ON THE INTERACTIONS OF AGGREGATES WITH SUPPLEMENTARY CEMENTING MATERIALS FOR DURABLE CONCRETE STRUCTURES



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Abstract

Supplementary cementing materials (SCMs) are an important part of modern concrete structures. Their use has many advantages (reduction of the cement amount, improvement of the durability and therefore CO_2 reduction). For example certain SCMs added to concrete mixtures can avoid the alkali-silica reaction (ASR). But such materials have a wide range of composition and therefore the mechanisms can be very differently. The knowledge of dissolution processes of aggregates and SCMs separate and together in alkaline solutions can help to understand the damage of concretes caused by ASR and the effects to avoid ASR in more details. Many dissolution experiments were performed in highly alkaline solutions (KOH) under CPT conditions (pH 14, 40°C) using aggregates in original grain sizes and Si and Al containing SCMs in different ratios. Also Calcium hydroxide was added to investigate the influence of calcium ions as a main part of the pore solution. The concentrations of soluble silica and alumina were determined by ICP-OES. Such dissolution experiments, with which an interaction was settled between the aggregate and the SCM via the alkaline solution, arose that under specific conditions the dissolution of aggregates was strongly influenced. Obviously both main constituents of concretes interact with each other. Additionally effects of the dissolved calcium ions must be considered. It was found that the efficiency depends on the amount and chemical composition of the SCMs used and on the reactivity of aggregates.

Keywords: SCMs, Aggregates, ASR inhibition, Dissolution behavior, Alkaline solution

1 Introduction

The addition of supplementary cementing materials (SCMs) in concrete has well known since many years and is accepted worldwide. The advantages can be clearly described:

a strong reduction of the cement amount, an improvement of the rheological properties, a formation of a more compact hardened cement stone structure and an increase of the durability of concretes in generally. Of course certain SCMs which are used in concretes can also avoid the alkali silica reaction. Microsilica is such a common material, which is used for ASR reduction. Fly ashes are also used but in this case the amount which is necessary to add is very high.

The past few years special alumina containing materials like metakaolin or others have become the focus. Also in this case effects like reduction of the pH value of the pore solution and alkali fixation in newly formed C-S-A-H-phases are discussed. But it seems that the effect and inhibition mechanism of ASR, especially with aluminum containing SCMs, is still not wholly understood and therefore current subject of international investigations [1]-**Chyba! Nenalezen zdroj odkazů.**7]. It seems that the effectiveness of SCMs in the cement stone matrix depends essentially also on the aggregate type. Obviously interactions between SCMs and aggregate take place which are determine the dosage of the required additive amount for safe prevention of ASR. These interactions between aluminium-containing additives and reactive aggregate should be investigated by means of dissolution experiments.

2 Materials and Methods

2.1 Aggregate and SCMs

Two aggregates with a different reactivity, a greywacke G9 and a rhyolite R2, were selected. The classification as reactive aggregates can be confirmed by the results of the concrete prism test (CPT).

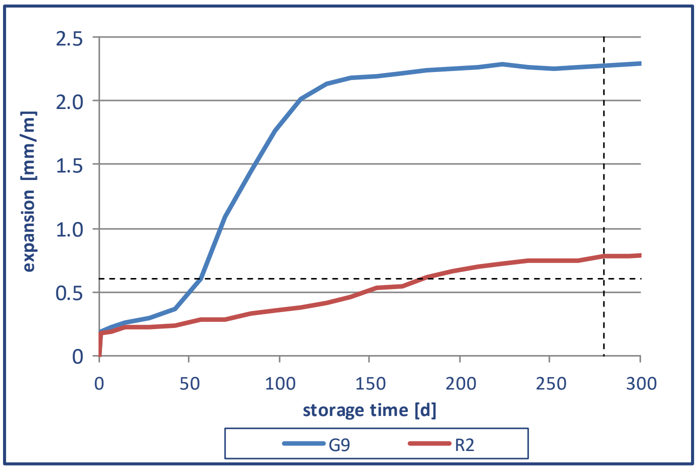


Fig. 1 Results of the CPT of aggregates G9 and R2

The limit is 0.6 mm/m after 9 months (dotted lines) stored in a fog chamber. As it can be seen in Fig. 1 both aggregates overstep the limit more or less. G9 is highly reactive, R2 is low reactive. Additional two alumi-num containing commercially available mineral admixtures were used, metakaolin (MK), called Powerpozz and a fly ash (FA). The chemical compositions are summarized in the following Tab. 1.

Tab. 1 Chemical composition of SCMs used

SCM	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O
FA	55.0	24.3	7.4	4.1	0.9	1.8
MK	55.0	41.0	< 1.4	< 0.1	< 0.05	< 0.4

The important difference is the alumina content, MK has approx. twice more than FA.

2.2 Methods for assessment and analysis

For the solubility investigations of the aggregates G9 and R2, the fraction 2/8 mm was used. 90 g of the aggregate were put into 900 g alkaline solution with a concentration of 1 Mol/L potassium hydroxide. The mixtures of grains and 1M KOH solution were stored in tightly sealed PE-bottles at 40°C till 300 days [8]-[9].

Corresponding to the CPT with 4 wt.% SCM related to the coarse aggregate content, 3.6 g MK and FA, respectively, were also stored in 1M KOH to determine their dissolution behaviour. Afterwards, the aggregates and SCMs were tested together in the same procedure, e.g. 90 g aggregate and 3.6 g SCM in 900 g KOH. And additionally an oversaturated $Ca(OH)_2$ solution was used to copy the pore solution composition. After 4, 14, 28, 56, 90 till 300 days, respectively, approximately 3 ml of solution were taken from the liquid phase, filtered through a 0.2 μm membrane filter and the SiO_2 and Al_2O_3 concentrations were determined by an ICP-OES spectrometer.

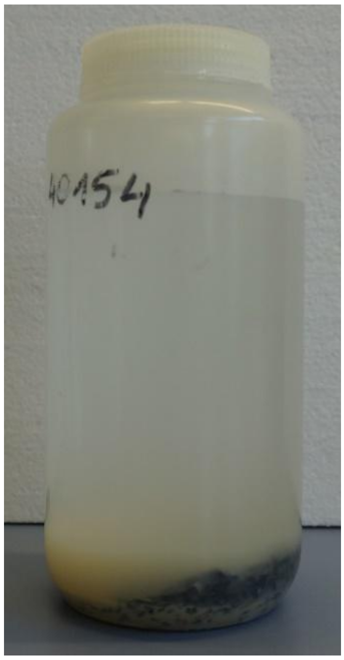


Fig. 2 Dissolution procedure

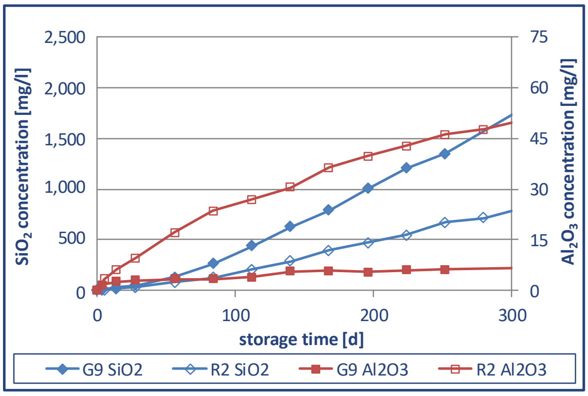
3 Results

3.1 Dissolution experiments

The following Figures present results of the dissolution experiments for both aggregates G9 and R2 and for the additives MK and FA separately and in mixtures. Such values are the basis for the discussion because the dissolved silica and alumina only can influence the structure formation process of the cement stone in presence of aggregates and SCMs.

As it can be seen in Fig. 3 G9 provides mainly SiO_2 into the alkaline solution under chosen conditions, the Al_2O_3 concentration reaches values of maximum 6 mg/L after 300 days only. In contrast R2 provides essential more Al_2O_3 and less SiO_2 than G9 in KOH solution.

MK provides a little bit more Al_2O_3 than SiO_2 but FA dissolves more SiO_2 and only less than the half Al_2O_3. The Si/Al ratio is marked in the figures and demonstrate the differences between both additives (for MK = 0.8, for FA = 2.4).



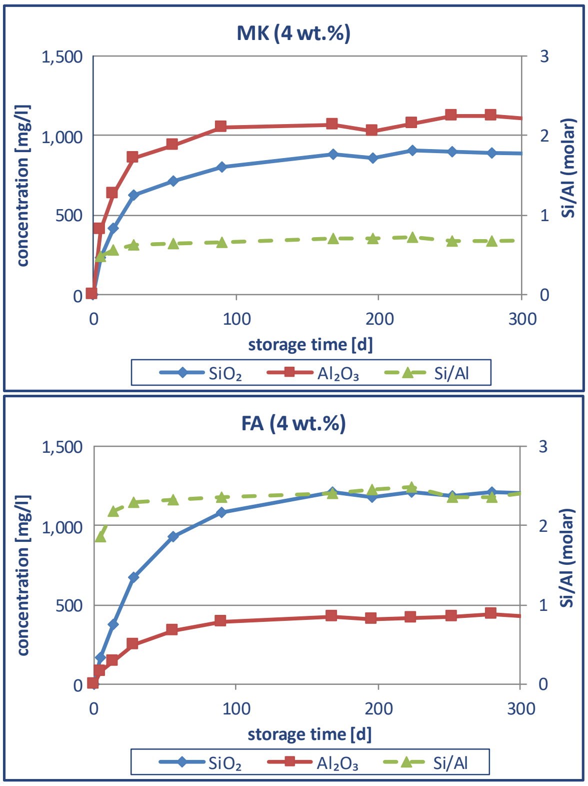


Fig. 3 Results of dissolution experiments of pure aggregates and SCMs

What happens if aggregates and SCMs are stored together in the alkaline solution. The results are demonstrated in Fig. 4.

Normally it can be expected that the measured concentrations are the sum of both curves for each combination but it is not so. The SiO_2 concentration for G9 in combination with MK is identical with the calculated sum till 100 days then there is a gap. Over the whole period of time the Al_2O_3 concentration is reduced and the reduction increases at later times. The same tendency can be measured for the combination G9 with FA, but the gap here is smaller. It can be assumed that the measured SiO_2 reduction indicates the formation of alumino silicates, because the Al_2O_3 concentrations also decrease. And it can be conclused already at this time that probably the effectiveness of MK should be higher than FA.

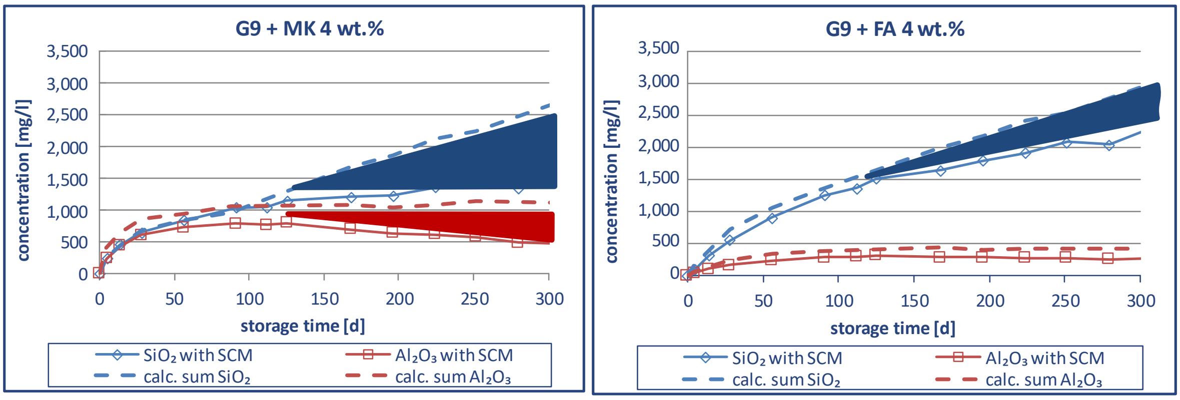


Fig. 4 Results of dissolution experiments of aggregates and SCMs together

But the crucial question is, how altered calcium the solubility behaviour of this complicated system? That`s why dissolution experiments of SCMs in a KOH solution with presence of $Ca(OH)_2$ were performed. Calcium ions change the concentrations dramatically (see Fig. 5).

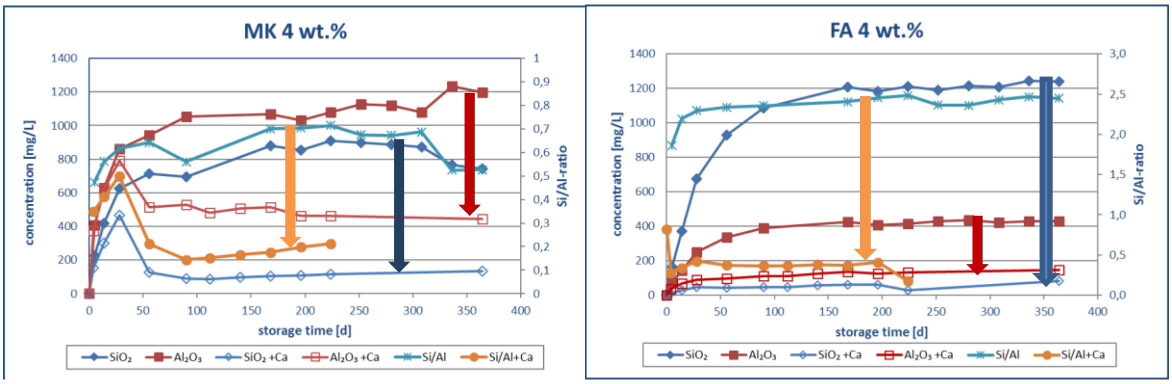


Fig. 5 Influence of $Ca(OH)_2$ on the dissolution of SCMs in KOH solution

For the system MK/KOH/$Ca(OH)_2$ applies: The maximum of dissolved SiO_2 and Al_2O_3 is at 28 d, then a reduction occurs in such a way that the SiO_2 conc. is reduced to a tenth and the Al_2O_3 conc. is halved compared with the Ca free system.

For the system FA/KOH/$Ca(OH)_2$ applies: The effects here are still stronger, the SiO_2 conc. is reduced to 1/20, the Al_2O_3 conc. is a quarter compared with the Ca free system.

It must be concluded that under Ca ion influence MK provides even more aluminum into the alkaline solution than FA, the Si/Al-ratio reduces from 0.7 to 0.25 for MK and from 2.5 to 0.5 for FA, an important fact for understanding the efficiency of MK in opposite to FA.

3.2 Transformation to the concrete mixture

The chosen dissolution conditions have a direct relation to the concrete mixtures. The value 4 wt.% in the solubility investigations mentioned above must be seen in relation to the coarse aggregate content. Converted to the binder and to the concrete mixtures the following data are valid (see Tab. 2).

Tab. 2 SCM content in relation to

coarse aggregate [wt.%]	cement content [wt.%]	concrete mixture [kg/m^3]
1	3.21	12.8
4	12.84	51.4
7	22.47	89.9
10	32.10	128.4

Based on these mixtures concrete prism tests (CPT) were performed. Also here only the results using 4 wt.% are shown. A strong reduction of the expansion with MK can be measured: from 2.30 mm/m to 0.20 mm/m for G9 and from 0.8 mm/m to 0.21 mm/m for R2 (Fig. 6). The absolute reduction values are smaller by using FA: from 2.30 mm/m to 0.65 mm/m for G9 and from 0.8 mm/m to 0.32 mm/m for R2.

Summarized it must be noted, in conversion to the concrete mixtures, that:

- for G9: 50 kg/m^3 FA are not enough, but 50 kg MK already!
- for R2: 50 kg/m^3 FA or 50 kg MK are enough, maybe the last one too much!

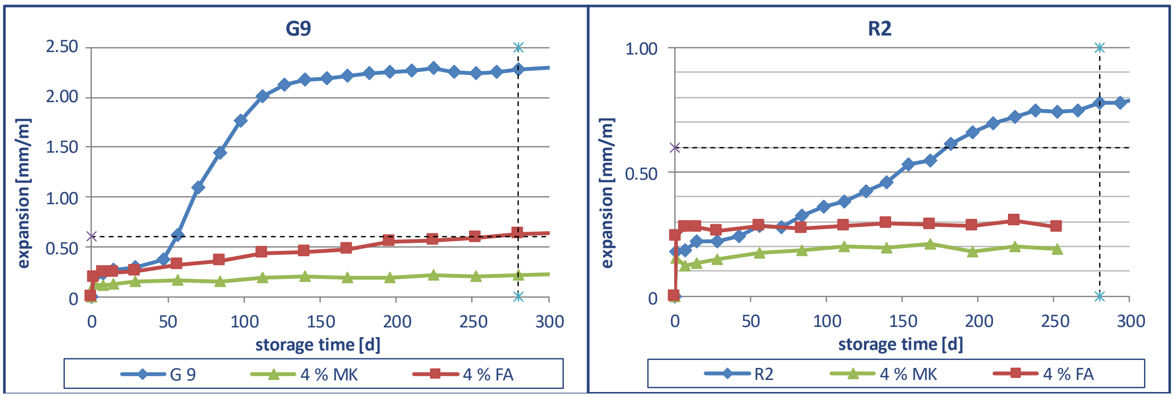


Fig. 6 Results of the CPT using MK and FA for both aggregates

4 Conclusions

Aggregates which provide aluminum and silica together in high concentrations into alkaline solutions are less expansive in concrete prism test than Al poor aggregates (self inhibition process). The molar Si/Al ratio based on dissolution experiments is a useful tool of SCMs, because it characterizes the formation of alumino silicate structures in the solution. MK with a ratio Si/Al < 1 has an aluminum excess and consequently a higher potential for preventing ASR than FA. But at this time of investigations a direct correlation between Si/Al-ratio and the expansion does not exist. Calcium ions in pore solutions lower the capacity of the SCMs because of competitive reactions, which also consuming dissolved aluminum. Obviously by using alumino silicate containing SCMs (e.g. MK) enough „free“ Al left for reducing ASR potential. But the optimal combination of aggregate and SCM depends on the dissolution behaviour of both the SCM and the aggregate.

Acknowledgement

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