WATER ABSORPTION AND VOLUME CHANGES OF ALKALI SILICATES IN FLINT MEASURED BY THERMOGRAVIMETRY

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ABSTRACT

Only the amorphous marked and micro-crystalline silica in aggregates causes alkali-silica reaction and expansion in concrete. One member of this group is flint. Using grains of flint which had been treated with alkali, it could be proved by means of thermogravimetry measurements at a temperature of 900°C that silica with lattice defects, such as flint, absorbs water differently. The absorption of water and the increase in volume of flint, is only possible in the presence of hydroxyl ions. Grains of flint stored in neutral NaCl/KCl solution did not show any increase in absorption. Contrary to this, flint stored in 1 normal NaOH/KOH solution showed a definite increase in the absorption of water.

Despite the numerous experiments with the alkali-silica reaction in concrete, one has not been able to give a full explanation for the expansion of the reactive aggregates. In this report we aim to prove that silica with lattice defects does infact absorb water and increase in volume, in the presence of alkali and hydroxyl ions. By the means of thermogravimetry we investigated the water sorption of flint as a representative of reactive silicas.

Bonded Water in Silicas and Flint

Depending on the nature and amount of the lattice defects, the silica minerals contain either more chemically bonded water (SiOH-groups) or molecular water. The most external or internal interfaces of reactive silica are covered with hydroxyl ions. More water can be added to the silanol groups due to further adsorption. Lange (2) described previously two sorts of molecular, adsorbed water in silicas:

SINGLE GROUP

DOUBLE GROUP

FIG. 1

Hydoxyl groups at SiO_2-interfaces (1)

1. Physically adsorbed water with slight activation energy and
2. Water bonded at the SiOH-groups with a high activation energy.

When heating in a vacuum, first the SiOH double groups are decomposed in the formation of reversible oxygen links and SiOH single groups. Following this, there is a further decomposition of the SiOH single groups. At 400 °C the silica lattice is displaced.

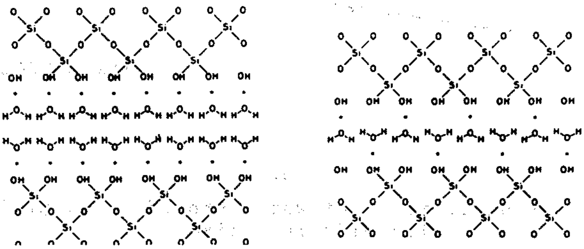

FIG. 2

Silanol groups and water layers at the quartzite interfaces in flint (3)

With respect to flint, Micheelsen (3) presumed that the interfaces of the quartzites, which build up the flint, are covered by single layers of SiOH-groups and that the neighbouring quartzites are bonded through several layers of water molecules. There are free SiOH-groups and oxygen links at the interfaces of quartzites in the ratio of 2:1. Overall, Micheelsen (3) found that the relationship between molecular water and the SiOH-groups in flint was 1:3.2.

The thermogravimetry measurements showed that the water in the fine flint grains is much more loosely bonded (see FIG. 3). The flint grains with the size of 0.05 - 0.07 mm release mainly the bonded water between a temperature of 400 °C and 600 °C. There are more external interfaces with slighter

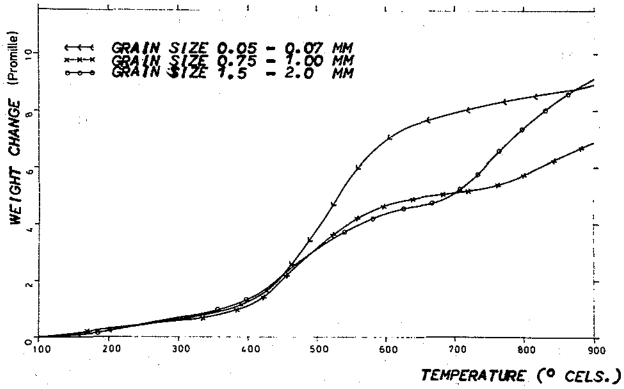

FIG. 3

Thermogravimetry of water stored flint grains with different sizes

activation energies in the fine flint grains.

Water Sorption and Expansion of alkali reactive Silicas

Hirche, Ludwig and Wolff (4) pointed out that the alkali-silica reaction depends mainly on following physico-chemical phenomena:

1. Diffusion of alkali ions and calcium ions to the reaction site in the silica grain

   Alkali ions and calcium ions diffuse along silica interfaces. Alkali ions diffuse more rapid because of its smaller size ($K^{+}_{solv.}$ =1.75 Å, $Na^{+}_{solv.}$ =2.17 Å, $Ca^{++}_{solv.}$ =2.75 Å) and of the stronger electrostatical interaction of the calcium ions with the lattice atoms.

2. Ion exchange of alkali and calcium at silica interfaces

The diffused cations Na^+, K^+ and Ca^{++} exchange against the protons of the silanol groups. Na^+ and K^+ exchange reversible, Ca^{++} exchanges irreversible. Calcium hydro-silicates will be concentrated at external interfaces, because of the exchange of calcium ions against alkali ions, too. The released alkali ions are available for further reaction at internal interfaces. There should be a surplus of alkali ions at internal interfaces.

3. OH-ion action with the silica lattice

Normally the silica interfaces are covered with a second layer of H_2O. Hydroxyl ions diffuse with the solvated cations to the reaction site. A water molecule of the second layer will be absorbed in the hydrate shell of the cation. The silica interface will be free now for the action of OH-ions. The hydroxyl ions react with the silica lattice and the cation-silica complexes. New silanol groups will be produced for further reaction.

4. Water sorption at the reaction site

With the formation of alkali hydro-silicates at internal interfaces the chemical potential of water near the reaction site decreases. Water will be transported to internal interfaces until the hydro-silicate is dissocated completely. The volume increasing of the waterless silicate to the voluminous alkali silica gel produces an increasing pessure in the silica grain and the surrounding hydrated cement paste.

The water sorption of alkali silicates in flint was studied with thermogravimetry investigation. Most experiments were conducted on fine and coarse flint grains which were stored in alkaline solutions few days. In Figures 4,5 and 6 the weight loss of the flint grains is given as a function of the temperature.

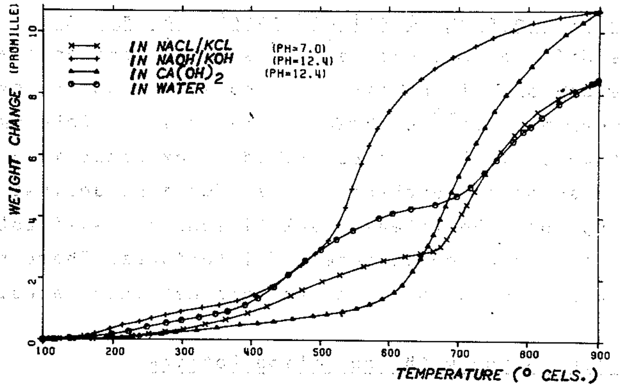

FIG. 4

Thermogravimetry of flint grains (grain size = 1.5-2.0 mm) stored in alkaline solutions

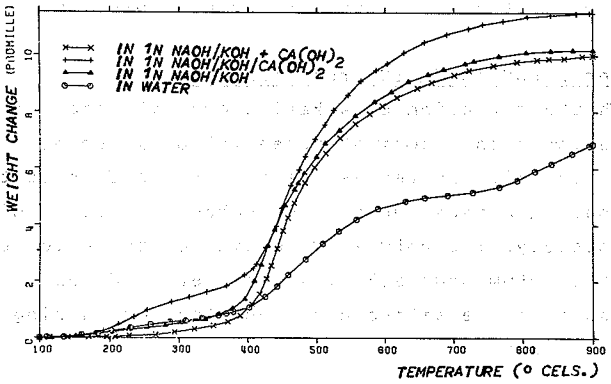

FIG. 5

Thermogravimetry of flint grains (grain size = 0.75-1.0 mm) stored in alkaline solutions

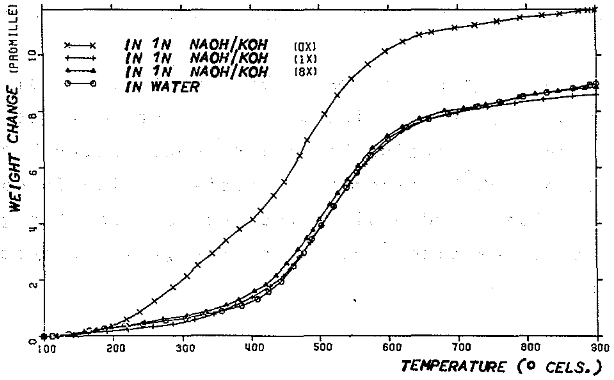

FIG. 6

Thermogravimetry of flint grains (grain size = 0.05-0.07 mm) stored in alkaline solutions

The results from these thermogravimetry investigations may be summarized as follows:

1. In presence of alkalis and OH-ions in solution the water sorption of flint grains increases (see FIG. 4). After heating in a vacuum the flint looses specially the bonded water between 500 °C and 600°C temperature.
2. In presence of calcium and OH-ions the water sorption of flint increases, too (see FIG. 4). The binding energy of water in calcium silicates is higher. The bonded water will be released between 650°C and 700°C temperature.
3. Storing the flint grains in an alkaliferous solution without OH-ions (= NaCl/KCl solution), one could not find any increasing water sorption.
4. Have we calcium ions in alkaline solutions the flint grains absorb water, too (see FIG. 5). The weight loss is similar to the measurements on flints stored in calcium free NaOH/KOH solution. Because of the small surface and of the short reaction time, the previously described ex-

change of calcium ions against alkali ions didn't occur (5).

5. The binding energy of water bonded at alkali silicate interfaces in fine flint grains is very low (see FIG. 6). The fine flint grains loose its bonded water between 200°C and 400°C temperature specially. The formation of the alkali hydro-silicates occured near the grain surfaces. One time flushing of the grains washed out all hydro-silicates.

Experimental procedure

All thermogravimetry investigations were made with an electro balance of Cahn-Instruments. The prepared flint grains were heated in a quartz tube under vacuum of 10^{-2} torrs. The heating temperature increased in steps of 2°C/min.

Before testing, the flint grains (0.05-0.07 mm, 0.75-1.0 mm and 1.5-2.0 mm) were stored 6 days in tridistillated water or in different alkaline solutions as follows:
NaOH/KOH solution (pH=12.4), $Ca(OH)_2$ solution (pH=12.4), 1n NaOH/KOH solution, 1n NaOH/KOH solution with addition of undissolved $Ca(OH)_2$, 1n $NaOH/KOH/Ca(OH)_2$ solution and NaCl/KCl solution (pH=7.0).

The flint specimens were contaminated partly through calcium carbonates. Heating calcium carbonates, we measure the releasing of CO_2 from 600°C to 900°C approximately. Due to the chemical analysis of the examined flint, we suggest that the different weight losses in the temperature range from 650°C to 900°C were caused partly through higher $CaCO_3$ contamination on the coarse flint grains. The maximum $CaCO_3$ contamination of flint minerals could be 0.80 percents in weight, the CO_2 contamination could be 0.35 percents in in weight.

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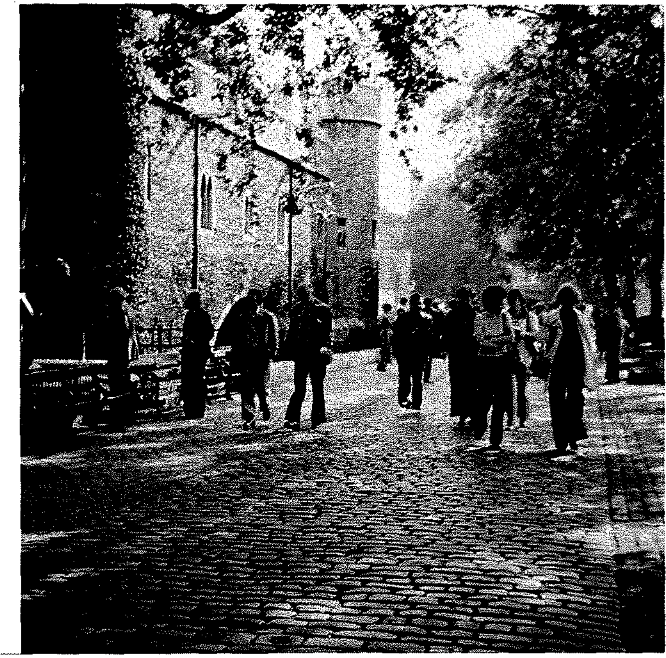

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