INFLUENCE OF PHONOLITE ROCK POWDER ON THE MITIGATION AT AN ALKALI-SILICA REACTION

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Abstract

In Germany the use of phonolite rock powder as supplementary cementitious material is not yet considered to avoid a damaging alkali-silica reaction. One reason is that the alkali content of phonolite rock powder is greater than 8 % by mass. To use the ability of phonolite rock powder to prevent a harmful ASR, it is necessary to understand the reaction of phonolite rock powder in the concrete. The paper attempts to answer the question whether the used phonolite rock powder has significant alkali content, which does not promote ASR in the concrete. The question whether the use of phonolite rock powder has a positive effect on the avoidance of harmful ASR should be answered.

Keywords: alkali-silica reaction, mitigation, supplementary cementitious material (SCM), phonolite

1   INTRODUCTION

It is well known that supplementary cementitious materials (SCMs) help to suppress ASR in concrete [1, 2]. One mechanism is, that the partial replacement of Portland cement with SCMs decreases significantly the concentration of alkali ions (K^+ and Na^+) and hydroxyl ions (OH^-) [3]. The second mechanism of using SCM is, for example pozzolans, to already bind the alkalis during the early stage of hardening in the C-S-H phases low in Ca or in zeolite-like phases that might form [4]. The Ca^{2+} ions of pore solution are bound in part by pozzolans. This leads to a reduction of the C/S ratio and to a stable binding or adsorption of alkalis in or to the C-S-H phases or in compounds in which the alkalis are virtually insoluble. Results on synthetic C-S-H phases show [5] that the alkali binding increases with decreasing C/S ratio in which the absorption of alkalis increases with increasing alkali concentration in the solution. A further aspect is that the alkali-silica gel is capable to swell only in a certain range of CaO content [6]. Measurements have shown [7] that a gel without CaO does not exert a swelling pressure whereas the maximum swelling pressure occurs with a CaO content of 10 %. Investigations with fly ashes showed [8], that fly ashes with lower content of CaO are more effective than those with high CaO content. Therefore, all SCMs, which bind $Ca(OH)_2$ formed during the C_3S and C_2S hydration, help to avoid a deterioration of concrete by ASR. It should be investigated whether the findings can be transferred to phonolite as supplementary cementitious material to suppress ASR.

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2 MATERIALS AND METHODS

2.1 Materials

Phonolite

Phonolite is a Tertiary igneous rock of volcanic origin. Due to its SiO_2 undersaturation, only feldspars and sodalites are formed, but no quartz [9]. The phonolite from Bötzingen on the Kaiserstuhl (a small group of mountains in the Upper Rhine Valley in SW Germany, NW of Freiburg) contains the minerals potash feldspar 32 % (orthoclase, sanidin), sodalite/hauyn as well as zeolite 45 %, pyroxenes 9 %, wollastonite 9 %, calcite 1 % and miscellaneous 3%.

The listing of the minerals showed, that the potash feldspar (orthoclase and sanidine ($K[AlSi_3O_8]$)), sodalite ($Na_8[Cl_2|(AlSiO_4)_6]$) and zeolite (e.g. natrolite ($Na_2[Al_2Si_3O_{10}] \cdot 2H_2O$)) dominate. Apart from these, pyroxenes, wollastonite and a very small quantity of calcite are also present. The chemical composition of phonolite is listed in Table 1.

Phonolite is mined at the quarry, crushed and pulverized to a Blaine fineness of 530 ± 50 m²/kg. 80 % of the particles are smaller than 40 μm. The fineness of the rock powder is thus similar to the fineness of cement. The density is approximately 2.60 g/cm³. Phonolite rock powder, as a naturally tempered pozzolan (Q), is used as a principal constituent of Portland pozzolan cement (CEM II/A-Q, CEM II/B-Q) in accordance with EN 197-1 [10]. Furthermore, it has been approved as an addition to concrete tempered phonolite rock powder "Hydrolith F200" [11].

Aggregate

One German reactive aggregate was used as the coarse aggregate in the mortar mixtures and the concrete mixtures. The alkali-reactive aggregate was quartz porphyry (QP) from a quarry in the middle of Germany. The composition of the aggregate has been described elsewhere [12]. A non-reactive natural sand was used as fine aggregate (0-2 mm) in the concrete mixtures.

Cement

Portland cement CEM I 42.5 R [10] with 0.48 % by mass Na_2O-equivalent ($C1_0$) and a Portland cement CEM I 32.5 R with 1.24 % by mass Na_2O-equivalent ($C3_0$) were used. The CEM II/B-Q cements ($C1_{30}$ and $C3_{30}$) have been prepared in the laboratory by mixing 30 % by mass of phonolite (Q) and 70 % by mass of the Portland cements. The designation and composition of the binders, Blaine fineness and density of the binders are listed in Table 1. The binders CEM II/B-Q are designated with (V) because they are not the commercial CEM II/B-Q.

2.2 Methods

General

The influence of phonolite as supplementary cementitious material should be investigated with the accelerated mortar bar test. Originally accelerated mortar bar test is a test method for aggregates that makes it possible to characterize the reactivity of an aggregate due to ASR. Therefore the test has to be adapted for the own investigations and the analysis of pore solutions and soluble elements of minerals of aggregates should confirm the results from accelerated mortar bar test. By means of the accelerated mortar bar test two different binders should be chosen for the concrete tests. Thus the efficiency of phonolite as supplementary cementitious material to mitigate ASR could be assessed.

Pore solution analysis

Cement pastes of water/cement ratio 0.45 were prepared from each binder ($C1_0$, $C1_{30}$, $C3_0$ and $C3_{30}$). These were cast into closable 250 ml PE cups and stored under sealed conditions at 20 °C for periods of 4 and 28 days. After the storage one cup of each mixture was cut open and the cylindrical cement stone specimens were mounted into a press. Under a pressure of up to 510 MPa the pore solution was extracted with a 0.45 µm filter and captured in PP tubes. To avoid carbonation the tubes were flushed with argon and immediately tightly closed. The OH^--concentration of the pore solutions was determined by titration with 0.1 n hydrochloric acid in the presence of phenolphthalein. The Ca^{2+}-, K^+- and Na^+-concentrations were determined by ICP-OES according to [13].

Accelerated mortar bar test

The accelerated mortar bar test according to [14] which is derived from [15] and [16] is used for the investigations. The quartz porphyry (8-16 mm) is crushed to 0.125 mm to 4 mm and used to produce mortar (three 40 mm x 40 mm x 160 mm mortar prisms) with each binder ($C1_0$, $C1_{30}$, $C3_0$ and $C3_{30}$). Prism expansions are measured after 1, 4, 8 and 13 days storage in 1 molar NaOH solution at 80 °C. The length of the prisms is measured at 80 °C.

Accelerated solubility and mobilization test

The quartz porphyry (8-16 mm) is crushed to a grain size of 0.25 to 0.5 mm, 1 to 2 mm and 4 to 8 mm according to [17]. These test fractions were put into synthetic potassium hydroxide solution to simulate the condition of a grain in mortar and concrete in respect of the concentrations of OH^-. According to [17] a 100 mmol/l synthetic hydroxide solution (KOH) was used. Additionally a 370 mmol/l and 1000 mmol/l KOH-solutions were used. The KOH-solutions correspond to pH-values of 13.0, 13.57 and 14.0. From the linear relationship according to [18] can be deducted that the pH-value of 370 mmol/l KOH solution is approximately the pH-value of pore solution of concrete (w/c = 0.45) after 365 days of hydration, which was produced by cement with total alkali content of 0.55 by mass Na_2O-equivalent. The KOH-solution of 1000 mmol/l is the highest possible concentration concerning OH^- of pore solution of concrete [6] which was produced by cement with high-alkali content. The temperature of the solutions was kept at 80 °C. This is the temperature level of accelerated mortar bar test. After 14 days storage in the alkaline solutions, concentrations of silicium (Si), aluminium (Al) , magnesium (Mg), iron (Fe), calcium (Ca) and sodium (Na) were measured.

Concrete test

The 40° C fog chamber test is similar to the internationally usual concrete prism test (RILEM AAR-3). For the experimental series two concrete mixtures with two different binders ($C3_0$ and $C3_{30}$) and quartz porphyry were produced with a water-cement ratio of 0.45 and a cement content of 400 kg/m³. An AB 16 grading curve [19] was chosen for the aggregate. 30 % by vol. of the aggregates consist of non-reactive sand up to 2 mm grain size while 40 % with grain size 2/8 mm and 30 % of grain size 8/16 come from the reactive quartz porphyry.

Beams with the dimensions of 100 mm x 100 mm x 500 mm are used for the expansion measurement. Cubes of 300 mm edge length are cast for the visual inspection of crack formation. Cylinders with 300 mm height and 150 mm diameter are tested in compression for the modulus of elasticity.

After mixing of each concrete mix, the specimens were stored in a steel mould at 20 °C and 95 % RH. After 24 h storage, the concrete prisms were demoulded and placed in a fog chamber at (40 ± 2.0) °C for 560 days. Measurements of the expansion are taken continuously. In addition, the specimens were visually inspected. Static modulus of elasticity was determined at 35, 70, 140, 280 and 560 days.

3   RESULTS

3.1   Pore analysis

The OH- and alkali concentrations as well as concentrations of calcium in pore solutions of pastes with $C1_0$, $C1_{30}$, $C3_0$ and $C3_{30}$ as binder are shown as function of hydration of 4 and 28 days in Figures 1 - 4. The results in Figure 1 and 3 show that the addition of phonolite to Portland cement reduces the concentration of potassium in the pore solutions after 28 days of hydration. In contrast to that, the addition of phonolite to Portland cement increases the concentration of sodium in the pore solution after 28 days of hydration. Figure 1 and 3 also show, that the addition of phonolite to Portland cement $C1_0$ increases the concentration of OH- while the addition of phonolite to Portland cement $C3_0$ reduces the concentration of OH- after 28 days of hydration. Figure 2 and 4 shows that the addition of phonolite to the Portland cements $C1_0$ and $C3_0$ reduces the concentration of calcium after 28 days of hydration.

3.2   Expansion in the accelerated mortar bar test

The mean expansions are plotted in the Figures 5 and 6 as function of time. Figure 5 shows the measurements of the mortar bar prisms with quartz porphyry and $C1_0$ and $C1_{30}$ as binders while Figure 6 shows the mortar bar prisms with quartz porphyry and $C3_0$ and $C3_{30}$ as binders. In both figures, the full dots belong to the mortars with $C1_0$ and $C3_0$ while the open dots belong to the mortar with $C1_{30}$ and $C3_{30}$. The criterion for alkali sensitive aggregates according to [20] is 1.0 mm/m after 13 days.

Figure 5 shows that at any time of measurement, the expansion of the mortar $C1_0$ is higher than that of the mortar $C1_{30}$. After 13 days storage the mortar $C1_0$ reached an expansion of 1.05 mm/m while mortar $C1_{30}$ reached an expansion of 0.44 mm/m.

Figure 6 shows that after 4 days storage, the expansion of mortar $C3_{30}$ is higher (0.57 mm/m) than that of mortar $C3_0$ (0.26 mm/m). In the course of time, the expansion of the mortar with $C3_0$ increases faster than that of the mortar $C3_{30}$. The mortar $C3_0$ reached an expansion of 1.65 mm/m while mortar $C3_{30}$ reached an expansion of 1.28 mm/m after 13 days.

3.3   Contribution by aggregate (soluble elements of rock-minerals) in KOH-solution

The contribution by aggregate (Si, Na, Al, Fe) is shown as function of concentration of 80 °C KOH-solution in Figures 7 and 8. The figures show that different concentrations of used KOH-solutions lead to less or more dissolution of different rock-minerals. Magnesium (Mg) and calcium (Ca) are not listed in the figures. The concentrations of Mg and Ca were always less than 0.1 mg/l.

3.4   Expansion and static modulus of elasticity in the concrete test

For the concrete tests the two binders $C3_0$ and $C3_{30}$, which showed the highest expansion in the accelerated mortar bar test, were selected.

The mean expansions are plotted in Figure 9 as function of exposition time. Figure 9 shows the measurements on the concretes with quartz porphyry and $C3_0$ and $C3_{30}$ as binders. The full dots belong to the concrete with $C3_0$ as binder while the open dots belong to the concrete with $C3_{30}$. The arrow marks the time when cracks with $\geq$ 0.2 mm width appeared at the edge of the 300 mm cube. The criterion for alkali sensitive aggregates according to [20] is 0.6 mm/m. The expansion of the concrete with $C3_0$ as binder reaches the critical mark of 0.6 mm/m after 280 days and increases up to 0.75 mm/m after 560 days. In addition, brown discoloration has been observed on the surface of the beams. The concrete cube shows also a crack $\geq$ 0.2 mm after 224 days. The concrete with $C3_{30}$ as binder always stays below the critical value of 0.6 mm/m. Brown discoloration has not been observed on the surface of the concrete beams and the concrete cube showed no cracks.

The static modulus of elasticity is measured by compression of cylinders. All values are the mean of three specimens. Figure 10 shows the results of the concretes with quartz porphyry as aggregate and $C3_0$ and $C3_{30}$ as binders respectively. The values of the static modulus of elasticity are normalized with respect to the reference value after 35 days of fog chamber storage at 40°C. It can be seen that the static modulus of elasticity of the concrete with $C3_0$ as binder decreases by 54 % after 560 days. Measurements on the concrete with $C3_{30}$ as binder have only been taken at the beginning of 35 days and at the end of 560 days. The two measuring points are connected with a straight line. The static modulus of elasticity of the concrete with $C3_{30}$ as binder shows only a decrease of 18 % after 560 days storage at 40 °C.

4   DISCUSSION

The investigated supplementary cementitious material (SCM) is phonolite with a CaO content of 9 %. When mixed with Portland cement CEM I ($C1_0$) which has a CaO content of 67 % the total CaO content of the binder amounts to 51%. If mixed with the Portland cement CEM I ($C3_0$) which has a CaO content of 64 % the total CaO content of the binder amounts to 49 %. When hydration takes place the SiO_2 combines with calcium oxide to form calcium-silicate hydrate (C-S-H). The SiO_2 content of the binder $C1_{30}$ and $C3_{30}$ comes to 31 % and 30 % respectively whereas the SiO_2 content of the Portland cements $C1_0$ and $C3_0$ is 23 % and 21 % respectively. The results showed that after 28 days of hydration less Ca^{2+} in pore solutions of pastes with $C1_{30}$ and $C3_{30}$ as binder are present than in the pastes with $C1_0$ and $C3_0$ as binder. Moreover the consumption of Ca^{2+} (ΔCa^{2+} = difference in mmol/l between 28 and 4 days of hydration) of the pastes with $C1_{30}$ and $C3_{30}$ as binder is significantly higher than with $C1_0$ and $C3_0$ as binder. This means on the one hand that in the binders $C1_{30}$ and $C3_{30}$ more calcium is needed to form C-S-H and less calcium can be bound in the alkali silica gel. Therefore the capability of swelling of gels is reduced and the resulted swelling pressure is lower. On the other hand, low calcium concentrations in pore solutions lead to lower expansions in the accelerated mortar bar test of mortars with $C1_{30}$ and $C3_{30}$ as binder than of mortars with $C1_0$ and $C3_0$ as binder. These calculations show that phonolite can help to reduce or even suppress the detrimental action of ASR.

Table 1 showed that the potassium content is higher than the sodium content of Portland cements. This is due to the constellation of deposits in Central Europe which is characterized by higher potassium contents as opposed to sodium contents [6]. The ratio of potassium to sodium of Portland cements with a high Na_2O-equivalent is therefore higher than with low Na_2O-equivalent. The addition of phonolite to Portland cement with high Na_2O-equivalent (with $K_2O >> Na_2O$) reduces the concentration of OH^- in the pore solution after 28 days of hydration. On the other hand the addition of phonolite to Portland cement with low Na_2O-equivalent (with $K_2O > Na_2O$) increases the concentration of OH^- after 28 days of hydration. Recently, experimental results obtained with phonolite have given indications that potassium (K^+) is firmly bound in the potash feldspar while sodium (Na^+) is partially bound in the zeolite. These experimental results have also shown that the fineness of phonolite has a big influence on the solubility of sodium (unpublished data).

In the accelerated solubility and mobilization test the well known influence of Na and thus of K/Na ratios in the pore solutions of mortar and concrete on the expansion behaviour of mortar and concrete with alkali-sensitive aggregates in laboratory studies [21] was not taken into account because only the alkali concentration and temperature of pore solution is important for the solubility of reactive SiO_2 and other rock-minerals [6]. Also calcium was not considered in the synthetic pore solution because calcium in the pore solution of mortar and concrete has only an effect on the capability of swelling of gels [6, 7] and not on the solubility of reactive SiO_2 and other rock-minerals. Generally it can be deducted from the accelerated soluble test that the concentration of OH^- and pH value respectively is the decisive factor for the solubility and mobilization of rock-minerals. The solubility and mobilization of rock-minerals leads to softening of

aggregates [12, 22]. This could indicate that softening could decrease or stop, if the alkalinity of the pore solutions dropped below a critical level.

The brown discolouring on the surface of the concrete specimens with $C3_0$ as binder stems from on the dissolved Fe ions from chlorite and hematite filled veins of quartz porphyry. This means that the concentration of OH^- of the pore solution of concrete with $C3_0$ as binder is higher than the concentration of OH^- of concrete with $C3_{30}$ as binder because no discolouring could be observed on concrete specimens with $C3_{30}$ as binder. These observations are consistent with the results according to [23]. A look to figure 9.2 in [22] shows that the solubility of hematite depends on concentration of pH and OH^- respectively.

Why cracking has occurred in concrete with $C3_0$ as binder and quartz porphyry and no cracking has been observed in concrete with $C3_{30}$ as binder can be explained with a two step process. The first step concerns the dissolution of the hematite and chlorite filled veins in the quartz porphyry for which a high alkalinity in form of high concentrations of OH^- is necessary (OH^- of $C3_0$ > OH^- of $C3_{30}$). The dissolution creates open cracks in the quartz porphyry. The second step concerns the formation of an alkali-silica gel which precipitates in the cracks. The gel depends on the availability of soluble silica of quartz porphyry and calcium in the pore solution (available Ca^{2+} of pore solution of $C3_0$ > available Ca^{2+} of pore solution of $C3_{30}$) because these two components are necessary for the formation of silica gel. When the gel forms and precipitates in the cracks the gel expands due to absorption of water and forces the crack to open as soon as the pressure is high enough and the critical stress intensity factor is reached [12]. In this context the stress intensity factor of aggregates depends on solubility and mobilization of rock-minerals which depends strongly on a high concentration of OH^- and pH value respectively as well as temperature. Only when all prerequisites are met cracking of the quartz porphyry will occur.

The modulus of elasticity has been determined from the stress-strain diagram between 5 and 30 % of the compressive strength. The results show that the static modulus of elasticity is very sensitive to the alkali reaction and is therefore a good indicator for ASR [18]. Cracks in the aggregate grains are compressed and therefore the static modulus of elasticity must decrease with the exposure time since the dissolution process is progressing. The static modulus of elasticity decreases with addition of phonolite to Portland cement. This could indicate that the alkalinity of the pore solutions of concrete with $C3_{30}$ as binder is lower than the alkalinity of the pore solutions of concrete with $C3_0$ as binder.

5   CONCLUSIONS

The investigations with one type of slow/late aggregate and 4 types of binder have brought up some new facts about alkali-silica reaction which have been found in accelerated mortar bar test, analysis of pore solution, accelerated solubility test and concrete prisms test during 560 days of exposure in the fog room:

i)   although the total alkali content of phonolite in the minerals is high, potassium is firmly bound in the potash feldspar and does not contribute to ASR

ii)   sodium is only partially bound in the zeolith and affects the concentration of OH^- of pore solution as a function of the used Na_2O-equivalent of Portland cement

iii)   the solubility of sodium of phonolite depends on the fineness of phonolite

iv)   it is possible by using phonolite as SCM to control expansion of mortar containing highly reactive aggregate in the accelerated test

v)   the SCM phonolite has beneficial effects with respect to expansion concrete prism and crack formation through the reduction of calcium concentration in pore solutions

vi)   replacement of Portland Cement with high alkali content by 30 % by mass phonolite can improve the mechanical properties (e.g. static modulus of elasticity) of concrete composites

vii)   the influence of higher Blaine fineness of phonolite (> 524 m²/kg) has not been investigated and needs further investigations

viii)   further investigations with the accelerated mortar bar test are necessary to pre-select binder and slow/late aggregate combinations, so that concrete performance tests have to be made only with suitable concrete combinations.

6   ACKNOWLEDGMENT

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TABLE 1: Chemical composition and $Na_2O_{equ.}$ of the binders in mass %, ratio CaO/SiO_2, Blaine fineness in m^2/kg and density in g/cm^3 of the binders as well as phonolite

Type	CEM I 42.5 R	CEM II/B-Q (V)	CEM I 32.5 R	CEM II/B-Q (V)	Phonolite
Designation	$C1_0$	$C1_{30}$	$C3_0$	$C3_{30}$	Q
LOI	2.31	3.17	2.91	3.59	5.26
SiO_2	22.82	31.42	20.54	29.88	52.45
TiO_2	0.20	0.26	0.24	0.29	0.38
Al_2O_3	3.77	8.66	5.46	9.85	19.66
Fe_2O_3	1.58	2.59	3.72	4.11	4.72
MnO	0.05	0.14	0.10	0.18	0.33
CaO	67.39	51.32	64.00	48.80	8.75
MgO	1.03	0.96	2.04	1.67	0.66
SO_3	3.34	1.83	3.10	2.12	0.12
P_2O_5	0.22	< 0.01	0.24	0.01	0.17
SrO	0.17	0.23	0.05	0.15	0.39
Na_2O	0.17 [1]	1.93 [2]	0.25 [1]	2.65 [2]	4.82 [2]
K_2O	0.47 [1]	1.28 [2]	1.51 [1]	1.27 [2]	4.59 [2]
$Na_2O_{equ.}$	0.48	2.77	1.24	3.49	7.84
CaO/SiO_2	2.95	1.63	3.12	1.63	–
Density	3.11	2.95	3.14	2.96	2.62
Blaine	376	384	338	404	524

[1] Determination of amount of alkali according to [24], clause 18, breaking down with hydrochloric acid (HCl) based on the insoluble residue < 3 %

[2] Determination of amount of alkali according to [24], clause 18, breaking down with hydrofluoric acid (HF) based on the insoluble residue > 3 %
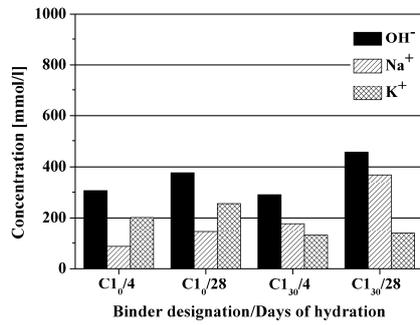
FIGURE 1: OH⁻ and alkali concentrations in pore solutions of pastes with $C1_0$ and $C1_{30}$ as binder after hydration of 4 and 28 days
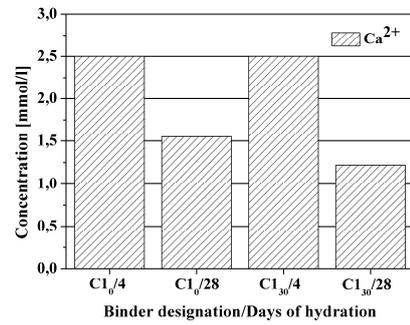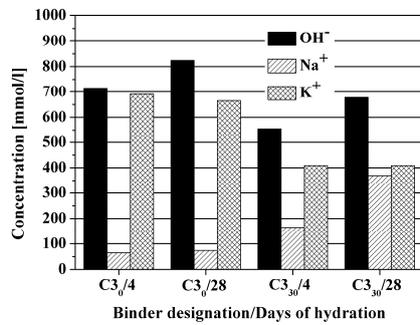

FIGURE 2: Calcium concentrations (Ca^{2+}) in pore solution of pastes with $C1_0$ and $C1_{30}$ as binder after hydration of 4 and 28 days

FIGURE 3: OH⁻ and alkali concentrations in pore solution of pastes with $C3_0$ and $C3_{30}$ as binder after hydration of 4 and 28 days
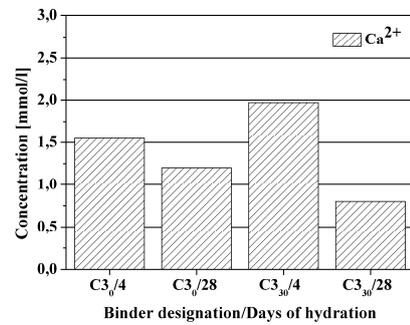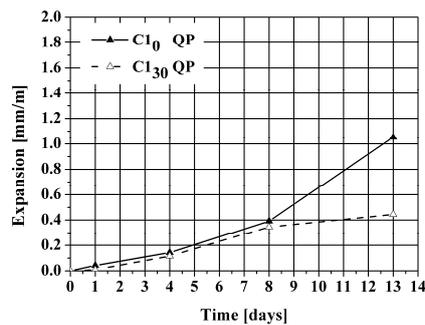

FIGURE 4: Calcium concentrations (Ca^{2+}) in pore solution of pastes with $C3_0$ and $C3_{30}$ as binder after hydration of 4 and 28 days

FIGURE 5: Expansion of quartz porphyry mortar with $C1_0$ and $C1_{30}$ as binder
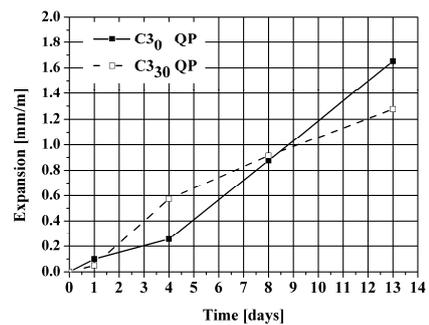
FIGURE 6: Expansion of quartz porphyry mortar with $C3_0$ and $C3_{30}$ as binder
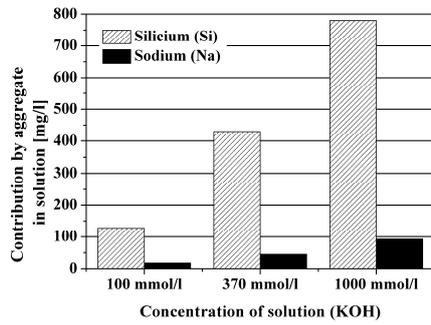
FIGURE 7: Contribution by aggregate (Si, Na)
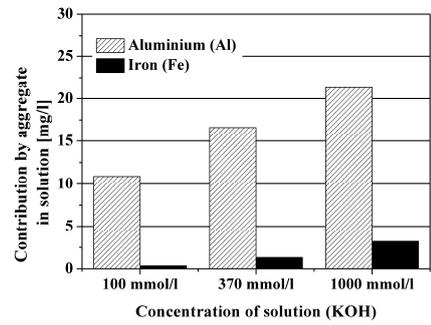in 80°C KOH-solution

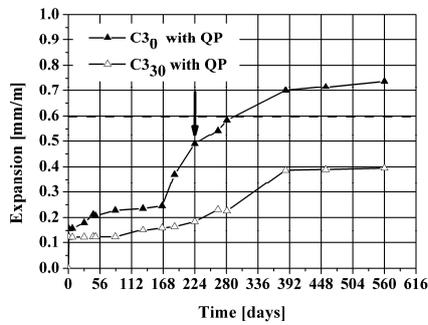FIGURE 8: Contribution by aggregate (Al, Fe)
in 80°C KOH-solution

FIGURE 9: Expansion of quartz porphyry concrete
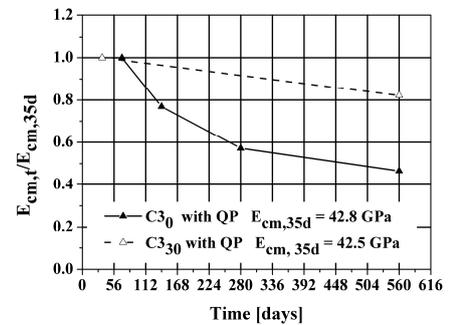with $C3_0$ and $C3_{30}$ as binder

FIGURE 10: Normalized static modulus of
elasticity of quartz porphyry concrete
with $C3_0$ and $C3_{30}$ as binder