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CONCRETE DURABILITY AND CaO/SiO_2 MOLE RATIO OF CSH

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ABSTRACT

CaO/SiO_2 mole ratio of calcium silicate hydrate (CSH) in Portland cement pastes has been studied by various authors using diverse techniques. Some of these authors claimed a mole ratio of 1.5 and others a higher ratio of about 1.7 to 1.8. However no attempt seems to have been made to correlate the claimed mole ratios to the chemical and mechanical properties of CSH especially the durability of hardened mortar or concrete. This paper addresses this correlation. It has been shown that the durability of Portland cement concrete requires a CaO/SiO_2 mole ratio of 1.5 and any excess CaO is detrimental to concrete durability under some circumstances. The reported CaO/SiO_2 mole ratios above 1.5 may be due to a contamination of the analyzed volumes or the excess CaO is so loosely bound that it may take part in some concrete break-down processes. Neither does a higher CaO/SiO_2 ratio in CSH adds to its strength giving property.

Hydration and strength development of Portland cement involves, among other reactions, the formation of calcium silicate hydrate (CSH) and $Ca(OH)_2$. It is a general assumption that CSH is the main strength giving component in a set Portland cement paste; this is particularly so in a hardened C_3S paste. Another general assumption is that CSH particles that form in Portland cement and C_3S pastes are identical in structure except for some substitution of other ions in the structure of CSH in the case of Portland cement paste. In a hydrating Portland cement, especially in hydrating C_3S, the formation of CSH and $Ca(OH)_2$ are related processes in the sense that the proportion of each increases with the degree of cement hydration. The processes are complementary to each other in the sense that for a given degree of cement hydration an increase in CaO/SiO_2 mole ratio of CSH lowers the proportion of $Ca(OH)_2$.

CaO/SiO_2 mole ratio of CSH has been studied by a number of workers using diverse techniques. The results so far obtained may be divided into two main groups. The workers using the phase equilibrium, the theoretically valid electron probe micro-analytical and the extraction techniques obtained a ratio of about 1.5 (fx. 1, 2, 3). Other workers, using mainly the analytical electron microscopic, dta and tga techniques have reported a variable CaO/SiO_2 mole ratio centred on 1.7 (fx. 4, 5). The literature cited above is not exhaustive but only indicative of the existence of claims of two values.

However, attention has already been drawn that all electron beam analytical techniques, including the analytical electron microscopic technique, analyze a volume of material which is very much larger than that of a single particle of CSH and the analyzed volume, in general, contains other phases of the paste e.g. $Ca(OH)_2$, C_4AH_x etc. The presence of the contaminating phases vitiates the analytical results and only under special conditions CaO/SiO_2 mole ratio of CSH could be estimated from a large number of spot analyses (6). Furthermore in all electron beam micro-analytical techniques the sample is liable to decompose due to the electron bombardment in high vacuum. In this respect the analytical electron microscopic technique is particularly severe; it has been reported that a hydrothermally prepared, well crystalline calcium silicate hydrate changed its CaO/SiO_2 ratio during the analysis (7). It will thus appear that CaO/SiO_2 ratio of CSH of set cement paste is still an open question.

Most of the above work have been carried out without any reference to the physical and chemical properties, especially the durability aspects, of the set products. The object of the present paper is to ascertain if the durability requirements of mortar and concrete yields any information on CaO/SiO_2 mole ratio of CSH.

Though CSH is the main strength giving component in hardened cement mortar and concrete, it does not directly take part in the durability of the end products. Calcium hydroxide is however involved in a number of durability mechanisms. Its presence is beneficial and is required to maintain the passivity of reinforcing bars in reinforced concrete structures. The presence of $Ca(OH)_2$ is, on the other hand, detrimental in at least three mechanisms of concrete break-down. These are the calcium chloride attack, alkali-silica reaction and expansion and the sulphate attack on concrete. Of the above three processes the first two will be examined below.
The sulphate attack will not be considered here the reason being that more than one mechanism is involved in this attack. For the same reason sea-water attack will not be considered.

1) The break-down of concrete structures in the presence of concentrated solutions of $CaCl_2$.
This is one of the most severe mechanism of concrete break-down. Prisms of concrete or mortar, even of very low water/cement ratio, would breakdown very quickly if placed in a concentrated $CaCl_2$ solution at temperature below about 20°C (8,9,10, 11). It has been shown that the breakdown is due to the formation and crystallization of a calcium oxychloride hydrate from $Ca(OH)_2$, which is present in concrete, and $CaCl_2$. Conjeaud, using three different cements, have been able to show that more than 90% of the breakdown at room temperature is independent of C_3A content of cements and is due to the dissolution of $Ca(OH)_2$ and the formation of a calcium oxychloride hydrate (12).

If however, mortar or concrete prisms are stored in a concentrated solution of $CaCl_2$ at about 40°C or above no damage occurs although $Ca(OH)_2$ is leached out of the prisms. If the leached prisms are then stored in a concentrated $CaCl_2$ at 20°C or below no damage occurs. The damage mechanism is thus solely connected with the presence of free $Ca(OH)_2$ in the prisms and is avoidable by leaching it out with the attacking agent. This leaching of $Ca(OH)_2$ from the prisms, if carried out at 40°C, does not affect the compressive strength of the prisms as can be seen from Fig.1 (11). From Fig.1 it can be seen that the prisms which are stored at or below 20°C i.e. below the crystallization temperature of calcium oxychloride hydrate lost a considerable part of their starting strengths. The compressive strength of mortar prisms stored in a 30% $CaCl_2$ solution at 40°C for 90 days is, on the other hand, very similar to the compressive strength of companion prisms stored at 20°C for the same length of time. This is in spite of the porosity created by the leaçhing of free $Ca(OH)_2$ from the prisms. This similarity of strengths of the leached and un-leached prisms indicates that CSH particles are not attacked during this leaching (see also the section on C_3S pastes below).

2) Alkali-silica reaction and expansion :
This is another process of concrete destruction. In this process concrete expands over a period of time and the expansion is associated with the formation of a gel. The in-situ electron probe micro-analyses of gel in different concrete structures showed that the gel is composed of $Na(K)_2O$-CaO-SiO_2-H_2O. It has also been shown that the presence of free $Ca(OH)_2$ is a pre-requisite of alkali-silica expansion although dissolution of reactive silica may continue in the absence of free $Ca(OH)_2$ (13, 14). The mortar prisms which have been leached free of $Ca(OH)_2$ with a hot 30% $CaCl_2$ solution do not expand though the prisms are made with a highly reactive sand (13). This again emphasis the role of free $Ca(OH)_2$ in the deterioration process and the efficiency of $CaCl_2$ leaching technique.

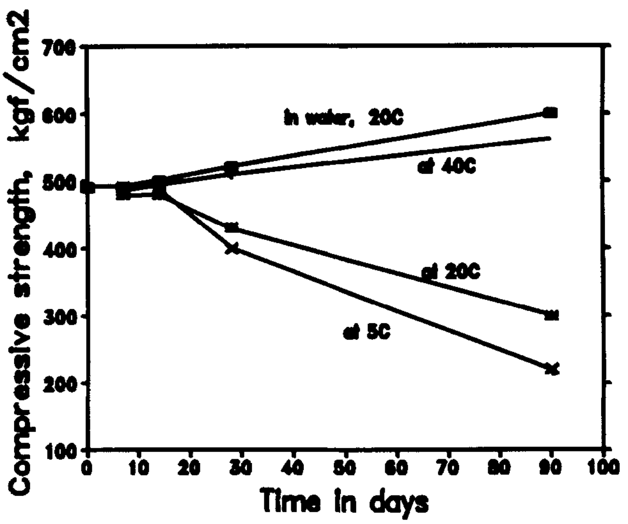

Figure 1. The compressive strengths of mortar prisms stored in 30% $CaCl_2$ solutions at different temperatures. All the prisms were pre-cured in water for 28 days at 20°C. Drawn after (11)

3) Leaching of fully hydrated C_3S pastes with a hot $CaCl_2$ solution : Results of leaching, with hot conc. $CaCl_2$ solution, of fully hydrated paste of pure C_3S have been reported (3). The results could be summarised as follows:

a) CaO/SiO_2 mole ratio of fully leached paste is about 1.5.

b) the x-ray diffraction diagrams of fully leached and virgin pastes could not differentiate between CSH phases of different samples. This observation emphasises the fact that leaching with $CaCl_2$ does not affect CSH particles.

Inferences:

Taking all the above results together following inferences could be drawn

i) from fully hydrated C_3S paste sufficient $Ca(OH)_2$ could be leached out so that the residue has a CaO/SiO_2 mole ratio of 1.5. This leaching of $Ca(OH)_2$ does not alter their x-ray diffraction pattern of CSH compared to that present in a virgin paste.

ii) if it is assumed that CSH in hydrated Portland cement is identical to that in C_3S pastes, except for some isomorphous replacement of SiO_2 by other elements, then the extraction by $CaCl_2$ solution has no affect on the strength giving properties of CSH as can be seen from Fig.1.

iii) as far as durability of cement mortar and concrete is concerned CSH has a CaO/SiO_2 mole ratio of 1.5. Any excess CaO is liable to cause a deterioration of concrete under appropriate conditions.

iv) the reported higher CaO/SiO_2 mole ratio i.e. 1.7 -1.8 is either due to a contamination of the analyzed volume by $Ca(OH)_2$ etc. or the extra CaO is so loosely bound that its extraction alters neither the strength giving property nor the x-ray diffraction pattern of CSH. The extra CaO is capable of taking part in the chemical reactions of concrete destruction.

Conclusion

In conclusion it could be said that the durability requirement demands a CaO/SiO_2 mole ratio of 1.5 for CSH in hardened Portland cement mortar or concrete. The presence of any extra CaO in CSH is harmful to mortar and concrete in the case of $CaCl_2$ attack or alkali-silica reaction.

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