrated by a mechanism of evaporation of the water at the atmospherically exposed concrete surface. If this accumulation of chloride is by absorption and desorption by water vapor, then we could infer that water vapor can travel within a seemingly water-saturated pile for a longitudinal distance of at least 10 ft (28). Apparently there could be voids in concrete where there is free passage of water vapor even though the capillary pores are filled with water.

If the indicated mechanism of chloride accumulation in concrete can be confirmed, then laboratory corrosion testing can be directed toward controlling those variables that can cause misleading test results. And, most important, the solution to economically preventing or forestalling the time to corrosion of steel in concrete can be determined in the laboratory.

SUMMARY AND CONCLUSIONS

Absorption

Concrete absorption, per se, does not appear to be a direct measure of ability of concrete to inhibit or prevent corrosion of embedded steel. However, it may be valuable in evaluating similar concrete mixes. That concrete absorption is not necessarily related to the time to corrosion of the steel is illustrated by the following two conflicting test results: (a) concrete absorption is reduced by increasing the cement factor, which increases the time to corrosion, and (b) concrete absorption is reduced by steam curing with a resulting decrease in the time to corrosion. Roughly, steam curing reduces volumetric concrete absorption by 0.3 percent (Fig. 3).

Concrete Sorption

A preliminary test of submerging one face of a concrete specimen in water was performed to confirm capillary action as the primary mode for transport of water into concrete. The concrete that had only one face in water absorbed nearly as much water as one that was entirely submerged. Therefore, capillary action must be a large factor in the movement of water into the atmospherically exposed area of concrete. In addition, the gain in weight of concrete that is simply exposed to high humidity confirms the hygroscopic adsorption properties of concrete (26) (Fig. 4). In effect, because all concrete samples were considered water-saturated at the beginning of the test, the varia-

tions in test results due to concrete variables are probably most related to the desorption characteristics of the concrete.

Active and Passive Potential

The total time that it takes for the half-cell potential of the steel to change from passive to active has been related to the total test period that it takes concrete to crack as a result of steel corrosion (21). In this study, the mean passive or noncorroding half-cell potential of the steel was about -0.19 volt to a saturated calomel reference cell. The mean value for the active or corroding potential on the day that the active potential was detected was -0.36 volt, which continued to increase after 4 weeks of measuring to a mean of -0.49 volt. As indicated by this and a previous study (21), the half-cell potential of steel follows a normal statistical distribution; therefore, there will be no absolute value that will precisely define an active or passive potential. However, based on the two studies, it appears that the potentials with a numerical value of less than about -0.22 volt to the calomel reference cell could empirically indicate a passive potential for about 95 percent of the measurements. Also, if the potential had a numerical value of greater than about -0.27 volt, then it could indicate an empirical active potential of the steel in approximately 95 percent of the measurements. The active potential does not indicate a rate of corrosion, merely that sufficient chloride is present to destroy the corrosion inhibiting or passivating effect of the concrete (Fig. 5).

Cement Factor

In all of the testing, as the cement factor was increased, the time to corrosion of the steel increased. The results of a regression analysis roughly indicate that the addition to the concrete mix of one sack of cement per cubic yard will increase the time to an active potential of the steel by roughly 70 percent for both the water- and the steam- plus water-cured concrete within the cement factor limits of 5 to 8 sacks per cubic yard (Fig. 6).

Length of Cure

Within the limits of the test, it was found that the length of water curing of the concrete had a pronounced influence on the time to an active half-cell potential of the steel. The longer the curing was, the longer the time to corrosion or to an active potential was. However, only a six-sack concrete mix was tested for this variable. Therefore, the length of concrete curing time may have more or less influence on the time to an active potential depending on the cement factor and even on extended times of water curing beyond the test period of 32 days.

The regression analysis of the data indicated that, by doubling the water curing time, the time to an active potential increased by 50 percent for both the water- and the water-plus steam-cured concrete (Fig. 7).

Water and Steam Curing

The steam curing of the concrete reduced the time to corrosion of the steel. With other variables equal, the regression analysis of the data indicated that the time to an active potential of the steel by steam plus water curing was about 60 percent of that by water curing alone (Fig. 8).

Admixture-Inhibitors

In this study, hydrated lime and sodium benzoate were used as corrosion inhibitors, and pozzolan was used as a concrete admixture. Test results did not clearly indicate that the lime had a significant influence, even though there was a small increase in the time to corrosion or active half-cell potential of the steel.

The use of sodium benzoate resulted in a marked increase in the time to corrosion. However, there was a significant reduction in mixing water requirements due to the

entrainment or entrapment of air. Therefore, the overall benefit of sodium benzoate is questionable until it is compared to a plain concrete made with the same amount of mixing water.

Although there was an increase in mixing water required for a given slump, the addition of a calcined, volcanic-tuff pozzolan resulted in a significant increase in the time to corrosion. This effect was greatest when the concrete was steam-cured. Based on the large coefficient of variation of test results for the water-cured concrete containing pozzolan, it is speculated that the apparent benefits of pozzolan may be increased with longer water curing than the 28 days used for this particular test; i. e., give the water-cured pozzolan and calcium hydroxide chemical reaction a chance to reach the same "maturity" of the steam-cured mix (Fig. 9).

Concrete Shrinkage

The major significance in the 14-day drying shrinkage tests was the large increase in shrinkage of the concrete containing pozzolan. Perhaps a reduction of the shrinkage might be achieved by using a coarser sand and by reportioning the mix so as to reduce the mixing water requirements (Table 12).

Chlorides in Concrete

Chemical analysis of the mortar at the steel-concrete interface showed a calculated concentration of 17.9 and 21.7 lb of chloride in the mortar portion of a cubic yard of concrete for the water- and steam-cured concrete respectively. Based on an assumed concrete absorption of 14 percent by volume, the evaporable water in the concrete could have contained salt in solution at a calculated chloride concentration of about 9 percent by weight at the steel-concrete interface.

Batch Variations

An analysis of variance was calculated for the batches of the six-sack, 28-day water- and the steam- plus water-cured concrete that was batched all in 1 day and those that were batched on a weekly basis.

For the steam-cured concrete, the test results indicated that there was no significant difference between the two procedures for casting concrete blocks. However, there was a significant difference found for the moist-cured concrete. It is speculated that for the moist-cured concrete the difference might be related to the vagaries of the test itself inasmuch as the difference between the means was about 22 percent of the 92-day average test time to active potential. This 22 percent variation in the means should also be compared to the approximate 30 percent coefficient of variation of the normal testing without regard to batching effect.

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