

# CHANGES OF PORE SOLUTION COMPOSITION UNDER ACCELERATED MORTAR BAR AND CONCRETE PRISM TEST CONDITIONS

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## Abstract

Accelerated tests of mortar bars and concrete prism were carried out at temperatures  $\geq 40^\circ\text{C}$  in order to reduce the test duration. Because the  $\text{OH}^-/\text{SO}_4^{2-}$  equilibrium is shifted to lower values with increasing temperature and alkali content of the cement, there exists the possibility of side reactions between sulphate ions from the cement and aluminate ions which can come from mineral admixtures and aggregates. Solubility measurements of two types of aggregates in sulphate free KOH solutions indicate that the temperature effect on the silica releasing rate is bigger than the inhibiting effect of the decreasing  $\text{OH}^-$  concentration. To avoid side reactions during aggregate test procedure, expansion measurements should be performed at  $40^\circ\text{C}$  in combination with adapted solubility measurements.

**Keywords:** pore solution, temperature, mineral admixture, solubility of aggregates

## 1 INTRODUCTION

From numerous investigations it is known that the hydration reaction of cements is influenced by temperature. This is valid for the hydration products as well as the composition of the pore solution [1]. Nevertheless, all test methods for ASR in mortar bars and concrete prisms in Germany are performed at higher temperatures in order to increase the reaction rate and to reduce the test duration [2][3][4]. Additionally to these methods two performance tests are applied [5][6] which give comparable results in evaluating the durability of concrete mixtures [7]. Since the reaction processes are rather complex and not fully understood, it is possible that the evaluation of the alkali sensitivity of an aggregate with different test methods is not well-defined.

From the investigations described in [8] it is known that one main factor for changes in pore solution composition is the decomposition of the calcium sulfoaluminate hydrates with increasing temperature leading to a lower  $\text{OH}^-/\text{SO}_4^{2-}$  ratio in the pore solution. These results were confirmed for concrete mixtures during the performance tests [9], where the shift of the  $\text{OH}^-/\text{SO}_4^{2-}$  equilibrium disturbs the evaluation of mineral admixtures regarding AAR prevention.

This paper deals with the pore solution composition of cement pastes underlying the same conditions as mortars and concrete samples in AAR test methods. The main target is to determine the influence of temperature and  $\text{OH}^-$  concentration on the solubility of two aggregate types and to investigate the effect of aluminate containing mineral admixtures at higher temperatures.

## 2 MATERIALS AND METHODS

### 2.1 General

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Two kinds of experiments were performed to gather detailed information on the AAR in concrete. Firstly, the pore solutions of hardened cement pastes were investigated in dependence on temperature. Secondly, the soluble amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  from the aggregates in KOH solutions were determined under similar conditions as in the cement pastes.

## 2.2 Materials and mixture proportions

Two Portland cements (type CEM I) with different  $\text{Na}_2\text{O}$  equivalent were used for preparing the cement pastes. The first was a test cement (CEM I 32.5R) doped with potassium sulphate to a  $\text{Na}_2\text{O}$  equivalent of 1.30 wt. %. The second cement CEM I 42.5R contained 0.89 wt. %  $\text{Na}_2\text{O}_{\text{eq}}$ . In the paper, they are called as TC (1.30) and CEM I (0.89). The pastes were obtained by mixing 100 g cement and 50 g distilled water by hand for 5 min, corresponding to a water/cement ratio of 0.5. In some pastes, 10.9 % of the Portland cement CEM I (0.89) were replaced by two kinds of mineral admixtures: first, a 50/50 mixture by mass of ELKEM microsilica (MS) and a highly  $\text{Al}(\text{OH})_3$  containing admixture (Serox) and second, an aluminosilicate type oven dust (FS1). The pastes were stored in tightly sealed PP bottles at 20°C, 40°C, 60°C and 80°C for 90 days.

For solubility measurements, we used two kinds of aggregates: a gravel (alkali sensitive) and a greywacke (slow-late rock) in the grain fraction 8-16 mm, which were separated from the original aggregate (provided by the producers) by sieving without any further breaking. After the sieving procedure, they were washed and dried at 110°C.

## 2.3 Methods for assessment and analysis

### *Separation of pore solutions*

After the 90 days storage, the cement stone samples were removed from the storage chamber and after coarse breakdown transferred in a special die. With a maximum power of 320 MPa, the pore solution was separated and filtered through a 0.2  $\mu\text{m}$  PTFE membrane filter.

### *Chemical analysis of the pore solution*

The original pore solution was titrated with 0.1 m HCl to determine the  $\text{OH}^-$  concentration. After diluting the pore solution with ultra pure water, the ion concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  were determined by ICP-OES with a PERKIN ELMER spectrometer OPTIMA 3000. An ion chromatograph DIONEX was used for the determination of the sulphate concentrations.

### *Determination of ettringite in the cement pastes*

A thermoanalytical DSC method described in [10] was used to determine the ettringite content quantitatively. One part of the 90 days hardened cement pastes was removed from the sample before pore solution separation und finely pestled by hand. Operating conditions of the METTLER /TOLEDO DSC/TG1 were set at a heating rate of 4 K/min from 40°C to 250°C in a nitrogen flow of 20 ml/min.

### *Solubility measurements*

Ninety grams of the aggregates were stored in 900 ml analytical grade potassium hydroxide solutions of different concentrations, corresponding to a ratio solution/solid of 10:1. The storage temperatures were chosen analogous to the cement pastes. After 28 days, the concentrations of dissolved  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were determined by ICP-OES. According to [11][12], the excess silicic acid ( $\text{SiO}_{2\text{exc}}$ ) content is calculated from the dissolved  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  content using the following formula:

$$\text{SiO}_{2\text{exc}} = \text{SiO}_2 - 1.4 * \text{Al}_2\text{O}_3 \quad (1)$$

Only this part of silicic acid is responsible for the damage of concrete. Table 1 contains the results of the solubility measurements.

### 3 RESULTS

Figure 1 shows the accumulated concentrations of the cations  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  in the pore solution of the two Portland cements in dependence on the temperature after 90 days. It can be established that the plots mainly depend on the alkali content of the cement and less on the temperature. The results of the equivalent anion concentrations  $[\text{OH}^-]$  and sulphate after 90 days of hardened cement pastes contain Figures 2 and 3. In contrast to the relatively constant cation concentrations with temperature, at above  $40^\circ\text{C}$  the pore solutions show a strong decrease in  $[\text{OH}^-]$  and a corresponding increase in  $[\text{SO}_4^{2-}]$ . In the temperature region from  $20^\circ\text{C}$  to  $80^\circ\text{C}$ , the  $\text{OH}^-$  concentration in pastes with CEM I (0.89) falls to 50.8 % and in TC (1.30) pastes to 44.2 % of the original value. Thereby, the difference between the two cements diminishes from 300 mmol  $\text{OH}^-/\text{L}$  at  $20^\circ\text{C}$  to 90 mmol  $\text{OH}^-/\text{L}$  at  $80^\circ\text{C}$ . In contrast to this behaviour, the difference in sulphate concentrations increases: from 12 mval/L at  $20^\circ\text{C}$  to 225 mval/L at  $80^\circ\text{C}$ . In the paste with TC (1.30), the increasing sulphate concentration in the pore solution is connected with the decreasing ettringite content in the solid phase, above at  $80^\circ\text{C}$  no ettringite could be detected.

The extremely high sulphate concentrations of 300 to 550 mval/L at  $80^\circ\text{C}$  in the pore solutions let expect having influence on the reaction mechanism when additional aluminate providing substances are present. This can be the case if mineral admixtures are used which contain a certain soluble aluminate content. Figure 4 shows this case for plain CEM I (0.89) cement pastes and with 10.9 wt. % aluminate containing admixtures at  $60^\circ\text{C}$ , Figure 5 respectively at  $40^\circ\text{C}$ . The sulphate concentrations measured in hardened pastes with the mineral admixtures are significantly lower (difference 60 – 90 mval/L) at  $60^\circ\text{C}$  than it can be calculated from the dilution effect (dotted line). Especially, the highly effective admixture FS1, regarding prevention AAR in concrete (since 8 years storage in a fog chamber at  $40^\circ\text{C}$  and 100° R.H. without any damaging reactions), reacts with sulphate at  $60^\circ\text{C}$ . Therefore it can be expected that a certain part of soluble aluminate is not available for AAR inhibition and the effect of the admixture is reduced. In comparison, the reduction of sulphate concentration in the corresponding pastes at  $40^\circ\text{C}$  is 30 mval/L only (see Figure 5). However this is the evidence that already at  $40^\circ\text{C}$  the side reaction mentioned above starts. Also in [13] the important role of alumina especially in determining the alkali-binding capacity of SCMs was discussed, however the precise role and the contribution of the alumina could not be clearly described. As Figure 6 shows, there is no reduction of the hydroxide concentration in CEM I (0.89) pastes at  $60^\circ\text{C}$ , when FS1 is used as a mineral admixture. A relatively small effect is achieved by mixing microsilica and Serox, likely caused by the silica part of the admixture. At  $40^\circ\text{C}$  (see Figure 7), the plots change in this way that both admixtures reduce the alkalinity of the pore solution to approximately 400 – 480 mmol  $\text{OH}^-/\text{L}$ . The results obtained at  $40^\circ\text{C}$  only are consistent with expansion measurements at the corresponding concrete.

Based on the fact that the solubility of aggregates depends on the temperature as well as the  $\text{OH}^-$  concentration, the results depicted in Figure 2 allow to correlate precisely these influencing factors for all cements. Therefore, the solubility experiments can be performed under more real conditions. In Table 1, this method is depicted for two aggregates in alkaline solutions adapted to the conditions being available in TC (1.30) cement pastes. Table 1 shows that the dissolved amounts of  $\text{SiO}_2$  from the aggregates are very different: the gravel emits significantly more  $\text{SiO}_2$  into the solution than the greywacke, whereas the  $\text{Al}_2\text{O}_3$  concentration seems to be less influenced, excepted the relative strong increase at  $80^\circ\text{C}$  with the greywacke. Between  $20^\circ\text{C}$  and  $40^\circ\text{C}$  within both aggregates, a doubling of the concentration of  $\text{SiO}_{2\text{exc}}$  can be detected.

At higher temperatures, the soluble amounts of  $\text{SiO}_{2\text{exc}}$  strongly increase, whereas the corresponding KOH concentration becomes lower. Figure 8 shows these results as an enhancement factor related to the values appearing at 20°C. Hence for temperatures above 40°C, the influence of temperature on the solubility is by far greater than that of the  $\text{OH}^-$  concentration. It is also remarkable that the aggregates react very differently, corresponding with the results of expansion measurements in concrete.

#### 4 DISCUSSION

The results depicted in Figures 1 and 2 confirm the general tendency that higher temperatures than 40°C considerably change the composition of the pore solution concerning the anion concentrations. It can be decided that up to 40°C only, the pore solution concentration corresponds to normal terms of use of concrete. Above this temperature, additional reactions like decomposition of calcium sulfoaluminate hydrates occur and disturb the evaluation of the aggregate and the impact of aluminate providing mineral admixtures. Cements, rich in alkali like TC (1.30), are especially liable to this effect because the stability of calcium sulfoaluminate hydrates is not only affected by temperature but also by the alkalinity of the pore solution [14].

At temperatures higher than 40°C, admixtures which provide aluminate into the pore solution preferred react with the sulphate ions in the pore solution, likely forming solid products. This part of bound aluminate is not available for binding dissolved  $\text{SiO}_2$  during AAR. The formation of an additional solid phase like ettringite can also cause an expansion of concrete, not directly connected with the tested AAR, but similar to delayed ettringite formation. The evidence of ettringite in such cement pastes with the mentioned admixtures will be a purpose of further investigations. Consequently, the increase of temperature above 40°C in concrete test methods regarding the hydration of the cement paste is not only an acceleration of the reactions, but a strong change in mechanism.

Based on these results, the release of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  from aggregates was investigated under  $\text{OH}^-$  conditions existing in the TC (1.30) pastes at different temperatures. Evaluating the contrary effects – lower  $\text{OH}^-$  concentration and higher temperature – it is shown that the effect of increased amounts of dissolved  $\text{SiO}_2$  is reached with temperatures  $\geq 60^\circ\text{C}$ , although the hydroxide concentration is lower. Because the dissolved  $\text{SiO}_{2\text{exc}}$  amounts are very different in dependence on the used aggregate, in future studies it seems to be possible to find out the optimal application range for every aggregate.

#### 5 CONCLUSIONS

Investigations of the pore solutions of hardened CEM I pastes with different alkali content show:

- The  $\text{OH}^-/\text{SO}_4^{2-}$  equilibria change to lower values with increasing temperature whereas the sum of cation concentrations remains nearly constant.
- These changes in anion concentrations are the stronger the higher the alkali content in the cement is.
- At 60°C, it was demonstrated that mineral admixtures which provide aluminate in to the alkaline solution react preferably with the sulphate ions in the pore solution. That is one reason for the difficulties in evaluating the effect of mineral admixtures. This reaction also should be taken into account when aggregates, providing aluminate in to the solution, have to be tested.
- Based on the fact that higher temperatures ( $\geq 60^\circ\text{C}$ ) more promote the solubility of the aggregate than the corresponding decreasing  $\text{OH}^-$  concentration inhibits this process, higher temperatures are useful for accelerated tests. But it is not sure which chemical reactions cause the expansion measured.

- Because the problem of the contrary effects - decrease of OH<sup>-</sup> concentration and increase of sulphate concentration - cannot be solved in cementitious systems, a separation of the test system seems to be successful. Further investigations in this direction are necessary.
- Expansion measurements are recommended to carry out at 40°C in order to ensure that only AAR causes the length changes of the concrete.
- At a second part, solubility measurements should be done in alkaline solutions without any sulphate content, whereas the OH<sup>-</sup> concentration conforms to that in the corresponding cement paste at the same temperature. This implicates the possibility of acceleration of the test duration without additional reactions.

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TABLE 1: Solubility of aggregates in KOH solutions corresponding to the conditions in cement pastes of TC (1.30) at different temperatures						
Aggregate	Solubility conditions		Concentration of dissolved species			Enhancement factor related to 20°C conditions
	KOH conc. mol/L	Temperature °C	SiO <sub>2</sub> mg/L	Al <sub>2</sub> O <sub>3</sub> mg/L	SiO <sub>2exc</sub> mg/L	
Gravel 8/16	0.92	20	74.6	12.8	57	1.0
	0.90	40	140	16.2	117	2.1
	0.50	60	5.098	33.4	5051	89.1
	0.41	80	11.099	5.5	11.091	195.6
Greywacke 8/16	0.92	20	38.9	3.2	34	1.0
	0.90	40	73.8	7.7	63	1.8
	0.50	60	243	16.7	220	6.4
	0.41	80	1.858	121.3	1.688	49.1

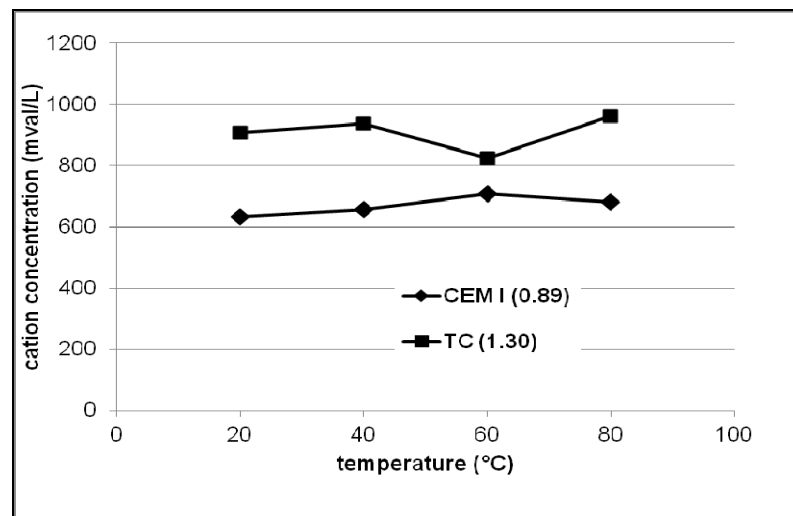


FIGURE 1: Cation concentrations in pore solutions of 90 days hardened Portland cement pastes in dependence on the temperature

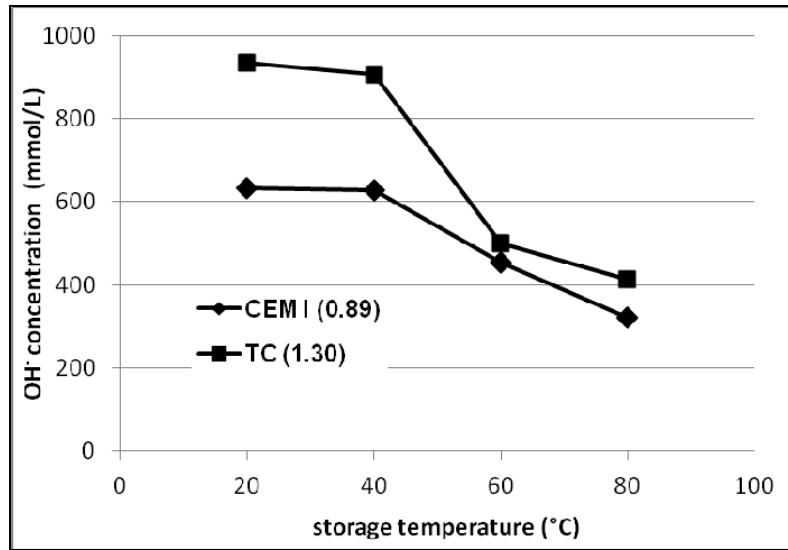


FIGURE 2: OH<sup>-</sup> concentration in the pore solution of 90 days hardened cement pastes in dependence on the temperature

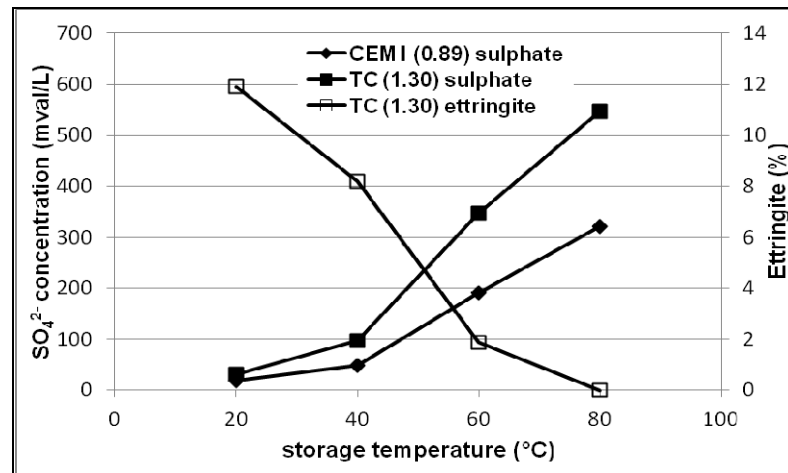


FIGURE 3: Sulphate concentration in the pore solutions and ettringite content of 90 days hardened cement pastes in dependence on the temperature.

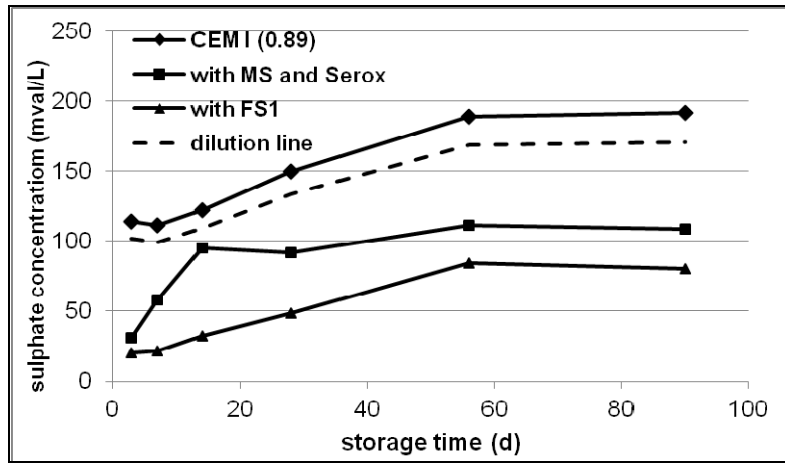


FIGURE 4: Sulphate concentration in the pore solution of plain CEM I (0.89) pastes and with 10.9 % mineral admixture at 60°C

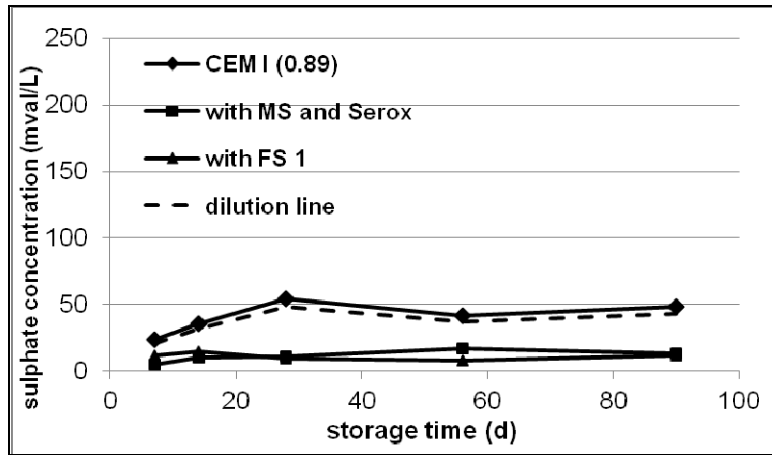


FIGURE 5: Sulphate concentration in the pore solution of plain CEM I (0.89) pastes and with 10.9 % mineral admixture at 40°C



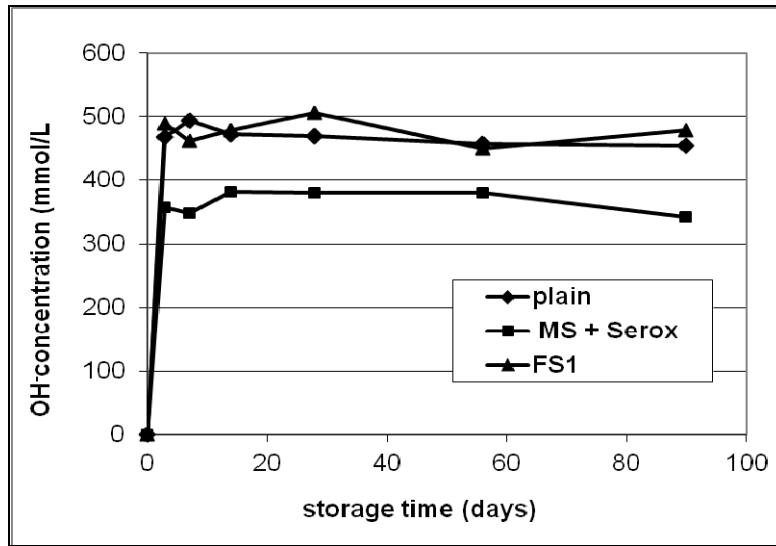


FIGURE 6: OH<sup>-</sup> concentration in the pore solution of hardened CEM I (0.89) pastes at 60°C

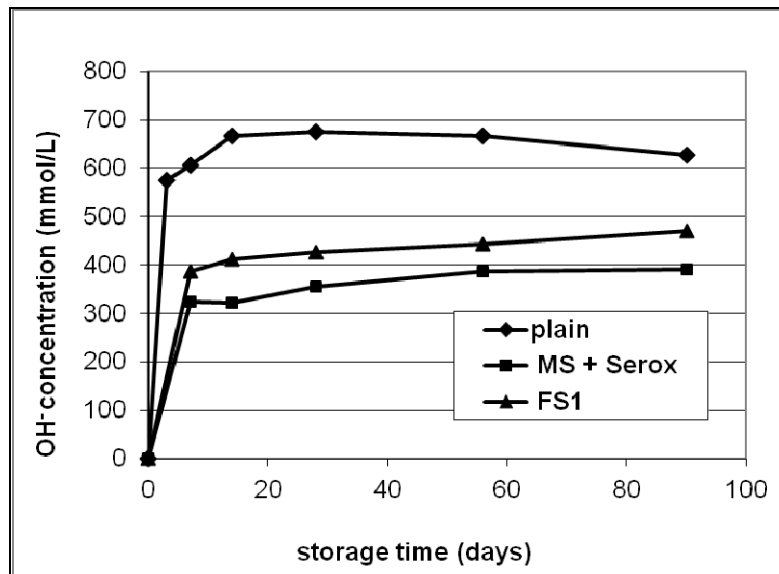


FIGURE 7: OH<sup>-</sup> concentration in the pore solution of hardened CEM I (0.89) pastes at 40°C

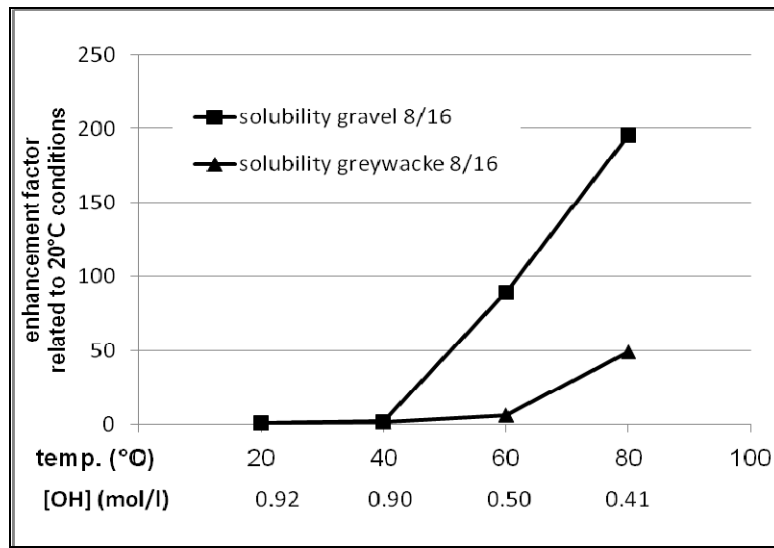


FIGURE 8: Combined influence of the KOH concentration **and** temperature on the dissolved amount of  $\text{SiO}_{2\text{exc}}$ , depicted as enhancement factor related to 20°C, 0.92 m KOH