NRC Publications Archive Archives des publications du CNRC

Influence of sea water solution on mortar containing calcium carbonate Ramachandran, V. S.; Feldman, R. F.; Beaudoin, J. J.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

Publisher's version / Version de l'éditeur:

Materials and Structures, 23, 138, pp. 412-417, 1990-11

NRC Publications Archive Record / Notice des Archives des publications du CNRC :
<https://nrc-publications.canada.ca/eng/view/object/?id=f28a7f5c-bad5-4a9f-9ce1-0c20cf04c083>
<https://publications-cnrc.canada.ca/fra/voir/objet/?id=f28a7f5c-bad5-4a9f-9ce1-0c20cf04c083>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site
<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Influence of sea water solution on mortar containing calcium carbonate

Ramachandran, V.S.; Feldman, R.F.; Beaudoin, J.J.

NRCC-32368

A version of this document is published in / Une version de ce document se trouve dans
Materiaux et constructions. Materials and Structures, 23, (138), pp. 412-417, November-90

The material in this document is covered by the provisions of the Copyright Act, by Canadian laws, policies, regulations and international agreements. Such provisions serve to identify the information source and, in specific instances, to prohibit reproduction of materials without written permission. For more information visit <http://laws.justice.gc.ca/en/showtdm/cs/C-42>

Les renseignements dans ce document sont protégés par la Loi sur le droit d'auteur, par les lois, les politiques et les règlements du Canada et des accords internationaux. Ces dispositions permettent d'identifier la source de l'information et, dans certains cas, d'interdire la copie de documents sans permission écrite. Pour obtenir de plus amples renseignements : <http://lois.justice.gc.ca/fr/showtdm/cs/C-42>

Influence of sea water solution on mortar containing calcium carbonate

VANGIS. RAMACHANDRAN, ROLFF. FELDMAN,
JAMES J. BEAUDOIN

Materials Section, Institute for Research in Construction, National Research Council Canada, Ottawa K1A 0R6, Canada

Normal Portland cement mortar discs containing precipitated or ground limestone at dosages of 0, 2.5, 5 and 15% were made at water/cement ratios of 0.42 or 0.60. They were hydrated in lime water or sea water solution for periods up to 1 year. The length and modulus of elasticity changes were monitored periodically. Some mortars containing CaCO_3 exhibited more than three times the expansion of the reference in sea water. The expansions were greater in samples containing fine CaCO_3 . The modulus of elasticity was especially low for samples containing precipitated CaCO_3 and exposed to sea water.

1. INTRODUCTION

Various types of by-products and waste materials such as fly ash, slag, silica fume and rice husk are used in concrete as additives with success. Limestone dust poses disposal and environmental problems and has been suggested for use as an additive to Portland cement. The Canadian Standard CSA CAN3-A5.M83 allows the addition of up to 5% carbonate for Type 10 normal Portland cement and this has been extended to Type 30 high early Portland cement.

Although a considerable amount of work has been carried out on the physical and mechanical properties of concrete containing limestone dust there are some conflicting results and also few data are available on the durability of concrete containing calcium carbonate. There is concern about the long-term durability of concrete containing lime dust [1].

Calcium carbonate addition not only influences the rate of hydration of the individual components of cement but also leads to the development of new compounds: for example the rates of hydration of C_3S and C_3A + gypsum are accelerated by the addition of CaCO_3 [2,3]. It can thus be expected to affect the physico-mechanical properties of cement paste. This may in turn have an influence on its durability.

Feldman and Ramachandran [4] have developed a non-destructive method of evaluating the properties of mortar discs exposed to various solutions. This method was adopted to determine the modulus and expansion of mortar bars containing 0 to 15% CaCO_3 of two finenesses and exposed to sea water for up to a year.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

2.1.1 Cement

Type 10 normal Portland cement was used having the following chemical composition: $\text{SiO}_2 = 19.83\%$, $\text{Al}_2\text{O}_3 = 4.18\%$, $\text{Fe}_2\text{O}_3 = 3.20\%$, $\text{CaO} = 60.06\%$, $\text{MgO} = 4.09\%$, $\text{Na}_2\text{O} = 0.45\%$, $\text{K}_2\text{O} = 0.89\%$, $\text{SO}_3 = 3.93\%$, free lime = 1.15%, and loss on ignition = 1.53%. The mineralogical composition was as follows: $\text{C}_3\text{S} = 49.93\%$, $\text{C}_2\text{S} = 19.18\%$, $\text{C}_3\text{A} = 5.66\%$, $\text{C}_4\text{AF} = 9.74\%$.

2.1.2 Sand

A laboratory concrete sand was used. The fineness modulus was 2.38. Sieve analysis according to sieve size (mm) and weight percentage passing (in brackets) was as follows: 5 (100); 2.5 (93.9); 1.25 (79.4); 0.63 (67.5); 0.32 (17.15); 0.14 (3.37).

2.1.3 Calcium carbonate

Two types of calcium carbonate were used. One type was a precipitated carbonate supplied by Anachemia. It had a surface area of $6.88 \text{ m}^2 \text{ g}^{-1}$ determined by the nitrogen adsorption method. The second type was obtained by grinding limestone to particle sizes finer than $15 \mu\text{m}$. The nitrogen surface area was $2.25 \text{ m}^2 \text{ g}^{-1}$. Particle size analysis was performed using a Sedi-graph particle size analyser. The particle size range

Fig. 1 Particle size distribution of (■) ground and (▲) precipitated CaCO_3 .

(diameter) for the precipitated material was 1 to 5 μm . The ground material had particles in the range 1 to 40 μm (Fig. 1).

2.1.4 Test solutions

Two solutions were used for sample exposure. One was a saturated lime solution. The other was a laboratory-prepared sea water containing 2.7% NaCl, 0.32% MgCl_2 , 0.22% MgSO_4 and 0.13% CaSO_4 .

2.2 Specimen preparation

Mortar mixes were prepared at water:cement ratios of 0.42 and 0.60. The cement:sand ratio for all mixes was 1:2.75. Calcium carbonate additions (ground and precipitated) were made in amounts of 0, 2.5, 5 and 15% by weight of cement. Superplasticizer (melamine type) was used for mixes at $w/c = 0.42$ containing 5 and 15% calcium carbonate. The amounts were 0.4 and 1% by weight of cement, respectively.

Mortar cylinders (76.2 mm diameter $\times$ 152.4 mm) were cast for each mix and cured for seven days at 100% RH. Cylinders from each mix were then sliced to produce 6 mm thick discs. The discs were cured at 100% RH for an additional seven days prior to immersion in the salt solution. Stainless steel Demec gauge reference points were positioned 50.8 mm apart on the specimen surface for length change measurements. The reference points were inserted in pre-drilled holes and secured with epoxy adhesive. In addition to the disc specimens, mortar cubes (50.8 mm) were cast for compressive strength determinations at 14 days.

2.3 Test methods

Mortar discs were placed in separate baths containing either lime solution or sea water. Deflection and length change measurements were made at several time inter-

vals up to 1 year. Deflection measurements were made on discs loaded at the midpoint and supported along the edge at points 120° apart. Loads applied using an Instron testing machine did not exceed 35% of the failure loads. The modulus of elasticity was calculated using the deflection data and elastic plate theory [5]. Length change measurements were obtained with a Demec mechanical strain gauge. The smallest division on the gauge corresponds to a strain of 2×10^{-5} .

Compressive strength measurements of mortar cubes were performed according to ASTM C190.

3. RESULTS AND DISCUSSION

3.1 Modulus of elasticity

Figs 2 and 3 present the results of the changes in moduli for mortars containing 0 to 15% CaCO_3 ground or precipitated, respectively, and prepared at $w/c = 0.42$ and 0.60. Values are plotted for intervals up to one year.

All samples prepared at $w/c = 0.42$ and containing ground CaCO_3 show similar or slightly higher moduli with respect to the reference containing no CaCO_3 (Fig. 2). Addition of 15% precipitated CaCO_3 drastically reduces the modulus (Fig. 3).

All samples increase in modulus with time of exposure in lime water. On exposure to sea water, generally, all the samples containing ground or precipitated CaCO_3 show lower moduli than the references (Fig. 2). All samples containing precipitated CaCO_3 showed a significant reduction in modulus with respect to the reference.

At $w/c = 0.60$ all samples, both reference and those exposed to sea water, generally showed lower moduli (Figs 2 and 3) than those fabricated at $w/c = 0.42$. Exposure to sea water of mortars ($w/c = 0.60$) containing precipitated and ground CaCO_3 results in even more drastic reductions in moduli than those observed for samples prepared at $w/c = 0.42$.

Fig. 2 Effect of ground calcium carbonate on modulus of elasticity of mortars exposed to sea water. (a) Reference, w/c = 0.42; (b) sea water, w/c = 0.42; (c) reference, w/c = 0.60; (d) sea water, w/c = 0.60. CaCO₃ (%): (▲) 0, (□) 2.5, (◇) 5, (△) 15.

Fig. 3 Effect of precipitated calcium carbonate on modulus of elasticity of mortars exposed to sea water. (a) Reference, w/c = 0.42; (b) sea water, w/c = 0.42; (c) reference, w/c = 0.60; (d) sea water, w/c = 0.60. CaCO₃ (%): (▲) 0, (□) 2.5, (◇) 5, (△) 15.

Fig. 4 Effect of ground calcium carbonate on expansion of mortars exposed to sea water. (a) Reference, $w/c = 0.42$; (b) sea water, $w/c = 0.42$; (c) reference, $w/c = 0.60$; (d) sea water, $w/c = 0.60$. CaCO_3 (%): (▲) 0, (□) 2.5, (◇) 5, (△) 15.

3.2 Length change

The results of the length change measurements for the same samples for which moduli measurements were carried out are presented in Figs 4 and 5. At $w/c = 0.42$ addition of ground CaCO_3 reduces the expansion values with respect to the reference, whereas samples containing precipitated CaCO_3 showed enhanced expansion values.

On exposure to sea water, all samples show rapid expansion. The samples containing precipitated CaCO_3 and 15% ground CaCO_3 show much higher expansions than the corresponding reference specimens. At $w/c = 0.60$ addition of both precipitated and ground CaCO_3 reduces the expansion relative to the reference sample.

On exposure to sea water the expansions for samples containing both ground and precipitated CaCO_3 are significantly higher than in the references. Generally, samples prepared at $w/c = 0.60$ containing CaCO_3 expand more rapidly when exposed to sea water than those prepared at $w/c = 0.42$.

The reference mortar samples exhibited expansions of 0.05 to 0.06% in lime water. These values were higher than was expected. Experiments were done to determine expansion values when pastes and mortars containing 0 and 5% CaCO_3 were autoclaved to 216°C, after pre-curing for 14 days. The expansion values (Table 1) were found to be in the range of 0.06 and 0.08%. This confirms that the expansion observed during exposure to sea water is not the result of MgO or CaO hydration. The expansion of most of the specimens containing CaCO_3 , when exposed to sea water, was greater than in the reference samples. This may be related to the formation of carboaluminate-enhanced formation of thaumasite and perhaps other processes.

The net length change of mortars in sea water depends on the following factors: the rate of reaction of individual compounds with CaCO_3 and their interaction with sea water, the amount of the reaction product, the types of reaction products, the solubility of the materials, pore structure and porosity of the matrix. These individual processes may either increase or decrease the length of the mortar specimens.

Fig. 5 Effect of precipitated calcium carbonate on expansion of mortars exposed to sea water. (a) Reference, $w/c = 0.42$; (b) sea water, $w/c = 0.42$; (c) reference, $w/c = 0.60$; (d) sea water, $w/c = 0.60$. CaCO_3 (%): (▲) 0, (□) 2.5, (◇) 5, (△) 15.

Table 1 Autoclave expansion of cement containing 0 and 5% ground calcium carbonate

Samples	Type 10*		Type 50†	
	0%	5%	0%	5%
Paste				
Hyd 1d	0.174	0.155	0.105	0.091
Hyd 14d	0.081	0.06	0.043	0.042
Mortar				
Hyd 1d	0.157	0.145	0.125	0.114
Hyd 14d	0.07	0.069	0.064	0.067

*Type 10 = normal cement

†Type 50 = sulphate-resisting cement

3.3 Compressive strength

The behaviour of mortars exposed to sea water could depend on their strength before exposure. Compressive strength results for all samples moist-cured for 14 days are presented in Fig. 6.

All samples prepared at $w/c = 0.42$ exhibited higher

strength than those prepared at $w/c = 0.60$. In general, strengths are not affected by the addition of 2.5 to 15% ground CaCO_3 but the addition of 15% precipitated CaCO_3 results in a decrease of approximately 50%. Although the compressive strengths (Fig. 6) are similar, in many cases, the samples containing both types of

Fig. 6 Compressive strength after curing for 14 days at 100% RH.

CaCO₃ exhibit much higher expansion than the reference samples when exposed to salt water (Figs 4 and 5).

4. CONCLUSIONS

1. Use of small-size mortar discs permits examination of the influence of a large number of test variables on their properties.
2. By using this method, the potential durability of a material such as cement with carbonate additions exposed to sea water can be predicted.
3. Most mortars containing CaCO₃ (both coarse and fine) have higher expansion values than the reference specimens when exposed to sea water. However, those containing coarse CaCO₃ show relatively lower expansions than those containing fine CaCO₃.
4. Of the samples exposed to sea water those made at w/c = 0.42 and containing 2.5 to 5% ground CaCO₃ exhibit the smallest expansion values, being comparable to those of the reference specimen.

5. Higher compressive strength does not necessarily correlate with better durability to sea water.

REFERENCES

1. Ramachandran, V. S. and Chun-mei, Z., 'Dependence on the fineness of calcium carbonate on the hydration behaviour of tricalcium silicate', *Durabil. Mater.* **4** (1986) 45-66.
2. *Idem*, 'Thermal analysis of the 3CaO·Al₂O₃-CaSO₄·2H₂O system', *Thermochim. Acta* **106** (1986) 273-282.
3. Mayfield, L. L., 'Limestone additions to portland cement - an old controversy revisited', *Cement Concr. Aggreg.* **10** (1988) 3-8.
4. Feldman, R. F. and Ramachandran, V. S., 'New accelerated methods for predicting durability of cementitious materials', in *Proceedings, 1st International Conference on Durability of Building Materials and Components*, STP 691, Philadelphia, USA (American Society for Testing, 1980) pp. 313-325.
5. Timoshenko, S., 'Theory of Plates and Shells' (McGraw-Hill, New York, 1940) p. 295.

RÉSUMÉ

Influence d'une solution d'eau de mer sur du mortier renfermant du carbonate de calcium

On a confectionné des disques de mortier de ciment Portland normal contenant du calcaire, à des dosages de 0, 2,5, 5 et 15%, les rapports eau/ciment étant de 0,42 ou 0,60. Leur hydratation a été réalisée dans de l'eau de chaux ou dans une solution d'eau de mer pour des cycles

allant jusqu'à une année. On a contrôlé périodiquement la longueur et le module d'élasticité.

On a constaté sur certains mortiers contenant du CaCO₃ une dilatation plus de trois fois supérieure à celle de l'échelle de référence dans l'eau de mer, la dilatation étant plus forte dans les éprouvettes contenant du CaCO₃ fin. Les éprouvettes renfermant du CaCO₃ précipité, qui avaient été exposées à l'eau de mer, présentaient un module d'élasticité particulièrement bas.