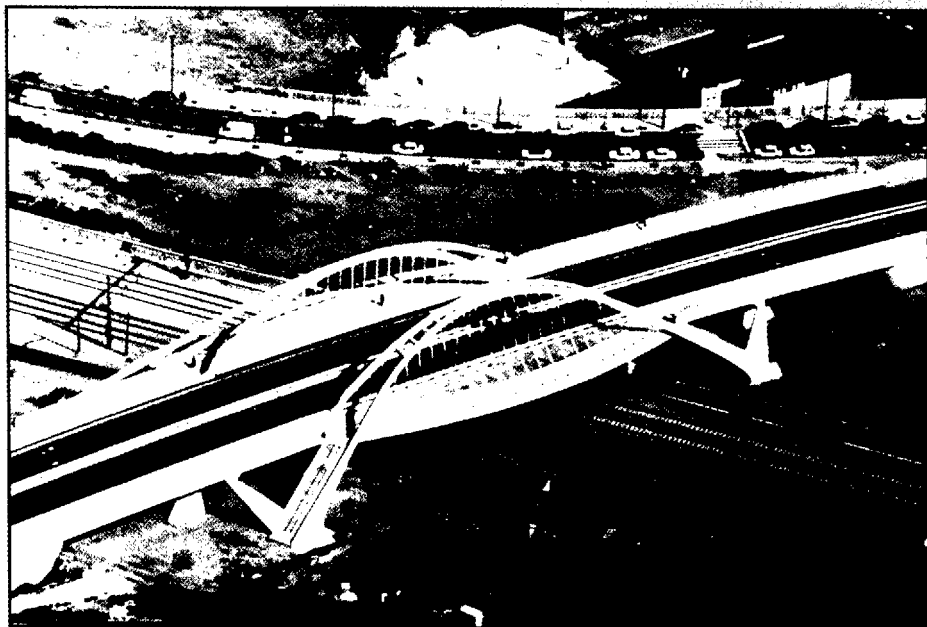


2000 CANMET/ACI

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**DURABILITY
OF
CONCRETE**

**DURABILITÉ
DU
BÉTON**

EDITOR • V. M. MALHOTRA • RÉDACTEUR EN CHEF

Durability of Concrete

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Volume II

Editor

V. M. Malhotra



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PREFACE

The Canada Centre for Mineral and Energy Technology (CANMET) of Natural Resources, Canada, Ottawa, has played a significant role in Canada for over 35 years in the area of durability of concrete. In August 1991, CANMET, in association with the American Concrete Institute (ACI), and the Institute for Research in Construction/National Research Council, Ottawa, sponsored the Second CANMET/ACI International Conference on Durability of Concrete. The conference was held August 4-9, 1991, in Montreal, Canada, and was a follow-up to the Katharine and Bryant Mather International Conference on Concrete Durability held in Atlanta, Georgia, April 27-May 1, 1987. The refereed proceedings of the Atlanta and Montreal conferences were published as ACI SP-100, and ACI SP-126, respectively.

In 1994, CANMET, in association with ACI and several other organizations in Canada and France, sponsored a third international conference on concrete durability. The conference was held May 22-28, 1994, in Nice, France, and the conference proceedings, consisting of 65 refereed papers, were published as ACI SP-145.

In 1997, CANMET, in association with ACI and several other organizations in Australia, sponsored a fourth international conference on the subject. The conference was held August 17-22, 1997, in Sydney, Australia. The two-volume proceedings of the conference consisted of 81 refereed papers, and was published as ACI SP-170.

In 2000, CANMET, in association with ACI, the Japan Concrete Institute, and several other organizations in Spain and Canada, sponsored a fifth international conference held June 4-9, 2000, in Barcelona, Spain. More than 120 papers from 35 countries were received and peer reviewed in accordance with the policies of the American Concrete Institute; 73 were accepted for publication. The accepted papers deal with all aspects of concrete durability.

In addition, several sessions dealing with sulfate attack, superplasticizers and supplementary cementing materials, and near surface testing for the durability of concrete were organized. To all those whose submissions could not be included in the symposium volume, the Institute and conference Organizing Committee extend their appreciation for their efforts and interest.

In addition to the papers that have been published in the refereed proceedings, more than 30 other papers were presented at the conference. A number of these were published as supplementary papers, and the authors of these papers are encouraged to publish in technical journals of their choice.

Thanks are extended to more than 20 members of the review panel that met in Torremolinos, Spain, in May 1999 to review the papers. Several other people also assisted in the review process, and their help is gratefully acknowledged. Without the dedicated efforts of the reviewers, it would not have been possible to have the proceedings ready for distribution at the conference. The cooperation of the authors in accepting reviewers' suggestions, and in revising their manuscripts accordingly is greatly appreciated. The authors are also to be commended for their prompt return of the revised manuscripts.

The help and assistance of A. Bilodeau (Chairman), B. Fournier, and R. Chevrier (members) of the slide review panel are gratefully acknowledged. Thanks are also extended to H. S. Wilson, M. Venturino, and G. D. Brearly for their help in processing the manuscripts. The contributions of the ACI staff are also recognized.

As an integral part of the conference, a special dinner to honor P. Scheißl was held to acknowledge his outstanding contributions to concrete durability over the last 25 years.

V. M. Malhotra
Editor

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SP 192-39

Influence of Fly Ash and Slag on Deicer Salt Scaling Resistance of Concrete

by C. Talbot, M. Pigeon, and J. Marchand

Synopsis: Over the past decades, numerous laboratory studies have clearly indicated that the use of supplementary cementing materials, and particularly fly ash, can significantly reduce the scaling durability of properly air-entrained concrete. Despite the great deal of research done on the topic, the reasons behind the detrimental influence of fly ash remain unclear. In order to bring more information on the subject, an investigation of the influence of fly ash on the deicer salt scaling resistance of concrete has been recently carried out. Test variables included water/binder ratio (0.40, 0.50 and 0.66), class of fly ash (two class C and a class CF), and the percentage of replacement of the cement by the fly ash (0, 20 and 40%). An additional series of mixtures was prepared with 25% slag as cement replacement. All deicer salt scaling tests were performed according to a modified version of ASTM C 672 on both troweled and sawed surfaces. The air-void characteristics of all mixtures were determined according to ASTM C 457, and the microstructure of selected mixtures was studied by means of SEM observations. All test results confirmed that the use of fly ash and slag can reduce the salt scaling durability of concrete as determined in the laboratory. The influence of fly ash and slag does not appear to be linked to their effect on the material pore structure. An explanation linked to its influence on the characteristics of the air-void network is suggested.

Keywords: air entrainment; fly ash; sawing; scaling; slags; spacing factor; troweling

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INTRODUCTION

In most cases, if sufficient curing time is allowed, the use of supplementary cementitious materials (SCM), causes a refinement of the pore size distribution of concrete [1-4]. Such a refinement should normally reduce the amount of ice formed in concrete during freezing. It should thus also, according to recent reports [5-6] on the relationship between ice formation and salt scaling resistance, increase the salt scaling resistance of concrete. Unfortunately, although a few good results have been reported [10], the use of SCM has generally been found to decrease this resistance [8-9]. A recent study of the amount of ice formed (in the temperature range of the salt scaling resistance test) in a number of concretes incorporating SCM has not indicated any very significant influence of the use of SCM on ice formation [7]. The reasons behind the generally poor scaling resistance of concretes containing SCM are therefore still unclear. It has been suggested that the 14 day curing period of the ASTM C 672 deicer salt scaling test does not allow sufficient time for the chemical reaction of the SCM. It was observed recently by the authors, however, that the use of a 28 day curing period did not significantly reduce the negative influence of SCM [7].

Very often, the results of deicer salt scaling tests indicate that the rate of deterioration of SCM concretes is more rapid during the first few cycles of freezing [11]. This phenomenon suggests that the use of SCM tends to promote the formation of a weak layer at the surface of concrete. In a recent investigation, a very porous surface layer was observed for all concretes examined, but the use of SCM was found to increase the thickness of this layer [12]. Results of salt scaling tests performed on sawed surfaces, however, showed that all SCM concretes had a lower scaling resistance than the reference mixtures [12]. The increase of the thickness of the porous surface layer can not therefore be the only explanation for the observed poor scaling resistance of SCM concretes.

A very simple hypothesis often suggested for the poor scaling performance of SCM concretes is the slow reaction rate of SCM. Considering that

their rate of hydration is negligible during the first 14 or 28 days, SCM can be considered as inert fillers which can influence the pore size distribution, but not the total porosity. The lower durability of concretes containing significant amounts of SCM as partial replacement for portland cement would therefore simply be due to their higher water/cement ratio. This paper presents the results of a series of tests performed to verify systematically this hypothesis. Both troweled surfaces and sawed surfaces were tested, in order to allow a better understanding of the influence of SCM.

RESEARCH SIGNIFICANCE

As the use of supplementary cementitious materials is becoming more and more common, in part because of environmental reasons, it is necessary to better understand the influence that the use of these products has on durability properties such as deicer salt scaling resistance.

TEST PROGRAM

Two canadian Type 10 cements from two different plants, three fly ashes and one slag were used to prepare 14 different mixtures, which were tested for deicer salt scaling resistance. Both sawed surfaces and troweled surfaces were tested. Three water/cement ratios were selected for the reference mixtures: 0.40, 0.50 and 0.66. The SCM mixtures were all prepared at a water/binder ratio of 0.40, using either 20% fly ash, 25% slag or 40% fly ash as partial replacement for portland cement. At such a water/binder ratio of 0.40, the water/cement ratio of the mixtures containing 20% fly ash was 0.50, and that of the mixtures containing 40% fly ash, 0.66. The choice of SCM for these experiments was based on previous tests [4].

CONCRETE MATERIALS, PROPORTIONING AND MIXING

The chemical analysis of the two Canadian Type 10 cements which were used are presented in Table 1. Table 2 shows the chemical analyses of the supplementary cementing materials. One of the three ashes can be considered as a Type F according to the ASTM C 618 classification, but the amount of CaO in this ash is higher than what is normally expected for a Class F ash. It is thus referred to in this paper as a CF ash. The other two are Class C ashes. The fine and the coarse aggregates (20 mm maximum-size) were from a local source near Québec city. Both contain mainly granitic materials. In all mixtures, a calcium lignosulfonate water reducer was utilized at a dosage of 2 to 2.25 ml/kg of binder. A synthetic detergent based air-entraining admixture was also used in all mixtures. The dosage varied between 0.15 to 0.5 ml/kg of binder, the higher values corresponding to the mixtures containing SCM, since air-entrainment is often more difficult in these concretes.

All mixtures were designed to contain approximately the same volume of paste (29%). As previously mentioned, the water/binder ratio of the SCM

mixtures was kept constant at 0.40, i.e. slightly lower than the value of 0.45 normally recommended by the ACI 201.2R-77(82) Guide to Durable Concrete for concrete exposed to severe conditions. The fly ashes were used to replace 20% and 40% by weight of cement, and the slag 25%. The target air content was $6\% \pm 1\%$ for all mixtures. The target slump for all SCM mixtures was relatively low (75 ± 25 mm), in order to reduce bleeding. The bleeding of each mixture was measured according to ASTM C 232. Table 3 presents the characteristics of the 14 mixtures which were prepared, together with the values of air content, slump and bleeding. Fig.1 presents the mixture identification code. For the reference mixtures without SCM, the code name indicates the water/cement ratio, i.e. 0.40, 0.50, or 0.66.

Mixing operations were carried out in a horizontal open pan mixer. The cement (and SCM if used) and the mixing water (including the water reducer) were first mixed to form a paste, and then the sand and the coarse aggregates were added with a little water containing the air-entraining admixture. The concrete was mixed for three minutes, allowed to rest three minutes, and then mixed for two more minutes.

SPECIMEN CURING AND TESTING

Nine 100 x 200 mm cylinders for compressive strength measurements (ASTM C 39) at 7 d, 28 d, and 91 d, three 75 x 225 x 300 mm slab specimens for the ASTM C 672 salt scaling resistance test on troweled surfaces, and one prismatic specimen for the spacing factor determination (ASTM C 457) were prepared from each mixture. An additional cylindrical specimen (150 x 300 mm) was also cast from each concrete for the salt scaling resistance test on a sawed surface (this cylinder was cut in three to expose a sufficient internal surface area for the test). The testing of sawed surfaces was decided in order to eliminate any surface effect due to finishing procedures and bleeding.

The slabs were cast in a single layer, using a rodding technique for placement as required in ASTM C 672, and finished with a wooden trowel. After casting, they were left to bleed (for 2 to 5 hours), and then the bleed water was brushed away and they were covered with moist burlap and plastic sheeting for approximately 20 hours. After demolding, they were placed in lime saturated water for 13 days (as mentioned in the introduction, previous tests had shown that increasing the curing period to 28 days had no significant influence on the scaling resistance). Drying for 14 days after curing was carried out in a room maintained at $23 \pm 2^\circ\text{C}$ and $50\% \pm 5\%$ RH. After the drying period, the top surface was covered with water for a 7 d resaturation period. A 3% NaCl solution was used during the freezing and thawing tests (freezing at -18°C for 16 hours and thawing at room temperature for 8 hours). The specimens were subjected to 5 cycles per week up to 50 cycles as recommended in ASTM C 672. The chloride solution was flushed and replaced every five cycles, and the scaling residues were collected. To prevent evaporation of the water from the surface, a plexiglas cover was placed over each test surface. A similar procedure was used for the tests on sawed surfaces.

RESULTS AND DISCUSSION

Table 4 presents, for all mixtures, the results of the compressive strength tests at 7, 28 and 91 days, the value of the air void spacing factor and the amount of scaling residues from both the sawed and the troweled surfaces after 50 cycles of freezing and thawing in the presence of a salt solution. The results of the scaling tests are described in more detail in Figures 2 to 5 which show the amount of scaling residues as a function of the number of cycles for the troweled surfaces of all mixtures made with cements A (Figure 2) and B (Figure 3), and for the sawed surfaces of all mixtures made with cements A (Figure 4) and B (Figure 5). These results represent, for each test condition, the average value for three specimens. The precision of these results can be described as follows: for all results lower than 0.25 kg/m^2 , the maximum difference between the individual values for the three specimens was less than 0.05 kg/m^2 , and for all results higher than 0.25 kg/m^2 , it was, with one exception, less than 25% of the average value.

Considering the type of materials that were used and the different mixture compositions, the compressive strength of all mixtures is quite satisfactory (Table 4). The values after 7 days are lower in the fly ash and slag mixtures, particularly those made with cement B, but, after 28 days, the strength of all SCM concretes are quite close to that of the 0.40 cement A or B reference mixtures. After 91 days, the strength of certain mixtures containing SCM are even higher than that of the two 0.40 reference mixtures.

The air void spacing factor is known to be of prime importance in relation to the frost and deicer salt scaling resistance. This is why all mixtures were designed to have a spacing factor approximately equal to the usual $200 \text{ }\mu\text{m}$ value. The results in Table 4 show that all mixtures containing SCM, and all reference mixtures but one, have a spacing factor lower than $200 \text{ }\mu\text{m}$. One reference mixture (A 0.66) has a spacing factor of $226 \text{ }\mu\text{m}$.

Even taking into account the fact that sawing exposes aggregate as well as paste, the amount of scaling residues from the sawed surfaces is in all cases quite small compared to that collected from the troweled surfaces (Table 4). The detailed results in Figures 2 to 5 show that the scaling process is relatively linear for the sawed surfaces, but not for the troweled surfaces. For these surfaces, the scaling process is always very rapid during the first few cycles (probably due to the loss of a weak and porous layer), but much slower afterwards. It is also very clear from the results that the use of SCM increases the deterioration due to scaling, not only on the troweled surfaces, but also on the sawed surfaces.

The difference between the amount of scaling residues collected from the sawed surfaces of all reference mixtures after 50 cycles and that collected from the same surfaces of all SCM mixtures is extremely evident. The highest value for the reference mixtures is 0.13 kg/m^2 , but the values for the SCM mixtures range between 0.24 and 0.74 kg/m^2 . The use of SCM thus increases not only the amount of deterioration of the troweled surfaces in the first cycles (Figures 2 and 3), but also appears to decrease the resistance of the basic concrete microstructure to scaling. At the same water/cement ratio (i.e. considering that SCM act as inert fillers), the reference mixtures have a much better scaling resistance than the mixtures containing SCM. In fact, even the amount of residues from the sawed

surface of the 0.66 mixture (with a spacing factor of $177\text{ }\mu\text{m}$) is very low. The simple hypothesis that the water/cement ratio increase due to the use of SCM is the basic cause of the lower durability of SCM concretes is thus insufficient to explain the results obtained, and there has to be another reason for the negative influence of SCM. It should be noted in this respect that there appears to be little influence of the type of SCM.

The size distribution of the air voids in three of the mixtures prepared for this study (A 0.4, A cf20 and A c120) was determined using simple image analysis procedures. The results are presented in Figure 6. The values obtained for the voids larger than $200\text{ }\mu\text{m}$ are not shown, since the number of these voids is extremely small. It can be seen on this Figure that the number of very small voids (between 10 and $50\text{ }\mu\text{m}$) is much higher for the two SCM concretes. A possible explanation for the lower scaling resistance of the SCM concretes could thus be that the very small air voids close to the surface become rapidly saturated during the process of freezing and thawing in the presence of deicer salts (ASTM C 672). If these voids do become saturated, they amplify the deterioration instead of offering protection.

CONCLUSION

The results presented in this paper show that the reduction of the salt scaling resistance of concrete due to the use of SCM can not be simply explained by the increase of the water/cement ratio. All reference concretes were found to have an adequate salt scaling resistance, including the 0.66 mixture. This reduction is not either simply due to the presence of a more porous zone at the surface (that can be easily attacked in the early stages of the scaling test), since it was also very clearly observed during tests on sawed surfaces. In terms of compressive strength, the refinement of the pore structure due to the use of SCM appears to compensate in good part for its much slower reaction rate than that of portland cement, but this is evidently not sufficient to prevent the loss of scaling resistance.

A possible reason for the poor scaling resistance of SCM concretes is the much larger number of very small entrained air voids. Close to the surface, these voids could become easily saturated during the test and thus enhance the observed deterioration. It is also possible that SCM concretes, which have a finer pore structure than normal concretes and thus a reduced paste permeability, require a lower spacing factor for adequate scaling protection. Further investigation, using techniques such as the one proposed by Pleau [14] to better characterize both the protection offered by the air void system and the loss of protection due to the filling of the smaller voids, should allow a clearer understanding of the mechanisms involved. More information is also required to determine if this phenomenon normally occurs under field conditions.

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TABLE 1 — Chemical analysis of cements (%)

Constituents	Cement A (%)	Cement B (%)
SiO ₂	20.64	21.42
Al ₂ O ₃	4.84	4.17
Fe ₂ O ₃	2.75	2.75
CaO	62.32	62.18
MgO	2.20	3.60
SO ₃	3.34	2.44
Na ₂ O	0.16	0.12
K ₂ O	0.75	0.42
TiO ₂	0.22	0.22
P ₂ O ₅	0.10	0.07
L.O.I.	2.35	2.12

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TABLE 2 — Chemical analysis of SCM (%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	SrO	LOI
cf	49.3	23.8	4.6	15.25	1.05	0.29	3.0	0.4	0.7	0.10	0.1	0.2	0.6
c1	42.0	20.6	5.79	19.97	5.08	2.29	1.2	0.4	1.2	0.16	0.5	0.6	1.3
c2	34.5	22.4	5.84	27.13	-	1.94	1.4	0.4	-	-	-	-	0.7
slag	36.5	10.1	0.6	33.60	15.6	3.80	0.5	0.5	0.7	-	-	-	-

TABLE 3 — Mixture proportions and fresh properties

Mixture	Cement	Water	SCM	Fine aggregate	Coarse aggregate	Slump	Bleeding	Air content
	kg/m ³	kg/m ³	kg/m ³	kg/m ³	kg/m ³	mm	%	%
A 0.4	408	163	—	732	1098	65	1.8	5.4
A 0.5*	358	179	—	722	1084	130	2.5	6.0
A 0.66*	262	173	—	775	1163	150	3.5	7.0
A cf 20	305	153	76	735	1104	50	2.2	5.1
A cf 40	233	155	155	735	1117	55	2.5	5.5
A c1 20	301	151	75	727	1090	65	2.0	7.2
A c2 20	317	158	79	736	1104	80	1.0	5.5
A slag 25	301	160	100	719	1079	70	0.7	6.3
B 0.4	405	162		728	1092	80	3.4	5.1
B 0.5	357	178		718	1077	175	4.0	7.4
B cf 20	302	151	76	729	1094	100	3.5	6.2
B c1 20	304	152	76	733	1100	75	1.9	6.5
B c2 20	311	156	78	723	1085	100	1.0	6.0
B slag 25	297	158	99	710	1066	90	2.3	6.1

*: no water reducer

TABLE 4 — Compressive strength, air-void spacing factor and salt scaling resistance

Mixture	Compressive strength (MPa)			Spacing factor (μm)	Salt scaling resistance 50 cycles (kg/m^2)	
	7 days	28 days	91 days		Sawed	Trowelled
A 0.4	36.3	47.9	48.8	196	0.09	1.09
A 0.5	25.6	34.4	38.2	226	0.06	0.74
A 0.66	13.5	20.7	24.2	177	0.13	0.97
A cf 20	32.0	43.5	51.5	175	0.74	2.01
A cf 40	23.5	37.8	47.0	180	0.45	2.90
A c1 20	28.0	37.9	44.1	173	0.48	1.80
A c2 20	33.9	45.1	51.8	179	0.63	2.77
A sl 25	32.7	44.1	49.0	191	0.46	1.88
B	35.3	47.7	51.2	195	0.10	0.96
B 0.5	23.5	33.0	39.5	162	0.08	0.86
B cf 20	25.3	38.7	47.9	156	0.30	2.18
B c1 20	27.1	39.1	47.0	145	0.24	1.89
B c2 20	24.7	38.8	46.6	148	0.59	2.21
B sl 25	24.7	45.3	48.1	147	0.64	2.06

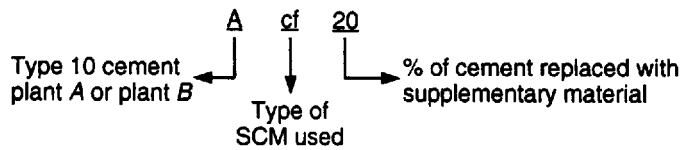


Fig. 1 - Identification code

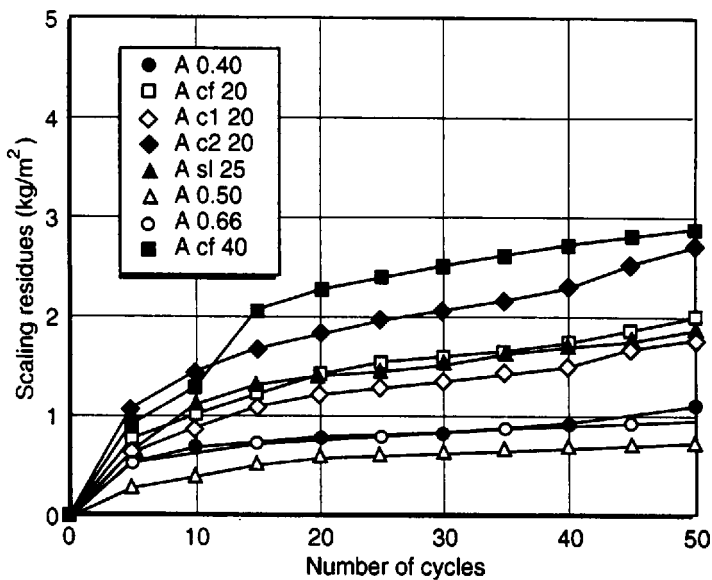


Fig. 2 - Salt scaling resistance of trowelled surfaces (mixtures with cement A)

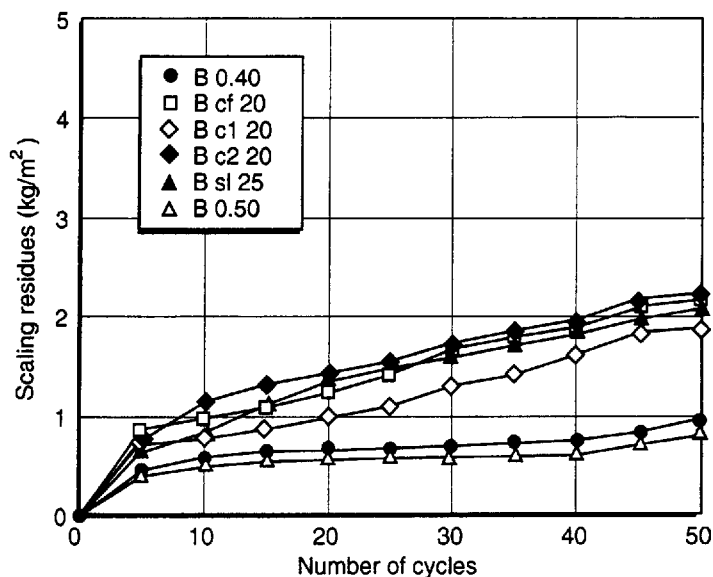


Fig. 3 - Salt scaling resistance of trowelled surfaces (mixtures with cement B)

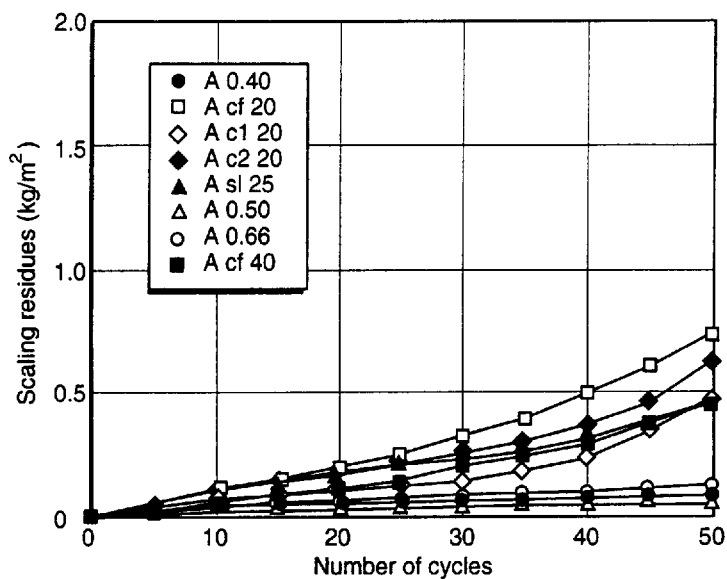


Fig. 4 - Salt scaling resistance of sawed surfaces (mixtures with cement A)

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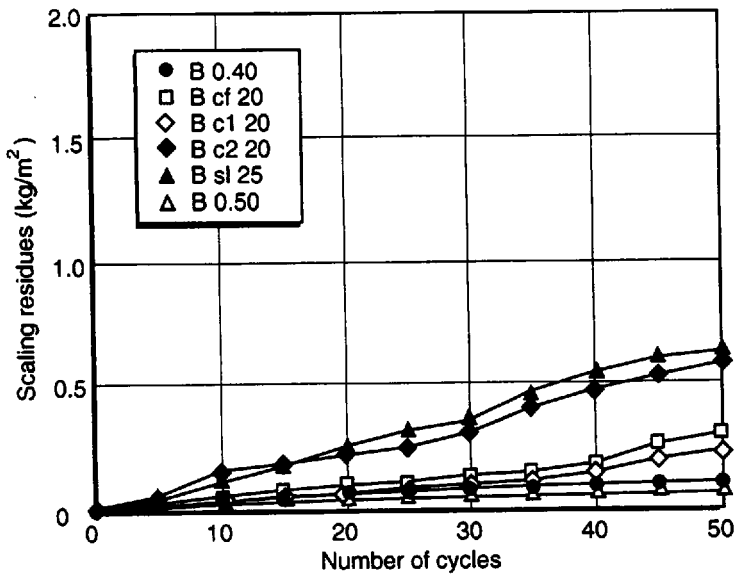


Fig. 5 - Salt scaling resistance of sawed surfaces (mixtures with cement B)

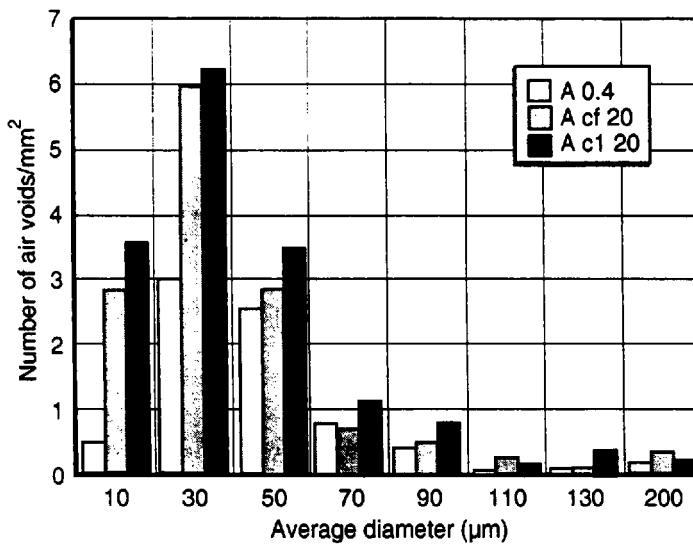


Fig. 6 - Air-void granulometry (<200μm)

SP 192-40

Durability of High-Performance Mortars Containing Contaminated Marine Sediments in Aggressive Environments

by G. Ferrari, T. Cerulli, P. Clemente, C. Pistolesi,
D. Salvioni, and F. Surico

Synopsis: Solidification/stabilization (S/S) is an effective management of toxic wastes, consisting in mixing a waste product with a binder and other ingredients, if any, to reduce the mobility or solubility of contaminants. In the present work, a contaminated marine sediment of the Venice lagoon was treated with cement, aggregates and different amounts of an acrylic superplasticizer to produce cement mortars with different W/C. The characteristics of the resulting mortars were evaluated by compressive strength, water permeability, observation of microstructure of the cement paste, and leaching of contaminants.

The durability in aggressive environments of the best performing mortar, corresponding to the mixture with $W/C = 0.38$, was evaluated in comparison to a reference mortar.

The results of the tests indicated that W/C affects not only the strength of the mortars but also improves the leaching characteristics of the stabilized waste. This could be ascribed mainly to the reduction of the microporosity of the mortars with lower W/C. The durability tests indicated that the mortar containing the sediment is less sensitive to the attack of $CaCl_2$ in comparison to the reference mortar, as confirmed by the higher strength after different periods of immersion in a 30 % aqueous solution of $CaCl_2$ at 5 °C. Furthermore, the linear expansion in sulphate solution seems not to be substantially influenced by the presence of the sediment. Thermal and XRD analyses suggested that these results could be ascribed to a pozzolanic effect of the sediment.

The results of the present work confirmed the possibility of producing high performance concrete by using the contaminated sediments of the Venice lagoon.

Keywords: durability; high-performance concretes; leaching; marine atmospheres; pozzolans; stabilization; superplasticizers; wastes

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INTRODUCTION

The Venice lagoon lies in the north of Italy. It was created more than 6000 years ago by the counteracting effects of the forces of the sea and the solid transport of the rivers. It extends over an area of about 550 km², it is bounded by the mainland on the north and by sandy littorals on the south, and mixes with the Adriatic sea by means of three openings. The mean depth of the lagoon is less than one meter, but there is a complex network of natural and artificial canals which allow the mixes. These canals, due to the effect of the tide and the transport of sediments, tend to be filled and need to be periodically dredged. The sludges resulting from the canals close to the city of Venice, which is located in the middle of the lagoon, and those close to the industrial area of Porto

Marghera, which faces the lagoon at north, are strongly contaminated by the discharges and consequently need to be disposed in restricted areas. For both economical and environmental reasons it is advisable to reduce the sludges disposal and to develop low cost technologies for their reuse under environmentally safe conditions.

One of the most promising technologies is the solidification/stabilization (S/S) process. This basically consists of mixing the waste product with a binder (cement for instance) and other ingredients, if any, to reduce the mobility or solubility of contaminants by producing a solid with no free liquid. By properly modifying the composition of the mixture, it is possible to obtain S/S-treated wastes which could be utilised as building materials for selected applications [1-3]. Furthermore, it is well-known that the leaching of contaminants occurs more quickly and to a higher degree in materials characterised by a high porosity [4]. Therefore, in order to reduce the loss of contaminants and to correspondingly improve the environmental compatibility of these reusable materials, it is advisable to reduce porosity as much as possible.

It is well-known that the reduction of W/C in concrete is the key factor to obtain materials characterised by high performance and durability. This can be achieved by adding to the cement mixture a superplasticizer which produces a sharp decrease of the viscosity of the fresh mix and, consequently, reduces the water demand ($W/C < 0.4$). By this way, it is possible to produce high performance concretes (HPC) which are characterised by a much lower porosity than normal concrete and, consequently, higher durability and strength. A further improvement of the durability and the watertightness of HPC is achieved by the addition of pozzolanic materials to the mixtures, such as silica fume or fly ash, which react with calcium hydroxide to form additional cementitious products, thus preventing the formation of expansive compounds, particularly when HPCs are exposed to aggressive environments.

In the present paper, the mechanical characteristics, the microstructure and the efficiency of the solidification/stabilization process of different superplasticized cement mortars containing contaminated sediments of the Venice lagoon were studied as a function of W/C.

In order to assess the durability behaviour, the mortar specimens were exposed to CaCl_2 or MgSO_4 both in form of aqueous solutions. Calcium chloride – as deicing salt used in winter time – is a very aggressive agent, particularly at low temperatures [5], since it reacts with $\text{Ca}(\text{OH})_2$ in cement paste and forms a destructive product, $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{H}_2\text{O}$ [6]. Magnesium sulphate, on the other hand, reacts with calcium aluminate hydrate and forms ettringite by producing expansive action.

The durability in aggressive environments of the best performing mixture ($W/C = 0.38$) was evaluated in terms of strength after different periods of curing in a 30 % CaCl_2 aqueous solution at 5 °C and in terms of linear expansion in a 5% MgSO_4 aqueous solution at 20 °C, in comparison with a reference mortar with the same W/C without the sediment.

EXPERIMENTAL

Materials

Characteristics of the Sediment -- The sediment used for the production of the mortars was collected in the Venice lagoon, near the industrial area. The sample was a black sludge (water content 56.9 %) and it was characterised by a strong sulphide smell due to the anaerobic conditions existing in the bottom of the canal. The mineralogical matrix of the sediment consisted of quartz, clays (illite, muscovite, etc.) and carbonates (calcite and dolomite), as detected by XRD analysis and confirmed by the literature [7]. The main contaminants were represented by toxic metals. The characteristics of the sediment are shown in Table 1. The metals concentration have been determined by atomic absorption spectrometry (AAS) after digestion of the sediment and complete solubilization of the mineral matrix; therefore the concentration values of Table 1 refer to the total metals content of the sediment.

Mortar Composition -- Different mortars were prepared by mixing the wet sediment with portland cement (Type V according to ASTM C-150 and Type CE I 52.5R according to ENV 197/1), silica sand (maximum diameter of 0.5 mm), and different amount of an acrylic superplasticizer [8] at dosages from 0 to 6 % by weight of cement. The fluidity of the mixtures was finally adjusted at approximately the same value (about 60-70 %, as measured by flow drop table test) by the proper amount of water, in addition to the amount already present in the sediment and the superplasticizer. By this way, mortars all containing the same amount of sediment (57 % of wet sediment by weight of cement) but characterised by different W/C were prepared. The compositions of the different mortars are shown in Table 2.

Test Methods

Compressive and Flexural Strength -- The mechanical characteristics of the different mortars were evaluated by measuring compressive and flexural strength on prism specimens (40 x 40 x 160 mm) after 28 days of curing at 20 °C

and 95 % r.h., according to the method described in the European norm ENV 196/1.

Watertightness -- The watertightness of the different mortars was tested, according to the European norm ENV 206, by subjecting cube specimens of the mortars (150 x 150 x 150 mm), previously cured at 20 °C and 95 % r.h. for 28 days, to an hydraulic pressure variable from 100 to 700 kPa on one side (100 kPa for 2 days, 300 kPa for 1 day and 700 kPa for 1 day). At the end of the test, the water penetration inside the specimens was measured on a fractured section perpendicular to the side of application of the water head.

Morphology and Microstructure -- The microstructure of the cement paste of the different mortars was studied on fractured areas using a Philips XL30 scanning electron microscope at magnification of 20,000x. The measurements of the specific surface area and pore size distribution of the different mortars were performed by a Coulter SA3100 gas sorption porosimeter on crushed samples of the mortars. By this technique, gas molecules of known size (nitrogen) are adsorbed on the surface of the sample. The quantity of gas condensed and the resultant sample pressure are recorded and used for subsequent calculations which are automatically performed according to the BET (Brunauer, Emmet and Teller) theory. The BET specific surface area, which include all internal pore within the approximate range of 0.4 to 200 nm diameter, is expressed in m^2/g .

Leaching Characteristics -- The leaching of toxic metals by the mortars containing the contaminated sediment was studied by two different techniques. In the first method, which is based on the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), the mortar specimens, including the mortar without the sediment (blank), were crushed and treated with 0.5 N acetic acid at pH = 5 for 24 hours in a weight ratio of the mortar to acetic acid of 1:20. The leachates were filtered and the concentrations of toxic metals were determined by atomic absorption spectroscopy (AAS). Comparative tests were also performed on the untreated sediment also in this case. The aim of this test was to simulate the leaching of the solidified wastes in a strongly aggressive environment and to evaluate their potential toxicity characteristics in extreme conditions. In the second method, which is based on the American Nuclear Society Test ANSI/ANS-16.1-1986, cylindrical specimens (25.4 mm height and 25.4 mm diameter) of the different mortars containing the contaminated sediment were produced and cured at 20 °C and 95% r.h. for 28 days. The specimens were then immersed, at room temperature, in different vessels containing 100 ml of distilled water. The leachates were sampled and entirely replaced at designated intervals with new quantities of 100 ml distilled water. The leachant-renewal cumulative schedule was the following: 2 hours, 7 hours, 1 day, 7 days, 1, 2, 3 and 10 months. On each collected fraction, the concentration of different toxic metals (As, Cd, Cr, Cu, Hg, Ni, Pb and Zn) leached from the specimens were

measured by atomic absorption spectroscopy (AAS). A comparative test was performed on an equivalent amount of the untreated sediment present in each specimen. Furthermore, in order to estimate the contribution of the other components of the mortar (cement and sand) to the leachate, a specimen of mortar without the sediment (blank) was tested under the same conditions. This test was not intended to simulate the long-term (several hundred to thousands of years) leaching behaviour, but served as a basis for indexing contaminant release of solidified-wastes forms in a short-term test under controlled conditions and in a defined leachant system.

Durability Tests -- Two different tests were performed to evaluate the durability in aggressive environments. In the first test, prism specimens (40 x 40 x 160 mm) of the best performing mortar and the reference mortar in which the sediment was replaced by an equivalent amount of fine silica sand, - both at the same W/C of 0.38 - were immersed, after curing at 20 °C and 98 % r.h. for 28 days, in a 30 % CaCl_2 solution at 5 °C. After different lengths of curing in this solution (7, 15, 30, 60, 90 days), the compressive strength of the mortars were compared, in order to evaluate the loss of strength due to the effect of CaCl_2 . In the second test, prism specimens (25 x 25 x 280 mm) of the best performing mortar and the reference mortar, in which the sediment was replaced by an equivalent amount of fine silica sand, - both at the same W/C of 0.38 - were immersed, after curing at 20 °C and 98 % r.h. for 14 days, in a 5 % MgSO_4 solution at 20 °C. At different times of exposure to this solution (up to more than 200 days) the linear expansion of the mortars was measured.

Thermal Analysis -- Thermogravimetric analysis was used to measure the percent of Ca(OH)_2 from hydration of a cementitious mixture having the same composition of the best performing mortar, in comparison with the reference composition without the sediment, both at W/C of 0.38. The measurements were made after 1, 2 and 7 days of curing at 20 °C and 98 % r.h.

RESULTS AND DISCUSSION

The mechanical characteristics of the mortars are shown in Table 3. These results indicate that both the flexural and compressive strength of the mortars containing the sediment are improved by the reduction in the W/C, as better illustrated in Fig. 1 for the compressive strength.

The results of the BET specific surface area and water penetration measurements on the different mortars are shown in Table 4: both these parameters decreased by reducing W/C. The relationship between BET and water penetration and their dependence on W/C are illustrated in Fig. 2: a reduction in the W/C, caused by the addition of the superplasticizer, produces a

decrease in the porosity of the cement matrix of the mortars, expressed by BET surface area. As a consequence, the mortars become more resistant to water penetration and less sensitive to external aggressive agents, and therefore more durable: as expected, at $W/C = 0.38$ the permeability of the cement mortar is negligible. The microstructure of the cement paste of the mortars characterised by W/C of 0.61 and W/C of 0.38 are shown in Figs. 3 and 4, respectively. From these Figs, the denser structure of mortar sample 5, characterised by a lower W/C (0.38) in comparison to mortar sample 1, characterised by higher W/C (0.61), is evident.

The results of the leaching tests on the different samples of mortar, performed according the U.S. EPA TCLP procedure, are reported in Table 5. Comparative tests on both the untreated sediment and the mortar without the sediment (blank), were performed. The results of the U.S. EPA TCLP test indicated that the S/S treatment of the contaminated sediment caused, with the exception of Cr, a sharp reduction of the metals concentration in the 0.5 N acetic acid leachates and that better results were obtained for the mortars characterised by $W/C < 0.45$. Table 5 shows that the concentrations of Cr in the leachates of the mortars are higher than the untreated sediment and even the mortar without the sediment (blank) is characterised by high concentration of this metal in the leachate (180 $\mu\text{g/l}$). This observation suggests that the cement matrix itself could be a source of leachable Cr. With this exception, the results of the TCLP tests seem to indicate that a cement matrix characterised by low porosity is essential to prevent the leaching of S/S treated wastes in strongly aggressive environment. The tests conducted according the ANSI/ANS-16.1-1986 method showed similar results. Due to the less severe conditions, with the exception of Cu, lower releases of contaminants were observed for the mortars containing the contaminated sediment, even after 10 months of immersion in distilled water, as shown in Table 6.

The benefits of the reduction of the W/C on the leaching characteristics of the mortars are quite evident for Cu, a metal which is amphoteric and becomes soluble at high pH. Fig. 5, in which the cumulative leachate after 10 months (according ANSI/ANS-16.1.1986) is plotted as a function of W/C , indicates that the stabilization of Cu is effective only when the W/C is not higher than 0.38.

Figure 6 shows the compressive strength of the best performing mortar and that of the reference mortar without the sediment, both at the same W/C of 0.38. The mortar containing the sediment did not show appreciable loss of strength after 90 days of curing in CaCl_2 solution. On the other hand, the reference mortar (without the sediment) showed a definite loss of strength after 20 days of aging.

These unexpected results suggests the possibility that the sediment could act as a pozzolanic material capable to prevent, like silica fume and fly ash, the

destructive effects of CaCl_2 . This hypothesis seems to be confirmed by the lower amount of Ca(OH)_2 developed by hydration of the cementitious mixtures containing the sediment, as shown in Fig. 7. Furthermore, XRD analysis of a fresh mixture of the sediment with 5 % of Ca(OH)_2 did not show the evidence of Ca(OH)_2 but presented an unidentified peak at an angle of $2\theta = 11$ (Fig. 8), not present in the original sediment sample (Fig. 9). This peak could be representative of the reaction product between Ca(OH)_2 and the clayey components of the sediment.

Figure 10 illustrates the linear expansion of the mortar containing the sediment in comparison with the reference. From this figure, it can be observed that the mortar containing the sediment is characterised by a higher expansion in the first period of curing in air, in comparison with the reference mortar without the sediment. This result could be ascribed to the expansive pozzolanic reaction of the clayey components of the sediment with Ca(OH)_2 originating by cement hydration. In any case, after the immersion in MgSO_4 solution, the slope of the two curves is similar, indicating no evidence of stronger sulphate attack due to the presence of the sediment in the mixture.

CONCLUSIONS

The results indicate that contaminated sediments of the Venice lagoon can be used to produce high-performance concrete (HPC). By the addition of high dosages of superplasticizer (4 - 6 % by weight of cement), it was possible to reduce the W/C and correspondingly improve the mechanical properties. Furthermore, also the porosity of the cement paste was reduced and the resulting HPC containing the sediment was impermeable to water up to 700 kPa, with a corresponding improvement of the durability of the mortars. The same parameters which affect durability are of paramount importance in determining the efficiency of S/S process and the environmental compatibility of S/S solidified wastes: a reduction of the porosity of the mortars caused a reduction of the leaching of contaminants, most in the aggressive environment. The sediment tested seemed to produce an improvement of the durability of the mortars in aggressive environments. These improvements could be ascribed to a pozzolanic effect of the sediment, as confirmed by thermal and XRD analysis.

The results of the present investigation should strongly encourage further research in order to the possibility to utilise HPC with contaminated sediments as building materials for special applications.

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Table 1. Characteristics and toxic metal contamination of the Venice lagoon sediment

PARAMETER	MEASURED VALUE
Solids content (%)	43.1
Na ₂ SO ₄ (%)	0.6
Mean particle size (μm)	13.28
Specific gravity (g/ml)	1.37
As (mg/kg of dry sediment)	35
Cd (mg/kg of dry sediment)	65
Cr (mg/kg of dry sediment)	149
Cu (mg/kg of dry sediment)	286
Hg (mg/kg of dry sediment)	46
Ni (mg/kg of dry sediment)	20
Pb (mg/kg of dry sediment)	626
Zn (mg/kg of dry sediment)	5415

Table 2. Composition and characteristics of the different mortars

MORTAR SAMPLE	DOSAGE OF SUPERPLASTICIZER (% of total soln. by wt of cement)	ADDED WATER (g)	TOTAL WATER (*) (g)	WATER CEMENT RATIO (W/C)	FLOW (%)
1	0	1420	3042	0.61	74
2	1	880	2537	0.51	69
3	2	540	2232	0.45	60
4	4	321	2083	0.42	61
5	6	50	1882	0.38	70

(*) Sum of the water contained in the sediment, water from the superplasticizer and added water.

Type V portland cement

Silica sand

Lagoon sediment (43.1 % solids)

Type of superplasticizer

5000 g

5500 g

2850 g (1228 g dry sediment + 1622 g H₂O)

Acrylic, 30 % active solution

Table 3. Compressive and flexural strength of the mortars containing the Venice lagoon sediment at different dosages of superplasticizer (28 days of curing at 20 °C and 90 % r.h.)

MORTAR SAMPLE	WATER- CEMENT RATIO (W/C)	FLEXURAL STRENGTH (MPa)	COMPRESSIVE STRENGTH (MPa)
1	0.61	6.8	52.8
2	0.51	8.8	54.0
3	0.45	11.3	56.0
4	0.42	12.5	59.5
5	0.38	13.8	70.6

Table 4. BET surface area and water penetration values of the mortars containing the Venice lagoon sediment at different dosage of superplasticizer and W/C

MORTAR SAMPLE	DOSAGE OF SUPERPLASTICIZER (% by mass of cement)	W/C	BET SURFACE AREA (m ² /g)	WATER PENETRATION (mm)
1	0	0.61	37.732	8
2	1	0.51	37.357	6
3	2	0.45	32.472	4
4	4	0.42	29.894	2
5	6	0.38	26.319	2

Table 5. Leaching characteristics of the different mortars containing the Venice lagoon sediment in comparison with the untreated sediment and the mortar without sediment (BLANK) according U.S. EPA TCLP Procedure.

METAL	SAMPLE						
	UNTREATED SEDIMENT	M 1 W/C = 0.61	M 2 W/C = 0.51	M 3 W/C = 0.45	M 4 W/C = 0.42	M 5 W/C = 0.38	BLANK W/C = 0.38
	LEACHING (µg/l)						
As	350	< 1	< 1	< 1	< 1	< 1	< 1
Cd	70	30	20	20	20	20	20
Cr	120	180	190	180	160	150	180
Cu	50	20	20	20	10	9	7
Hg	4	< 1	< 1	< 1	< 1	< 1	< 1
Ni	100	60	60	50	50	50	50
Pb	1500	80	60	50	40	30	40
Zn	23500	200	150	70	55	50	50

Table 6. Cumulative leaching after 10 months of the different mortars containing the Venice lagoon sediment in comparison with the untreated sediment and the mortar without sediment (BLANK) according ANSI/ANS-16.1-1986 method

METAL	SAMPLE						
	UNTREATED SEDIMENT	M 1 W/C = 0.61	M 2 W/C = 0.51	M 3 W/C = 0.45	M 4 W/C = 0.42	M 5 W/C = 0.38	BLANK W/C = 0.38
	LEACHING (µg/l)						
As	64	3	< 1	< 1	< 1	< 1	< 1
Cd	8	< 1	< 1	< 1	< 1	< 1	< 1
Cr	2	46	62	48	33	54	66
Cu	21	21	21	21	12	9	7
Hg	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Ni	2	2	1	< 1	< 1	< 1	< 1
Pb	37	< 1	3	< 1	7	3	8
Zn	761	< 1	< 1	< 1	< 1	< 1	< 1

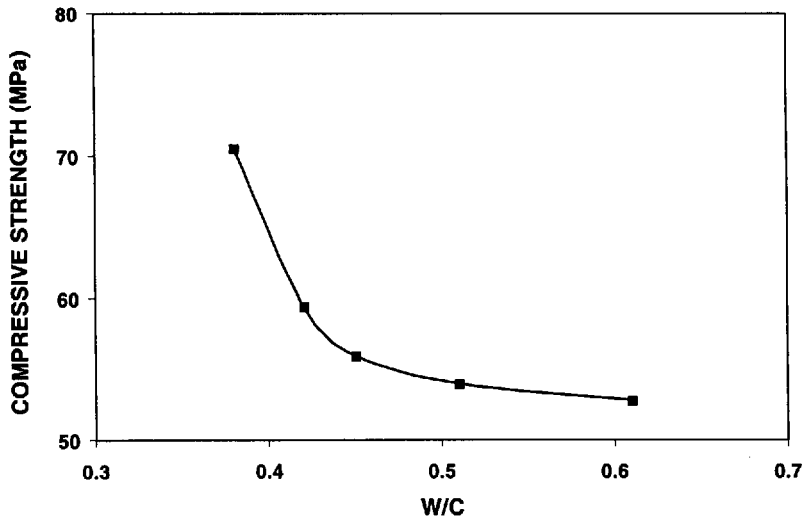


Fig. 1. Compressive strength of different mortars containing the Venice lagoon sediment as a function of W/C.

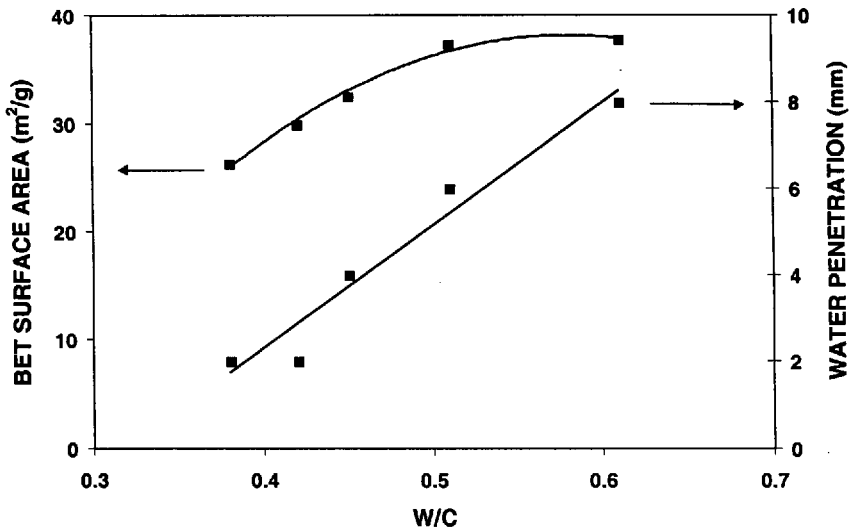


Fig. 2. BET Surface Area and water penetration of the different mortars containing the Venice lagoon sediment as a function of W/C.

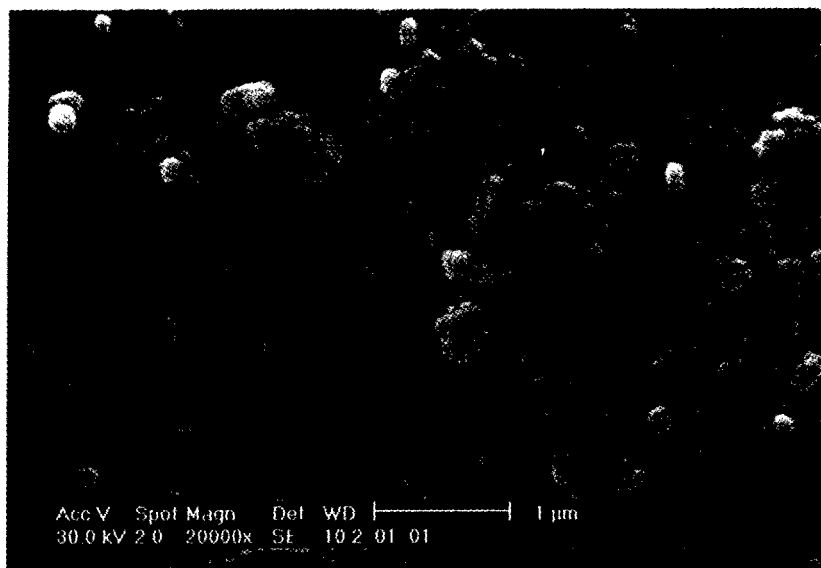


Fig. 3. SEM image of fracture area of mortar sample 1 containing the Venice lagoon sediment ($W/C = 0.61$).

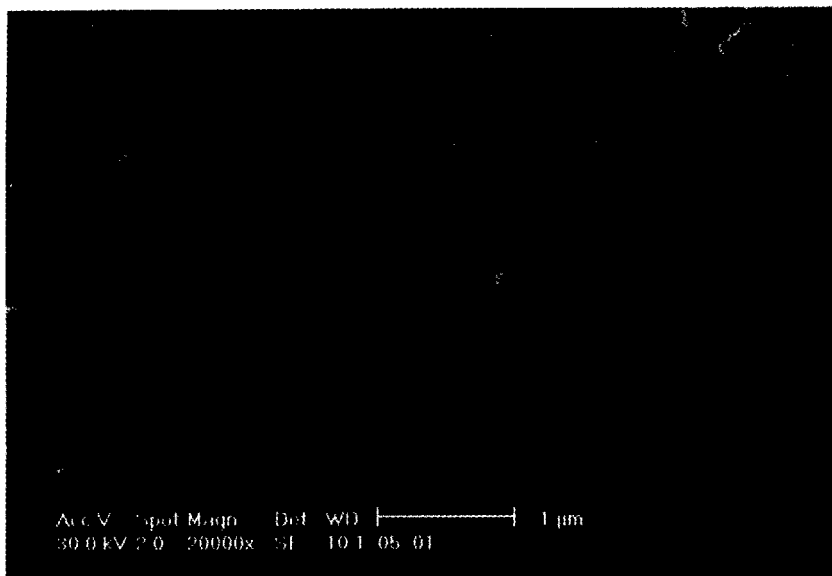


Fig. 4. SEM image of fracture area of mortar sample 5 containing the Venice lagoon sediment ($W/C = 0.38$).

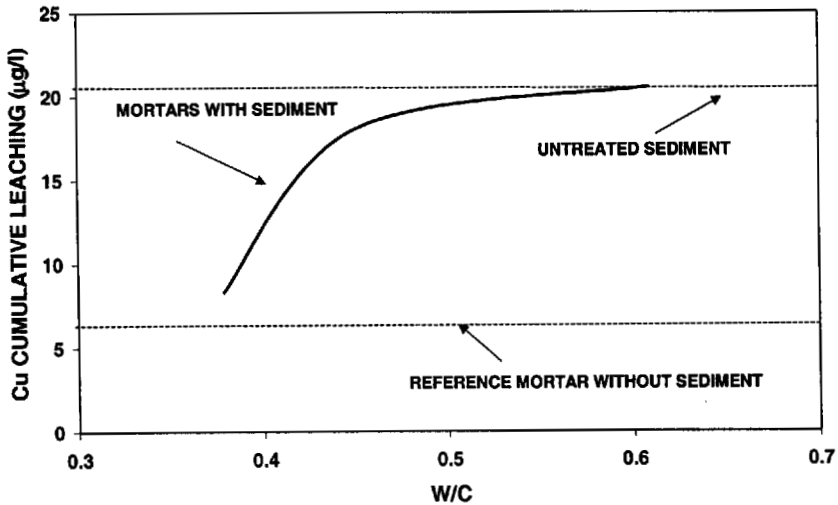


Fig. 5 - Effect of W/C on the cumulative leachate of Cu after 10 months (ANSI/ANS 16-1-1986).

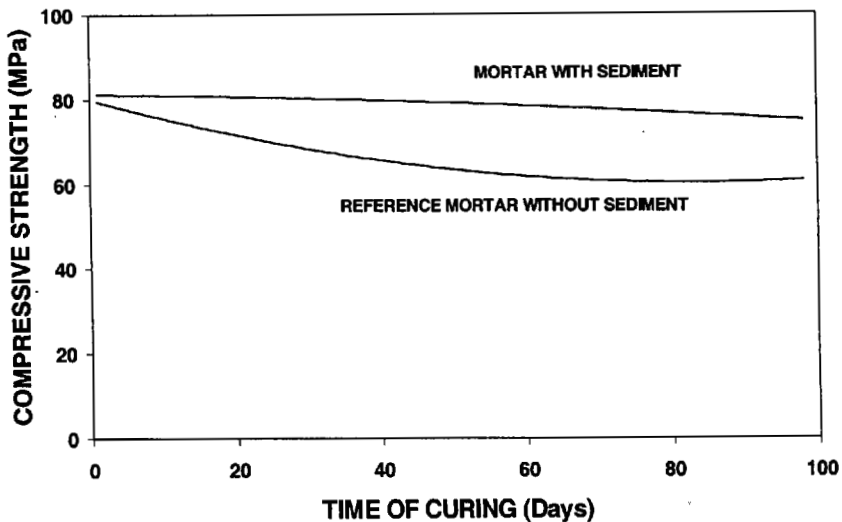


Fig. 6 - Compressive strength of specimens of the mortars with and without the sediment (W/C = 0.38) cured in 30 % CaCl_2 solution at 5 °C.

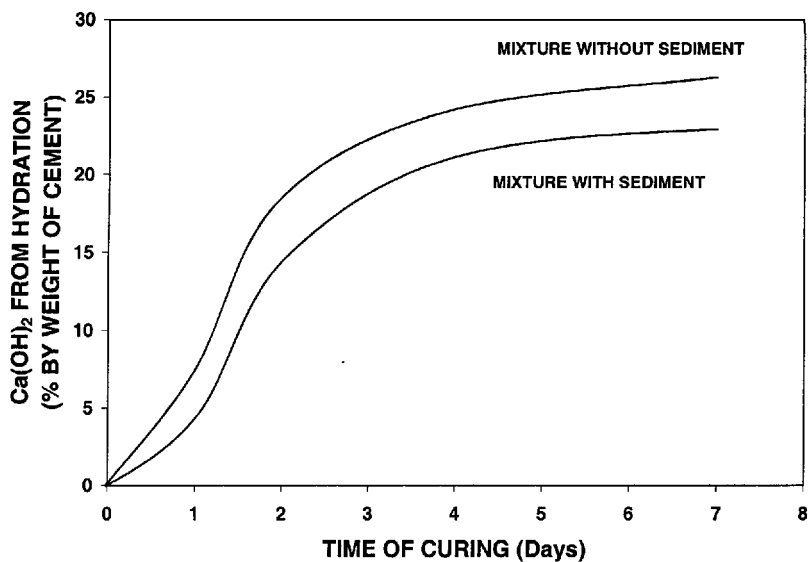


Fig. 7 - Developments of Ca(OH)_2 from cement hydration for cementitious mixtures with and without the sediment ($W/C = 0.38$).

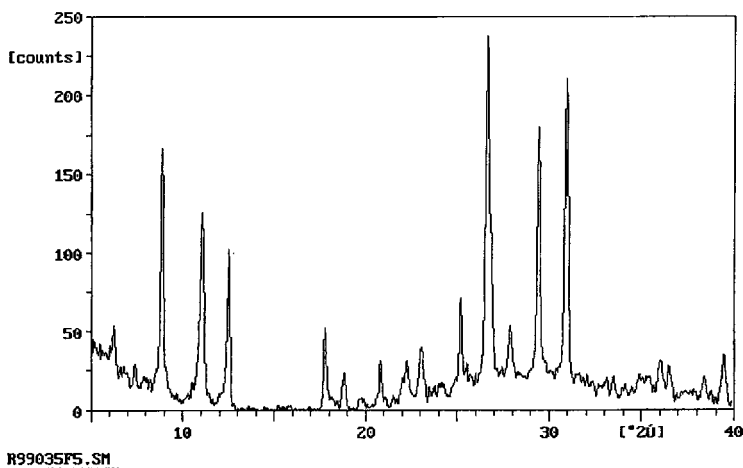


Fig. 8 - XRD analysis of the mixture of the sediment with 5 % of Ca(OH)_2 .

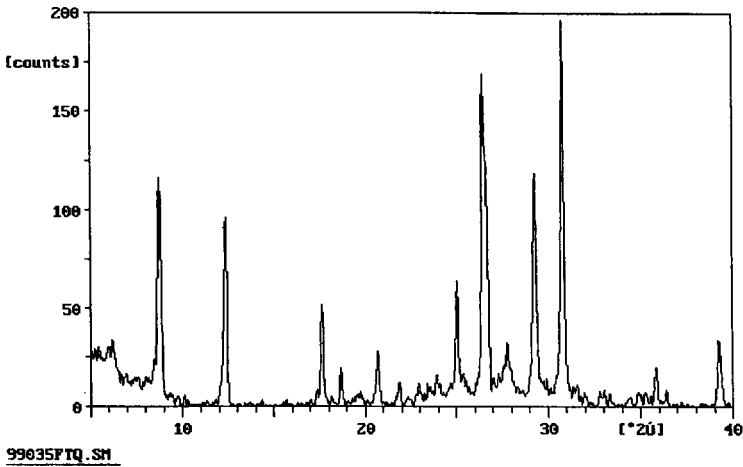


Fig. 9 - XRD analysis of the sediment of the Venice lagoon

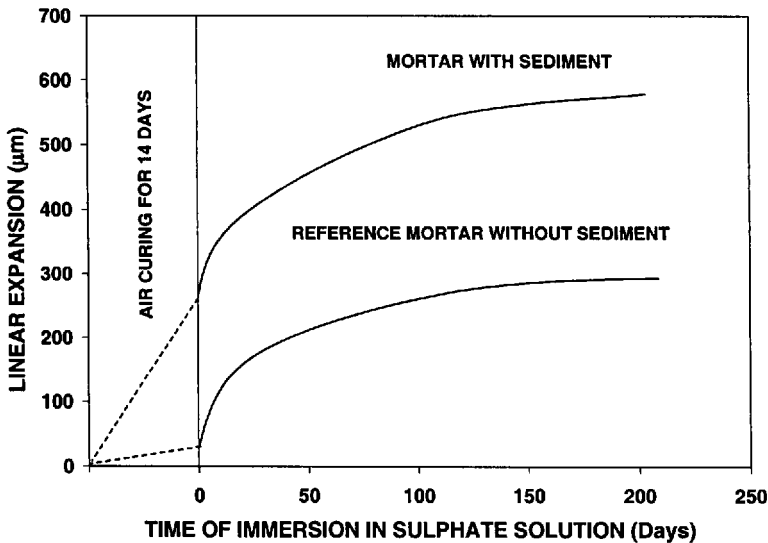


Fig. 10 - Linear expansion of specimens of the mortars with and without the sediment ($W/C = 0.38$) cured in 5 % $MgSO_4$ solution at 20 °C.

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Freezing and Thawing Hysteresis Effects in Experimental Analysis of Frost Deicing Salt Resistance of Cementitious Materials

by J. Kaufmann

Synopsis: Hysteresis effects are very frequent in experimental studies of porous building material. In the case of frost deicing salt resistance, hysteresis effects between freezing and thawing were reported in calorimetric and expansion experiments. They often were explained by a difference in the active pore diameter.

However, our calorimetric and ultrasonic pulse velocity measurement show much smaller hysteresis effects which support another explanation: supercooling. A model based on non-connected pore water which may supercool was developed to explain the experimental differences.

This model allows a reinterpretation of experimental expansion data. The moment of damage formation in frost deicing salt resistance tests can be studied.

The analysis of the causes of hysteresis effects therefore leads to improved models of frost deicing salt damage mechanisms.

Keywords: calorimeters; deicers; expansion; hysteresis; ice formation; ultrasonic tests

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INTRODUCTION

In experiments with porous materials hysteresis effects between adsorption and desorption are well known from sorption measurement [1]. Similar hysteresis effects were found between freezing and thawing in frost deicing salt experiments. The origin of such hysteresis is explained in literature by the influence of the pore shape on the freezing and the melting point of the pore water or can be explained by local supercooling. In our experiments where special attention was put on the initiation of ice nucleation, much smaller hysteresis effects were found. This leads to an improved analysis of experimental data.

POSSIBLE ORIGIN OF HYSTERESIS EFFECTS ON FREEZING AND THAWING OF PORE WATER

Influence of pore shape on the freezing/melting point

The freezing/melting point of the pore solution is depressed by dissolved alkali or chloride ions in the case of deicing salt application. Additionally the water in pores of small diameters is owing to surface-tension effects at a lower energy level than free water. When pore water freezes, the solid-liquid interface curvature depends closely of the pore diameter and therefore the freezing and the melting point of pore water is depressed compared to bulk water.

Relations between pore size and freezing/melting point of the pore water can be derived from thermodynamic models. Freezing is assumed to be limited by homogeneous nucleation within each pore.

First thermodynamic descriptions were developed by Everett [2] [3], Haynes [4] and Hill [5] [6] [7] where the validity of Gibbs-Duham equation [8] was assumed. The assumption of homogeneous layers implies the separation of two phases through a boundary region. When the relation of surface to volume of a phase becomes considerable, surface effects become important and it is no longer possible to consider a defined volume for each phase [9]. The Gibbs -Duham equations are only approximately valid.

In his thermodynamic model, which is based on the concepts of Landau-Lifschitz [10], Setzer [9] takes into account that between the internal surface of the solid matrix and the pore ice there exists an unfrozen adsorbed water layer of some molecules thickness. He derives the following relation:

$$(1) \quad (s_w - s_i) dT = (v_w - v_i) dp + (\gamma_{sw} - \gamma_{si}) \frac{V_{\text{pore}}}{n} d\left(\frac{1}{R_H}\right)$$

where γ_{sw} : surface energy between solid and pore-water
 γ_{si} : surface energy between solid and pore-ice
 $v_w(v_i)$: molar volume of water/ice
 $s_w(s_i)$: molar entropies of water/ice

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R_H : hydraulic radius ($= \frac{dV}{dA}$) of ice crystal
 V_{pore} : pore volume
 n : number of moles in the pore

$$\begin{aligned}
 \text{with } (\gamma_{sw} - \gamma_{si}) &\equiv \gamma_{wi} \\
 (s_w - s_i) &\equiv \frac{H_0}{T}
 \end{aligned}$$

and H_0 being the molar enthalpy of fusion one can find [11]

$$(2) \quad \frac{\Delta T}{T_0} = \frac{\gamma_{wi} V_i}{H_0 R_H}$$

where: ΔT : freezing/melting point depression
 T_0 : bulk freezing point

Similar relations were found earlier by different authors [12] [2].

Brun [13] finds a similar equation as (1) from Gibbs-Duhem equations. In his quasi macroscopic approach he calculates $\Delta S = (s_w - s_i)$ using macroscopic values. Assuming that the solidification process is by ice nucleation (growth of a critical embryo) and by integrating (1) he obtains from calorimetric data of porous Vycor glass a temperature dependent relationship for γ_{wi} . Additionally a layer of unfrozen water of 8 Å thickness (Brun [14]) is taken into account.

Finally, he obtains a relation between pore radius R_p and freezing and melting point depression ΔT for spherical pores:

$$(3) \quad R_p = \frac{-64.67}{\Delta T} + 0.57 \quad [\text{nm}] \quad 0 > T > -40^\circ\text{C}$$

The apparent solidification energy can be calculated as:

$$(4) \quad W_a = -5.56 \cdot 10^{-2} \Delta T^2 - 7.43 \Delta T - 332 \quad [\text{J/g}] \quad 0 > T > -40^\circ\text{C}$$

The shape of the pores influences the curvature of the liquid-ice interface (e.g. R_H). Therefore some corrections in the case of other pore forms have to be considered.

This leads to the possibility of explaining the hysteresis effects between freezing and thawing of pore water.

For freezing, nucleation from spherical ice nuclei (for each pore) is assumed. Brun therefore finds no deviation from equations (3) and (4) in the case of solidification (freezing). In the case of fusion (melting) the ice fills the whole pore space and the hydraulic radius of the melting ice is therefore assumed to be different. For cylindrical pores for example he derives for the melting point depression:

$$(5) \quad R_p = \frac{-32.33}{\Delta T} + 0.68 \quad [\text{nm}] \quad 0 > T > -40^\circ\text{C}$$

$$(6) \quad W_a = -0.155 \cdot 10^{-2} \Delta T^2 - 11.39 \Delta T - 332 \quad [\text{J/g}] \quad 0 > T > -25^\circ\text{C}$$

A shape factor can be introduced [13] [15].

Setzer [16] also explained the big hysteresis found in calorimetric tests with a different surface curvature (or hydraulic radius) of an ice embryo when freezing from the surface curvature when melting (Fig. 1).

Local supercooling

Let us now assume that no ice nucleation within the concrete specimen occurs, but that an ice front is penetrating the pore space from outside that means from a site where ice nucleation is initiated. This could be either by homogenous or heterogenous (ice formation nuclei) nucleation.

Let us call R_i the pore radius with freezing point of its pore water being T_i according to the pore size - freezing point relation. At a temperature $T_1 < T_0$ all pores which are connected to the surface by a larger radius than R_1 (all neck entrances are larger than R_1) are allowed to freeze (Fig. 2). The nucleation is guaranteed by the existing ice at the surface so that in these pores no supercooling occurs. At a lower temperature T_2 all pore water of the pores which are connected to the surface by pores with necks larger than R_2 will freeze and so on.

As we see, some pore space, although containing very large pores may not freeze because the ice front cannot penetrate them, as all pores which would connect them to the ice front have necks which are too small. Big "regions" therefore may supercool and freeze at much lower temperatures than they would if they were connected by larger pores.

When they finally get connected at a lower temperature (or nucleated) their pore water would freeze all together which could be interpreted as freezing of pore water of the smaller pores. The effect is similar as in mercury intrusion porosimetry (MIP).

The probability for the existence of such regions containing supercooled water increases when large pores have small entrances only and with the distance from the surface.

Interfaces of aggregates (in concrete) or fine cracks (may be introduced by drying, shrinkage, etc.) change the situation drastically, although their influence to the total porosity may be small. They can be considered as larger pores forming a network of connected pores which freeze at temperatures near the freezing point of water. For example, vacuum evaporation at modest temperature of 50°C of hardened cement paste can lead to a fine network of micro cracks. This was observed both with a scanning electron microscope (SEM) and a confocal microscope. The probability of supercooling of big regions even at large distance from surface hence is strongly reduced.

The supercooling of whole pore regions can lead to a big hysteresis between freezing and thawing [1]. Bigger amounts of pore space freeze at lower temperatures than they would according to the pore-size freezing-point relation. On the other hand the pore ice thaws exactly at the melting temperature according to pore-size melting-point relation as no superheating is possible.

The assumption that no nucleation in pores with no direct contact with the ion front occurs is supported by the experiments of Bigg [17] who measured big supercooling of small water drops.

EXPERIMENTAL RESULTS

Specimens

The specimens consisted of normal portland-cement concrete. Two different concrete mixtures were studied with various experimental techniques in detail.

Concrete cubes (200 by 200 by 200mm) of the following mixtures were fabricated (Table 1) and demolded after 2 days and then stored at 20°C/70% RH before they were cut at an age of 1-2 years and stored at different humidity conditions.

Calorimetry

DSC (differential scanning calorimetry) results -- Our DSC results of small volumes of cement paste (40 μ L) show a typical phase change (freezing) at about -20°C and another at -40°C (fig 3). At thawing, the peak at -40°C disappears and only one thawing peak near 0°C is found. Similar results were found by Beddoe [15].

In DSC experiments with a small amount of water (water drops) [18] also a phase transition (freezing) around -20°C was detected. As the water amount of 0.5 - 5mg still was large enough to neglect the freezing point depression owing to the surface tension, only supercooling can explain the low phase transition temperature. We think that, for this reason, the freezing peak at -20°C for a cement-paste specimen (Fig. 3) also has to be attributed to strong supercooling. For this purpose supercooling has to be prevented in calorimetric experiments. Supercooling can be limited by the use of larger specimens or the application of ice nuclei.

Improved DTA (differential thermoanalysis) results -- The use of larger specimens (cylinders, 18mm diameter, 10mm high) was possible using another calorimetric apparatus with a different measurement technique (DTA-type). The heat flow between the specimens and the bottom (copper block) of the calorimeter which is put into a programmable Lauda bath with constant cooling and heating rate (5°C/h) was registered continuously. To prevent the specimens from supercooling, special ice nuclei were used to initiate heterogeneous ice formation at the specimen surface. Cholesterol melted and recrystallised between two mica glass covers and then sprinkled on one specimen surface proved to be an effective ice nuclei with freezing initiation temperature at up to - 0.7 °C.

The apparatus and the method used are described in [19] and more in detail in [20].

The apparent heat capacities $C_{pA \text{ corr}} = C_{pA} - C_{pA \text{ ref}}$ the difference between the measured heat capacity of the specimen and the measured heat capacity of a reference (concrete dried at 110°C) in function of the specimen temperature of specimens saturated under water of mixture 1 and

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2 are given in Fig. 4. The thawing is given with reversed signs so that the values for freezing and thawing are comparable.

While the melting curve looks quite similar as in the DSC result, the freezing curve is significantly different from the DSC result. The first phase transition at freezing starts very close to 0°C. The second freezing peak is found near -40°C, also observed in the DSC tests. The temperature of the specimen was calculated from the calorimetric output signal and the temperature of the calorimeter. A test where the specimen temperature was measured by fixing a thermocouple at its center showed very good agreement with the calculated temperature [20].

Apart from the freezing peak at about -40°C which disappears in the thawing curve, only minor hysteresis between freezing and thawing was detected. Somewhat higher values were found for thawing than for freezing in the temperature region -8°C to -30°C. The freezing peak at -40°C seems to appear in the thawing curve in this temperature region. Above -8°C somewhat smaller values are found for thawing than for freezing, indicating a small hysteresis effect.

Ultrasonic Pulse Transit Time Measurement

The pulse transit time between a transducer and a receiver placed on two opposite sides of a concrete specimen (200 by 200 by 10mm) was measured. The specimen previously stored at different relative humidities until mass constancy was subjected to freezing and thawing cycles in an air driven climate chamber. The freezing/thawing rate in the air was kept constant at 10°C/h.

Because of the increased ultrasonic velocity of ice (3828 m/s) compared to that of water (1485 m/s) the pulse velocity increases when the pore water undergoes a phase change.

The experimental details are described elsewhere [21] [22].

In Fig. 5 the pulse velocities as a function of the specimen temperature are given for specimens of the same mixture proportions but stored at different relative humidities prior to testing.

No significant differences between freezing and thawing curve were detected.

Expansion Measurement

The expansion of a thin concrete plate (150 by 150 by 10mm) with the application of a frost medium layer at the upper surface in function of the concrete interface temperature is given in Fig. 6 for the case of water as frost medium and in Fig. 7 in the case of a 3 mass-% NaCl solution as frost medium. More experimental details are given in [23] [20]. Because of the applied frost medium layer supercooling is reduced, mostly to less than 3°C.

Significant hysteresis between freezing and thawing is observed. At the same time the remaining deformation (above 0°C) owing to damage is important.

The use of thin plates proved to have big advantages studying specimen expansion under frost deicing salt attack [23]. However, significant bending of the thin concrete plates was observed. Bending was much larger when a

salt solution instead of pure water was applied as frost medium [20]. This indicates that the expansion of the concrete layer near the frost medium interface (surface) most probably was larger in the case of a salt solution, which conforms to the results generally found in literature. As the expansion was measured between two lateral faces (parallel to the frost medium surface), bending effects influenced the observed length changes. Hence, this is the reason why the measured expansion as given in figs. 6 and 7 is smaller when a salt solution was applied as frost medium (fig 7) than with water as frost medium (fig 6).

DISCUSSION

In our DSC measurements where, without ice nuclei application, no phase transition upon freezing until -20°C was found. Similar DSC results were presented by Beddoe and Setzer [15]. Bager and Sellevold [24][25] also reported a freezing peak at about -20°C . In all these cases big hysteresis effects between freezing and thawing were found.

In the improved calorimetric tests (DTA) two main differences to these results are obvious. First, the initial phase transition occurred near 0°C and not at lower temperatures in the region of about -20°C and second, only a small hysteresis between freezing and thawing was found.

Supercooling of pore water was prevented in these experiments by the application of ice nuclei at the surface of the specimens. The nucleation in the inside of the specimen could be influenced by the improved nucleation at the specimen surface. This leads to the conclusion that the ice is penetrating the specimen like an ice front. This also was found by Bager and Sellevold (Bager [24][25]).

These differences between the different results of calorimetric tests should be explained by the different specimen (here: concrete ; Bager [24] [25] and Beddoe [15]: hardened cement paste), specimen dimensions (Bager [24][25] cylinders $\varnothing$ 14.6 mm, $l=65$ mm; Beddoe [15] cubes $l=1-2$ mm), apparatus (Bager [24][25] Setarm calorimeter (DTA), Beddoe [15] Perkin-Elmer (DSC)) or other experimental details.

While the theory of the influence of the pore shape does not explain these experimental differences, local supercooling theory could. The connectivity of the pores depends upon the material and the distance to the surface. The probability of supercooling of pore water increases with increasing length of the specimen as the mean distance to the surface increases. Even if ice nuclei are applied on the surface of these specimens the probability of supercooling in the inside increases. Without ice nuclei supercooling is significantly larger than what is seen in the DSC results.

The specimens used in our experiment were short ($l=10$ mm) and were mainly concrete specimens with a connecting network of larger pores at the interface between the aggregate and the cement paste matrix. Local supercooling in the inside therefore is less probable.

Very small hysteresis also was found in ultrasonic pulse transit time measurements which confirms the results of the improved calorimetric tests (DTA).

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This leads to the assumption that local supercooling in the case of concrete (at least for "small" specimens with sufficient ice nucleation at the surface) is not important and that the pore water freezes and melts at almost the same temperature.

In the expansion tests bigger hysteresis is found. At the same time significant remaining expansion ΔL_{remain} (permanent residual) owing to damage formation was measured.

In earlier expansion experiments performed by Powers [26], apart from some supercooling effects, much smaller hysteresis between freezing and thawing was measured. Unfortunately in their experiments the effect of supercooling was not limited by the application of ice nuclei. In these experiments it is most probable that the damage had a minor influence. The volumetric expansion was measured in a toluene filled vessel, so that the toluene might have refilled any induced microcracks. Hence, the damage actually did not influence the measured volume changes. That might also be the reason why they observed almost no remaining deformation in their experiments.

In our experiment, damage formation contributes to the measured expansion. Together with the above observation that only very small hysteresis between freezing and thawing of pore water exists this leads to a new interpretation of the expansion results. The hysteresis observed in the expansion measurement can be attributed to progressive damage formation during the frost cycle.

The difference δL between the length at freezing and at thawing for each temperature of one frost cycle is supposed to represent only the damage formed through the temperature cycling at lower temperatures.

The damage can be induced by different damage mechanisms: hydraulic or hydrostatic pressure, ice lens segregation, osmotic pressure as well as by thawing effects owing to ice dilatation [27]. We assume that the final damage is the result of a combination of different mechanisms. A damage model is proposed in [20].

The damage mechanisms may be separated into:

- a) freezing initiation mechanisms (hydraulic and hydrostatic pressure) and
- b) transport mechanisms (osmosis, ice lens segregation, and ice dilatation effects)

While the freezing initiation mechanisms mostly depend on the ice formation rate, the transport mechanisms mostly depend on the difference between minimum temperature and freezing point, and the duration of the frozen state. This separation is not very sharp.

The difference δL between freezing and thawing of the expansion of one cycle with frost medium water and the one with frost medium 3% NaCl solution are plotted in Fig. 8. Both curves qualitatively look very similar. The absolute values should be considered as relative values only, as specimen bending, possibly owing to the gradiental freezing (ice penetration front), influenced these results.

Above the freezing point of the frost medium (water: 0°C ; 3%NaCl: -2°C) the remaining deformation ΔL_{remain} (damage) is seen. The increased values near the freezing point indicate some relaxation effects.

At temperatures below the freezing point the difference δL between freezing and thawing first is smaller but reaches at about -3°C the values of the remaining expansion ΔL_{remain} ($>5^{\circ}\text{C}$). The difference δL gets maximal at about -4°C .

At lower temperatures the difference δL becomes smaller. The decrease is softer in the case of the salt solution. Below -10°C an almost linear behavior is found.

While the maximum in the case of the salt solution as frost medium is reached just after freezing is initiated, the maximum is approached continuously with water as frost medium. With frost medium water the temperature region between 0°C and -4°C seems to be of minor importance for damage formation. Nevertheless, as can be seen from calorimetric data (DTA), a large amount of ice is formed during freezing at temperatures above -4°C . The freezing initiation a) seems to be soft enough to accommodate the excess water without important damage formation. At the same time, owing to the high freezing point, the transport mechanisms b) are optimised in relation to duration and temperature difference.

With a 3% salt solution as frost medium, the maximum of the difference δL is reached soon after freezing initiation. This indicates that the frost damage mechanisms of type a) and b) are optimised. A rapid freezing effect (freezing initiation a)) is combined with a maximal duration of the transport mechanism effects b).

The slower decrease of the difference δL with decreasing temperature compared to the case of pure water may be the result of an increased importance of osmosis or other damage mechanisms related to the salt content.

With salt solutions of higher salt concentrations no maximum was found: the difference δL decreases constantly with decreasing temperature. The freezing initiation mechanisms certainly are important but the transport mechanisms might be reduced owing to the lower freezing point.

CONCLUSIONS

In calorimetric measurement it is crucial to prevent the pore water from supercooling. This can be achieved by the application of ice nuclei at the outer surface.

Only minor hysteresis between freezing and thawing is then found in calorimetric tests and in pulse transit time measurement. Hence the difference between freezing and melting point of pore liquid in concrete is much less than previously thought.

The differences to the results of other researchers can be explained with local supercooling.

Hysteresis effects in expansion tests can be attributed to progressive damage formation. This allows an improved analysis of expansion data.

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