PORTLAND CEMENT COMPOSITION AND ITS EFFECT ON THE DE-ICING SALT FREEZE-THAW DURABILITY OF PAVERS

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SUMMARY

Components of Portland cement that influence de-icing salt freeze-thaw durability are examined in this paper. They are considered to be:

1. Hydration products that are soluble, or soluble under certain conditions, allowing leaching to take place. The increase in pore size will allow additional disruptive pressure to build up during freezing.
2. Hydration products that will react with chloride ions, penetrating into the cement paste. Some of the new compounds, such as chloroaluminates are expansive. Alumina is available from the hydration of C_3A.
3. Particle size. This plays an important role, for less than 2 μm or more than 30 μm are of little value for the production of durable paste. The most useful size range is from 4 μm to 20 μm. Hydration and carbonation of particles less than 2 μm will take place before delivery. They will have an adverse effect on the brightness of pigments, for they will act as a grey dilutant.

Suggestions are made for the modification of the composition of Portland cement, and a method for determining the relative value of different commercial brands is proposed.

1. INTRODUCTION

The cost of repairing concrete that has been damaged by de-icing salt is a major problem in North America, but little attention has been paid to the actual composition of the cement itself and how the components influence performance. This paper attempts to look at some of the variables. Sodium chloride is the de-icing salt used in Canada.

2. DE-ICING SALT MECHANISM OF FAILURE

An understanding of the mechanisms by which de-icing salt causes concrete to deteriorate when freezing and thawing is necessary if we are to evaluate the variables in the chemical and physical properties of Portland cement. A de-icing salt solution of sodium chloride will influence:

1. The degree of saturation. A salt solution will result in a greater degree of saturation in the pore structure.
2. The mechanism of freezing. Water will freeze out of solution as the temperature drops until finally a salt crystal remains. This slow freezing and expansion of water in solution will block the channels between voids with ice, pressure building up in the voids as the temperature drops further.
3. The availability of chloride ions react with the hydration products the cement paste.

3. CEMENT CHARACTERISTICS THAT INFLUENCE DE-ICING SALT PERFORMANCE

1. The chemical components that form soluble hydration products, and ones that are soluble under certain conditions.
2. The compounds that will react with chloride ions (2.3 above).
3. Particle size.

This paper covers Portland Cement composition, items 3.1, 3.2 and 3.3.

4. LEACHING

Soluble salts such as potassium and sodium sulphate will migrate into the surrounding solution during the freezing and thawing process but the majority of leaching is calcium hydroxide. Effluorescence is a similar migration of soluble salts caused by wetting and drying. Again, calcium hydroxide is the main component, carbonating on reaching the surface to form white calcium carbonate. The pore structure of the concrete paste will be changed when leaching takes place, porosity and permeability will

increase and the larger void volume will allow greater pressures to build up during the periods of freezing. We have had leachate in solution analyzed after a 50 cycle de-icing salt freeze-thaw test. It contained 95% calcium carbonate derived from calcium hydroxide. Forrester [1] has shown that the amount of calcium hydroxide in a liquid phase is greater at lower temperatures, hence the problems of efluorescence in the winter months.

5. CEMENT COMPOSITION

5.1 The Four Mjyor Components of Portland Cement

1. Tricalcium silicate: C_3S. Also known as Alite.
2. Dicalcium silicate: C_2S. Also known as Belite.
3. Tricalcium aluminate: C_3A.
4. Tetracalcium aluminoferrite: C_4AF.

Both tricalcium silicate and dicalcium silicate produce calcium silicate hydrate and calcium hydroxide when combined with water, but Czemin [2] has calculated that the extra calcium in tricalcium silicate produces close to 40% by weight of calcium hydroxide when fully hydrated: dicalcium silicate only 18%. Cements containing higher percentages of C_3S, smaller amounts of C_2S result in higher early strengths and many concrete specifications are written on the basis of a required strength at 28 days. Cement manufacturers have increased C_3S levels over the past fifty years in order to allow the user to reduce the weight of cement required for a specified strength. This has increased durability problems in colder climates because higher water:cement ratios have often been the result of lower cement contents. Also, these cements with high C_3S contents produce more calcium hydroxide.

5.2 Phase Composition

Bogue [3] published his empirical formula for phase composition in 1929, and it is still used by cement manufacturers to calculate phase percentages for customer's reports. The formula does not allow for change of composition due to the rate of cooling, the effect of fluxes and of limestone addition during the clinker grinding operation. Table 1 from a paper of Odler, Abdul Maula, Nudling and Richter [4] shows phase composition percentages for a number of German clinkers obtained by different methods and by calculation using the Bogue formula. The results show that the actual C_3S percentage will be higher than the Bogue calculation for commercial cements, the C_2S figure lower, but that the figures will be reasonably close for laboratory clinker. As we have no way of knowing accurately the exact composition of commercial cement that is delivered, we are unable to calculate the amount of calcium hydroxide that will be produced by hydration.

5.3 Chemical Reaction

Chloride and sodium ions disassociate by entering cement paste. The sodium ions are available to interact with reactive siliceous aggregate, continuing an alkali aggressive reaction. Chloride ions are the basic cause of the rusting of steel in reinforced concretes, for they neutralize the alkalinity of the protective environment provided by calcium hydroxide, allowing the steel to oxidise. Chloride ions are slow to penetrate into the cement paste, but the performance on the surface area of pavers is the key to de-icing salt durability. Both calcium hydroxide and alumina react with chloride ions, forming chloroaluminates, calcium chloride, ettringite crystals and complex compounds. The formation of ettringite crystals is expansive and will cause some scaling. Calleja [5] suggests that deterioration caused by chemical reaction may be greater in denser concrete.

TABLE 1

PHASE COMPOSITION OF GERMAN PORTLAND CEMENT CLINKERS

SAMPLE	C3S + C2S			C3S			C2S	
	Bogue %	Opt Mic %	Ohem Ex %	Bogue %	Opt Mic %	X-Ray %	Bogue %	Opt Mic %
Z-35-1	75.3	73.9	79.8	43.9	72.3	59.0	31.4	1.6
Z-35-2	75.1	74.3	79.6	25.9	54.4	61.5	49.2	19.9
Z-35-3	74.5	81.6	81.4	27.8	73.6	55.0	46.7	8.0
Z-35-4	75.0	72.9	79.2	36.5	63.2	51.5	38.5	9.7
Z-35-5	76.0	81.7	79.2	46.8	76.1	63.0	29.2	5.6
Z-35-6	77.9	83.8	82.3	41.6	67.6	59.5	36.3	16.2
Lab Clinker	80.0	86.5	81.8	70.0	71.2	72.5	10.0	15.3

Bogue Potential phase composition calculated by Bogue method.

Opt Mic Phase composition based upon examination under optical microscope.

Chem Ex Phase composition based upon selective chemical extraction.

X-Ray Phase composition based upon X-ray detraction of clinker powder specimens.

6. PARTICLE SIZE DISTRIBUTION OF CEMENT

Locher [6] suggests that very fine particles make little contribution to the hardening process, hydration and carbonation taking place in storage before they can be used to produce concrete. Gypsum and in some cases limestone added during the grinding process are softer than clinker, and will tend to increase the percentage below 2 μm. Dimitriey, Vlasova and Yudovich [7] state that particle sizes over 30 μm are of no value, for they do not hydrate adequately. They recommend the use of jet mills for the best results when grinding clinker. Rose, Hope and Ip [8] in their technical report, *Strength and Durability of Concrete*, evaluated the performance of 26 different cements and blends with two types of aggregate. The work focused on the 28-day strength and the 50-Cycle salt scaling loss. Statistical analyses were performed on test data consisting of chemical and physical properties of the cements: properties of fresh concrete; compressive strength, salt scaling loss and air void parameters of mature concretes. No consistent set of variables correlated to the compressive strength, but a definite pattern of 50-cycle salt scaling loss was found related to particle size distribution. An increase in the percentage of particles less than 2 μm caused more scaling, and the percentage between 4 μm and 20 μm had a very strong negative correlation - i.e., increase of this percentage reduced scaling. Also, they suggest that a longer set time will result in concrete with a superior salt resistance. They relate G3A to short set time and the formation of tricalcium chloro aluminate with chloride ions. They recommend the use of cements with a high proportion of particles between 4 and 20 μm and a low G3A content.

Uniformity of colour is a problem for all paver manufacturers. Cement particles that have hydrated and carbonated before use will be a grey dilutant for pigments. Cement "G" in a mix using 200 kg of cement and 6 kg of pigment will add 15 kg of dilutant, or two and one half times the weight of colour; cement ”K" only 3 kg. Cement ”K" will produce brighter colours. What if the percentage of particles less than 2 μm varies from load to load? Is this the key to colour variation? Table 2 gives particle size distribution for the cements evaluated by Rose, Hope and Ip.

TABLE 2

CEMENT PARTICLE SIZE DISTRIBUTION

Sample	% passing 2 μm	% passing 4 μm	% passing 20 μm	% 4 to 20 μm	% passing 30 μm	% 2 to 30 μm
A	6	14	55	41	71	65
B	6	15.5	57.5	42	73	67
C	7	19	58	49	83.5	76.5
D	6.5	20.5	68	47.5	81.5	75
E	6.5	15.5	54.5	39	69	62.5
F	6	15	59.5	44.5	76	70
G	7.5	15.5	55	39.5	70	62.5
H	4.5	15.5	62.5	47	79	74.5
I	4.5	14.5	62	47.5	78	73.5
J	6.5	15	57.5	42.5	73	66.5
K	1.5	11	58.5	47.5	73.5	72
L	3	12	57	45	72.5	69.5
M	2	12	61	49	78	76
N	6	17	58	41	72	66
O	4.5	14	56	42	70	65.5
P	5.5	15.5	58.5	43	75	69.5
Q						
R	4.5	15	62	47	78	73.5
S	6	16.5	63	46.5	79	73
T	5.5	18	68.5	50.5	83	77.5
U	4	13.5	57.5	44	74	70
V	5.5	16	56.5	40.5	73	67.5
Z-1	6	21.5	78.5	57	91	85
Z-2	4.5	21	80	59	94	89.5
Z-3	7	23	80	57	92.5	85.5
Z-4	6.5	22.5	79.5	57	92	85.5

Diff.	Highest and lowest passing	2 μm	400%
Diff.	Highest and lowest passing	4 μm	109%
Diff.	Highest and lowest between	2 & 30 μm	51%
Diff.	Highest and lowest between	2 & 20 μm	43.2%

7. CONCLUSION

Paver manufacturers in Northern climates must appreciate the variables in Portland cement that have an effect on durability performances. Cement producers are unlikely to change their product to suit our needs, but usually we have a choice of different brands. Also, we are able to modify cement composition. Blast furnace slag has a lower calcium to silica ratio, and produces less calcium hydroxide on hydration. Partial substitution of slag for cement will greatly reduce the amount of calcium hydroxide, and slags often have a better particle size distibution. Slag with a high silica content will have extra silica available to produce a secondary hydration reaction with calcium hydroxide, forming calcium silicate hydrate. Silica fume provides this secondary reaction

but we have found that it takes place after some efluorescence has already formed on the paver surface in winter. Fly ash will provide available silica, but it is dangerous because high alumina levels may result in poor performance.

The hypotheses of Locher and Dimitriev are confirmed by Rose. Hope and Ip, so it is logical for paver manufacturers to value available brands of cement on the basis of the percentage of useful particles, say between 2 and 30 μm. Cement "Z-2" has 89.5% within this useful range; more than any other brand, and so should be used as the reference brand. The value of another brand will be the cost of brand "Z-2" times the percentage of 2 to 30 μm of the other brand divided by the percentage of 2 to 30 pm of brand "Z-2". For example, if brand "Z-2" costs $100.00 per tonne, then brand "G" will be worth $100.00 x 62.5/89.5 = $69.83 per tonne. The user of brand "G" should expect to use 43% more cement in order to obtain the same durability as obtained with brand "Z-2". However, it must be realized that increasing the quantity of a cement such as "G" will add even more grey dilutant to coloured pavers and may bring the total alumina content to dangerous levels.

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