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DURABILITY OF CONCRETE STRUCTURES EXPOSED TO $CaCl_2$ BASED DE-ICING SALTS

by

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ABSTRACT

The authors point out that in addition to the steel corrosion, calcium chloride can specifically act as an aggressive agent for concrete through the formation of calcium oxychloride ($3CaO \cdot CaCl_2 \cdot 15 H_2O$). This product is formed by reaction of $CaCl_2$ diffusing through the cover and $Ca(OH)_2$ produced by cement hydration.

The main purpose of the present paper was to study the influence of the cementitious system (portland cement with and without a pozzolanic addition) on the damaging effect caused by $CaCl_2$ used as a de-icing agent.

In order to block both steel corrosion and concrete deterioration, the reduction of the water/cement ratio in the concrete mix should be accompanied by the utilization of slag cement or pozzolanic cement. The slag content should be at least 50% of the cement, whereas silica fume (> 15% by weight of cement) instead of fly ash (30%) should be preferred.

Keywords: Freezing and thawing. Chloride penetration. Slag. Fly ash. Silica fume. Durability.

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INTRODUCTION

Calcium and sodium chloride are widely used as de-icing agents to remove ice from concrete pavements. It is well-known that both these products can promote the corrosion of the steel reinforcement because of the chloride ion (Cl^-) can penetrate through the concrete cover (1). In addition to this general damaging effect on steel reinforcement, calcium chloride ($CaCl_2$) can also attack the cement matrix of concrete (2). Sodium chloride (NaCl) is not an aggressive agent for plain concrete unless reactive aggregates are present (3).

The specific attack of concrete specimens caused by $CaCl_2$ has been demonstrated by Chatterji (2) and confirmed by Berntsson and Chandra (4). Collepardi and coworkers (5-8) have found that this attack is accompanied by the formation of the hydrated calcium oxychloride as shown by the following reaction:

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \longrightarrow 3CaO \cdot CaCl_2 \cdot 15H_2O$$

When initially exposed to CO_2, the carbonated concrete or mortar specimens are not damaged by the subsequent action of $CaCl_2$ since $Ca(OH)_2$ is transformed into $CaCO_3$ and $3CaO \cdot CaCl_2 \cdot 15H_2O$ cannot be formed (8).

Concrete deterioration caused by penetration of $CaCl_2$ occurs quickly at low temperatures, such as 5-10°C, which is higher than the freezing temperature and therefore this effect cannot be confused with the deterioration of concrete from freezing and thawing. However, reinforced concrete structures exposed to $CaCl_2$ as de-icing salt may deteriorate in practice from simultaneous action of three different mechanisms:

- *(i)* corrosion of reinforcing steel (electrochemical action), which can cause the concrete cover to spall;
- *(ii)* freezing and thawing action acting on concrete not provided with an adequate air-void system;
- *(iii)* formation of the oxychloride in the cement matrix, as described above.

In field concrete structures the above three mechanisms occur simultaneously and this can explain why the chemical attack of $CaCl_2$ on cement paste has been masked for a long time. Although in the past the specific role played by de-icing salts in concrete structures exposed to cold climate was recognized (9), it was generally assumed that the deicer action was physical rather than chemical (10).

The main purpose of the present paper was to study the influence of the cementitious system (portland cement with and without a pozzolanic addition) on the damaging effect caused by $CaCl_2$ used as a de-icing agent. Because of reduction in lime content in the concrete as a consequence of the pozzolanic reaction, increased resistance of concrete to $CaCl_2$ attack can be expected.

An other purpose of the paper was to study the influence of air entrainment on the specific action of $CaCl_2$ in the absence of freezing and thawing cycles which could mask the chemical effect of the attack.

A third purpose of the paper was to study the effect of water/cement (*w/c*) of the concrete mixture on the damaging action of $CaCl_2$. A reduction in the porosity of concrete should reduce the penetration of $CaCl_2$ and therefore a reduction in the chemical attack caused by this salt could be expected by decreasing the *w/c*.

MATERIALS AND TEST PROCEDURES

The composition and the characteristics of the concrete mixtures are given in Tables 1 and 2. Normal portland cement was used alone or with a partial replacement by silica fume (15%), fly ash (30%) or ground blastfurnace slag (50%). Table 3 shows the physical properties and chemical analysis of the portland cement, silica fume, fly ash and slag. Natural sand and gravel (maximum size = 19 mm) were used for making concrete. Three different *w-c* ratios (0.40 - 0.50 - 0.60) were adopted for the normal portland cement concretes and only one (0.40) for the mixtures with mineral admixtures.

The dosage of a superplasticizer (40% of sulphonated naphtalene polymer in aqueous solution) was adjusted to produce concrete mixtures at about equal slump (210-230 mm).

An air-entraining agent (based on Vinsol Resin) was used to produce air-entrained concrete with a minimum air content of 6% according to ACI recommendations (11) for severe exposure. Only two air-entrained concrete mixtures (*w/c* = 0.40 and 0.50 with normal portland cement) were made with an air content of about 5%, corresponding to ACI 201 recommendations for moderate exposure. Both non-air-entrained and air-entrained cubic concrete specimens (100 mm) were cured at 20° C and R.H. of 95%.

Compressive strengths were measured at 1, 7 and 28 days (Table 1) in accordance with Italian standard test method (compressive stress rate of 0.5 MPa/s). After 28-day curing age, the concrete specimens were immersed in a 30% $CaCl_2$ aqueous solution. During the first two weeks the temperature of the $CaCl_2$ solution was kept at 40°C in order to accelerate the $CaCl_2$ diffusion into concrete (1). Then, the temperature was changed from 40°C to 5°C in order to favour the damaging effect caused by the $CaCl_2$ chemical action (2).

The compressive strength versus time of contact with $CaCl_2$ was determined at various ages ranging from 0 to 300 days. Since the un-reinforced specimens were always kept at a temperature higher than 0°C, the above mentioned deterioration mechanisms *i* and *ii* (due to corrosion of steel and frost action, respectively) were of course excluded. Therefore, the reduction in compressive strength versus time of exposure to $CaCl_2$ was adopted as a measurement of the chemical attack caused by $CaCl_2$.

RESULTS AND DISCUSSION

Compressive strength versus time of immersion in the $CaCl_2$ solution is shown in Fig. 1 for normal portland cement concrete mixtures and in Fig. 2 for the concrete mixtures containing mineral admixtures. Figure 3 shows typical photographs corresponding to sound and severely damaged concrete specimens after 300 days of permanent exposure to the 30% $CaCl_2$ solution.

Normal Portland Cement Concretes

Figure 1 summarizes the compressive strength results of normal portland cement concrete mixtures for three *w-c* ratios (0.40 -0.50 - 0.60) with and without air entrainment (Table 1).

In non-air-entrained concretes the damaging effect caused by the chemical action of $CaCl_2$ increases with a decreasing *w/c*. In the concrete with *w/c* of 0.40 or 0.50 the strength reduction after 300 day of exposure to $CaCl_2$ is about 80% or 75% respectively. With *w/c* of 0.60 there is a negligible reduction in strength after the same period of exposure to $CaCl_2$.

Therefore, for this special aggressive action, the general statement that concrete durability is improved by reducing the *w/c* is not confirmed. This disagreement can be explained in two different ways:

a) a lower *w/c* means a higher cement content (Table 1) and therefore a higher amount of $Ca(OH)_2$ in the concrete, which corresponds to a higher amount of $3CaO \cdot CaCl_2 \cdot 15H_2O$ responsible for the chemical action;

b) a lower *w/c* also means a lower capillary porosity in the cement matrix and therefore a higher disruptive hydraulic pressure caused by the oxychloride formation. According to this assumption, the oxychloride attack is based on an expansive physical action (very similar to that caused by ice formation) although the product is generated through a chemical process.

In air-entrained concretes the reduction in compressive strength as a function of time of contact with $CaCl_2$ is negligible or absent, provided that the air volume is higher than the value (6% for maximum aggregate size of 19 mm) recommended by ACI (11) for frost-resistant concretes devoted to "severe exposure" (outdoor exposure with moisture prior to freezing or where deicing salts are used). For instance, the reduction in the air content from 6.5% to 4.9%, in the concrete with *w/c* of 0.40, dramatically reduced the concrete resistance to $CaCl_2$ attack. Similar results have been obtained for the influence of air-entrainment in the normal portland cement concrete with a *w/c* of 0.50.

Therefore, independent of the freezing and thawing action, it is confirmed that the air content recommended by ACI for moderate exposure (5% for maximum aggregate size of 19 mm) appears not to be adequate when $CaCl_2$ is used as a deicing salt. This means that the air volume recommended by ACI (11) for concrete structures exposed to the $CaCl_2$ treatment is very critical and should be strictly met particularly in the surface portion of concrete that is in contact with

$CaCl_2$. This also means that the new recommendations of the European standard normes, ENV 206 (12), for concrete structures exposed to freezing and thawing *and* deicing salts (class of exposure: 3), do not appear to be adequate, since the maximum *w/c* of 0.50 would be accompanied by a minimum air content of 5% for a maximum size aggregate of 16 mm, and 4% air content for a maximum size aggregate of 32 mm. The results of the present work indicate that these values of the air content, for durable concretes in class of exposure 3, should be increased by 30-40% in order to be closer to the more reliable air content recommended by ACI (11) for the equivalent class of exposure ("severe exposure").

The fact that proper air-entrainment is required to produce durable concrete exposed to $CaCl_2$ (independent of the freezing and thawing effect) seems to be in agreement with the assumption (*b*) above for non-air-entrained concretes: higher *w-c* ratios appear to be more beneficial for concretes exposed to the $CaCl_2$ attack (in the absence of frost action) since a higher capillary porosity would reduce the disruptive stress caused by the oxychloride formation; proper air bubbles distribution is paradoxally more important for a low porosity concrete (*w/c* = 0.40 - 0.50) rather than for a very porous concrete (*w/c* > 0.60). It seems that air bubbles act as an important stress-release system for the disruptive hydraulic pressures generated by the ice formation as well as by the expansive chemical production of the oxychloride. On the other hand, it has been found that air entrainment improves the resistance of concrete to deterioration by sulfate attack (13) and reduces the alkali-aggregate expansion of mortar specimens even though extensive reaction occurs (14). From a practical point of view, by taking into account even the protection of rebars from the corrosion process, the best concrete mixtures for reinforced structures

exposed to frost action and to $CaCl_2$ as deicing salt should include a *w/c* as low as possible to reduce the capillary porosity and therefore the chloride diffusion through the concrete cover (1), and a minimum air content as recommended by ACI for "severe exposure" (11).

In other words a suitable microstructure of cement paste for frost-resistant concrete exposed to deicing salts should contain a proper air bubble system dispersed in a cement matrix with a capillary porosity as low as possible.

Blended Cement Concretes

Figure 2 shows compressive strength versus time of $CaCl_2$ exposure for blended cement concrete mixtures where portland cement was partly replaced by fly ash, silica fume or ground slag (Table 2). The *w/c* of 0.40 was adopted for these mixtures in order to produce concretes which, in the absence of air-entrainment, would be potentially in the most vulnerable situation to which the normal portland cement concrete mixtures without mineral additions (Fig. 1) were, when exposed to $CaCl_2$ attack.

The results shown in Fig. 2 indicate that, with a certain amount of mineral admixture replacing portland cement, concretes become $CaCl_2$ resistant even in the absence of entrained air. For a given initial compressive strength (about 50 MPa) silica fume and slag appear to be a little more effective than fly ash in producing durable concretes which are $CaCl_2$-resistant.

Preliminary tests carried out on non-air-entrained concretes with percentages of mineral additions lower than those shown in Table 2 (15% of silica fume, 30% of fly ash and 50% of slag) indicated that durable concretes could not be produced for the $CaCl_2$ attack. Therefore, it seems that the reduction of the lime content under a certain threshold value is an essential requirement to produce $CaCl_2$-resistant concretes particularly in the absence of an adequate air void system.

The reduction of lime in the cement paste of blended cement concretes is due to two simultaneous effects: the reduction of portland cement content (and consequently of the $Ca(OH)_2$ produced by cement hydration) and the combination of $Ca(OH)_2$ with the mineral addition by the pozzolanic reaction.

The higher the reactivity of the pozzolan, the lower is the amount of pozzolan required to produce $CaCl_2$-resistant concrete. This explains why the percentage of portland cement replaced by mineral addition, in order to produce $CaCl_2$-resistant concrete, increases from 15% for silica fume to 30% for fly ash and to 50% for slag. In the case of silica fume there is also an additional beneficial effect of reduction in the permeability of cement paste, which reduced the $CaCl_2$ penetration into concrete.

In the presence of air entrainment, concrete mixtures made with fly ash or silica fume or ground slag as partial replacement for portland cement, were $CaCl_2$-resistant similar to the corresponding non-air-entrained concretes (Fig. 2). Therefore, for the aggressive action of $CaCl_2$, air-entrainment would not be so important as it is for normal portland cement concrete without

mineral admixtures (Fig. 1). However, in practice the air-entrainment is always required also for blended cement concrete mixtures in order to make them frost-resistant, because field structures are exposed to freezing and thawing cycles in addition to $CaCl_2$ attack.

Although air entrainment for "severe exposure" requirement is able to enhance the durability of concretes to frost action, more durable concrete structures can be made when blended cements with fly ash, silica fume or slag are used. In fact, local reduction in the air content of the concrete surface, exposed to $CaCl_2$ as deicing salt, could cause significant damage when normal portland cement is used without mineral admixtures. Moreover, blended cements can also give more durable concretes even when NaCl-based deicing salts are used. The presence of fly ash, silica fume or slag can also reduce the risk of the damage caused by the alkali-aggregate reaction, which appears to be more severe for surface concrete structures exposed to large amounts of NaCl used as a deicer (3).

CONCLUSIONS

Concretes exposed to $CaCl_2$ appear to be severely damaged, even in the absence of freezing and thawing cycles, when non-air-entrained concrete is produced with normal portland cement.

The effect can be ascribed to the formation of an oxychloride ($3CaO \cdot CaCl_2 \cdot 15H_2O$) which causes disruptive hydraulic pressure.

The air-entrainment recommended by ACI for "severe exposure" (frost action and deicing salts) is sufficient to produce durable concrete. However, if the air content is insufficient, concretes are not $CaCl_2$-resistant, unless fly ash, silica fume and slag are used to replace part of portland cement. Both air-entrainment and the use of mineral admixtures allow durable concrete to be produced in a more reliable way. In such a case these concrete would also be more resistant to NaCl-based deicing salts if potentially alkali-reactive aggregates are used.

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Table 1 - Composition and Characteristics of normal portland cement Concrete Mixes

INGREDIENT:	BATCH QUANTITIES (Kg/m^3)							
Portland Cement	390	370	375	325	305	310	270	255
Water	156	148	150	163	153	155	162	153
Sand	745	700	720	810	780	795	890	870
Gravel (19 mm max)	1130	1095	1110	1105	1070	1080	1060	1020
Air entrain. agent	-	0.250	0.200	-	0.205	0.165	-	0.180
Superplasticizer	4.7	4.4	4.5	3.9	3.7	3.7	3.2	3.1
w/c	0.40	0.40	0.40	0.50	0.50	0.50	0.60	0.60
air volume (%)	2.2	6.6	4.9	2.1	6.3	4.8	2.7	6.3
slump (mm)	220	215	225	220	230	220	210	220
Compressive strength (MPa) at the age of:								
- 1 day	12	10	11	7	5	6	4	3
- 7 days	38	33	35	27	22	24	20	16
- 28 days	50	41	44	42	34	36	30	24

Table 2 - Composition and Characteristics of Blended Cement Concrete Mixes

INGREDIENT:	BATCH QUANTITIES (Kg/m^3)					
Portland Cement	273	259	327	310	190	180
Fly ash (30%)*	117	111	-	-	-	-
Silica fume (15%)*	-	-	58	55	-	-
Slag (50%)	-	-	-	-	190	180
Water	156	148	154	146	152	144
Sand	735	710	745	715	750	721
Gravel (19 mm max)	1105	1060	1120	1075	1125	1080
Air entrain. agent	-	0.370	-	0.360	-	0.240
Superplasticizer	4.7	4.4	6.9	6.6	4.6	4.3
w/c **	0.40	0.40	0.40	0.40	0.40	0.40
air volume (%)	1.8	5.9	2.0	6.1	1.9	6.0
slump (mm)	210	220	215	225	220	225
Compressive strength (MPa) at the age of:						
- 1 day	8	6	12	10	11	9
- 7 days	36	29	40	34	37	32
- 28 days	51	41	54	43	52	42

** The percentage of mineral admixture is referred to the total amount of cement + mineral admixture.*
*** The amount of mineral admixture is taken into account for the w-c ratio.*

Table 3 - Physical Properties and Chemical Analysis of Cement and Mineral Admixtures.

	Portland Cement*	Fly ash	Silica fume	Slag
Physical Tests				
Fineness - passing 45 μm (%)	87	90	100	86
- Blaine m^2/Kg	380	400	1800	375
Specific Gravity	3.15	2.18	2.20	2.70
Chemical Analysis (%)				
SiO_2	21.23	44.0	92.0	37.0
Al_2O_3	6.89	28.0	0.6	20.0
Fe_2O_3	5.94	9.0	1.5	0.6
CaO	60.83	4.0	0.3	39.0
MgO	2.16	2.0	0.8	3.0
Na_2O	0.10	0.7	0.4	-
K_2O	0.63	0.8	0.6	-
SO_3	1.62	1.0	-	0.4
Loss on ignition	0.60	7.0	3.8	-

* *Compressive strength (MPa) mortar specimens (w/c = 0.50): 3 day = 32 MPa; 7 day = 44 MPa; 28 day = 50 MPa.*

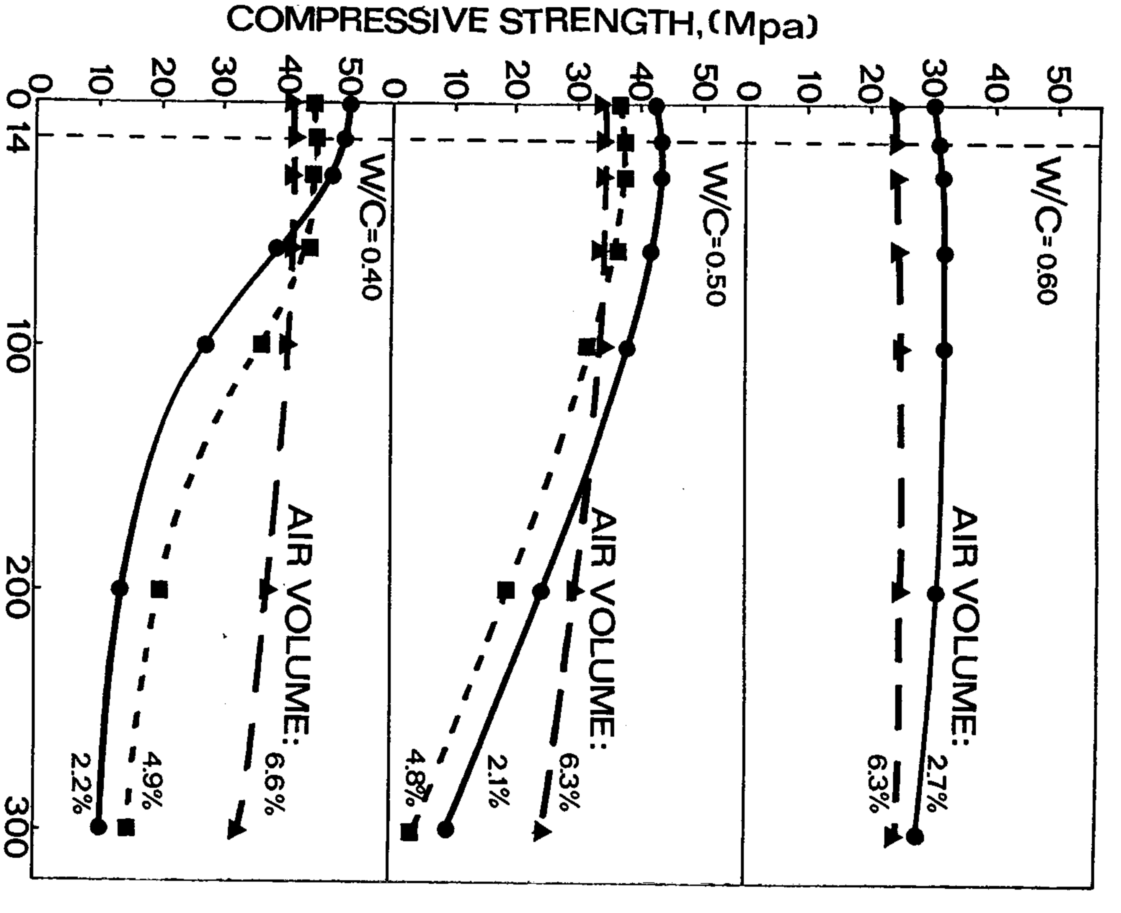

Fig. 1 - Compressive Strength Versus Time of Immersion into a 30% $CaCl_2$ Solution of 28-day Cured Portland Cement Concrete Specimens (Table 1). After 14 Days of Immersion the Temperature was changed from 40°C to 5°C.

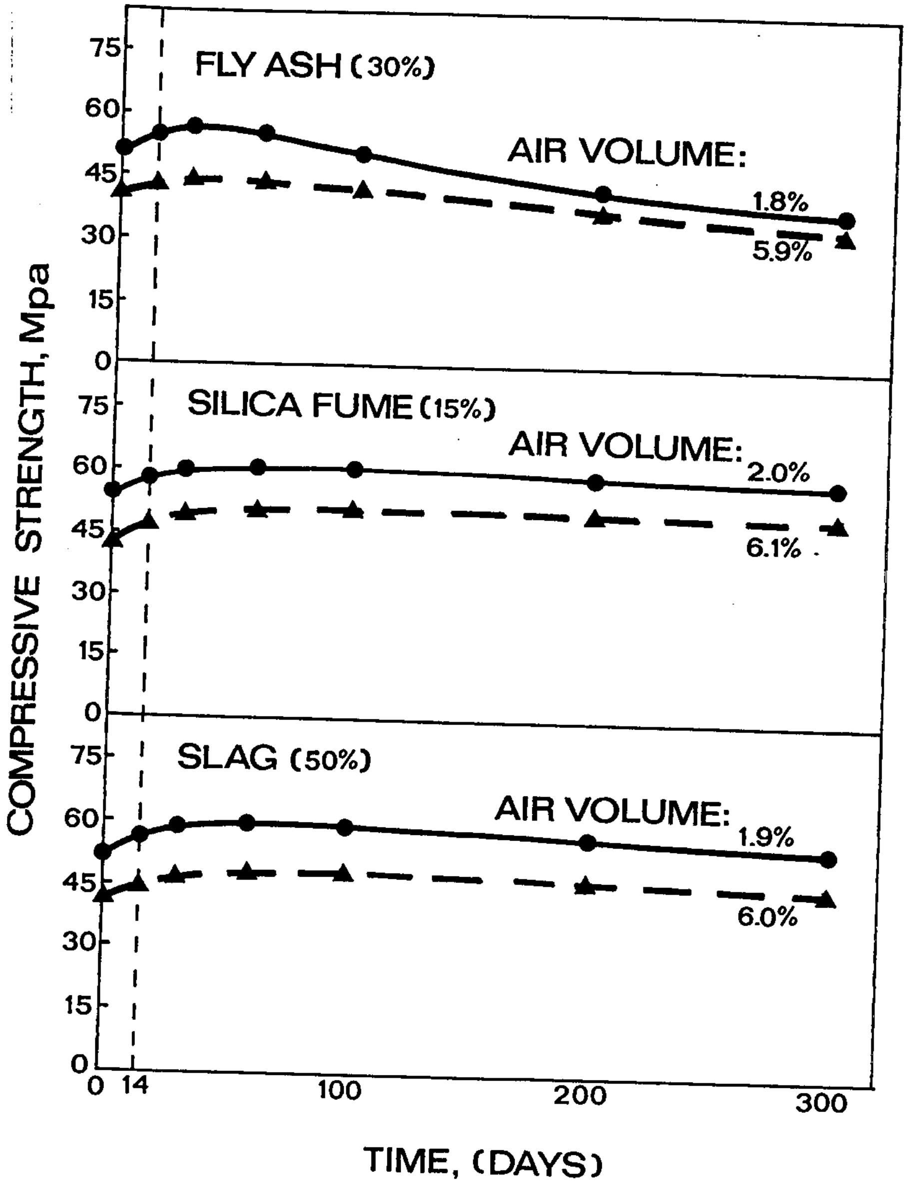

Fig. 2 - Compressive Strength Versus Time of Immersion into a 30% $CaCl_2$ Solution of 28-day Cured Blended Cement Concrete Specimens (Table 2).After 14 Days of Immersion the Temperature was changed from 40°C to 5°C.

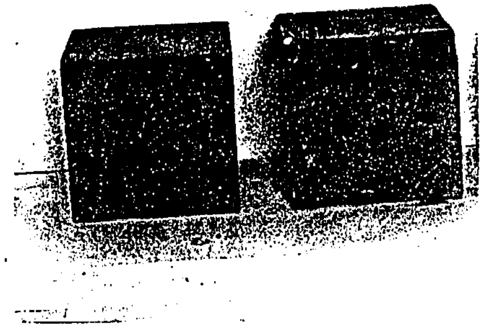

Fig. 3 - Non-Air-Entrained Concrete Specimens (w/c = 0.40) after 300 Days of Permanent Exposure to $CaCl_2$; left: Sound Specimen with 50% of Slag; right: Destroyed Specimen without Mineral Addition.