

Fundamental study on ASR kinetics – effect of temperature on aggregate reactivity and pore water composition

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Abstract

As part of the Norwegian R&D project "ASR – Reliable concept for performance testing" (2014-2019; labelled "KPN-ASR") a fundamental study on ASR kinetics has been performed. The main aim of the study is to assess the consequences of elevating the exposure temperature as a means for accelerating ASR during performance testing. On one hand the increased temperature accelerates the alkali-silica reactivity of various aggregates, but on the other hand the increased temperature accelerates also the fly ash reaction leading to lower effective alkali content and pH in the concrete pore solution and potentially a reduction in the reactivity of the aggregates. Hence, what is the net outcome of elevating the temperature from 20 to 38 or 60 °C on ASR performance testing?

For the laboratory test program, four coarse aggregates with different ASR reactivity and alkali releasing properties were included, ranging from non-reactive to extremely fast reactive. Two binders were used; 1) A high alkali OPC binder and 2) The high alkali OPC binder where 20 wt.% was replaced with a low CaO siliceous fly ash.

The study included the following tests on the 8 mortar mixes (including the four aggregates and the two binders); chemical composition and pH of the pore-water, and calcium hydroxide (Portlandite) content (only for the limestone aggregate mortars). Expansion was measured for the 8 corresponding concrete mixtures. The fine aggregate in the concrete mixes was a non-reactive, non-releasing limestone.

Keywords: *alkali release; ASR; kinetics; pore-water.*

1. INTRODUCTION

Alkali-silica reaction (ASR) is one of the major deterioration mechanisms for concrete structures. ASR in concrete is caused by the reaction of reactive siliceous minerals in the aggregates with alkali in the pore solution, mainly provided by the cement, when the concrete is exposed to a moist environment. The reaction leads to the formation of alkali-silica gel (ASR-gel) that absorbs water and expands. Subsequently, the expanding ASR-gel leads to expansion and cracking of the concrete. ASR is normally a slow reaction. In Norway, with a relatively cold environment and mainly moderately reactive aggregates, it might take 10-20 years before one can see signs of expansion and cracking on a structure.

Therefore, accelerated ASR laboratory concrete prism tests (CPTs) have been developed to assess whether aggregates or concrete mixes are safe to use. A lot of work has been done in this field during the last 20-30 years, the last 10-15 years mainly focusing on developing reliable performance tests [1]. One main finding is that sufficient replacement of part of the Portland cement with fly ash is able to mitigate ASR reactions in concrete containing reactive aggregates. In Norway, performance testing has shown that a 20 wt.% replacement of Portland cement with fly ash would be able to mitigate ASR in concrete with all known reactive Norwegian aggregates. However, recent findings from Canada and US have reported deleterious expansion of field exposed concrete blocks containing 20 wt.% fly ash, even though the concretes passed the 38°C CPT (using CSA A23.2-28A or the corresponding ASTM C-1293 [2]) [1,3], indicating that we might not be on the safe side using 20 wt.% fly ash for our most reactive aggregates. However, the 38°C Norwegian CPT (NCPT) [4] is documented to leach less alkalis during the exposure time (the main source of error during performance testing) due to the larger prism cross section (100 mm) [5] and is thus assumed to be better correlated to field behavior [1]. Another potential reason for the discrepancy between laboratory performance testing and field observations might be the

overestimation of the mitigating effect of fly ash during the laboratory testing. The elevated exposure temperature during ASR performance testing will on one hand accelerate the alkali-silica reactivity of the aggregates, but on the other hand it will also accelerate the fly ash reaction leading to lower effective alkali content and pH in the concrete pore solution and potentially a reduction in the reactivity of the aggregates. The question is whether the accelerated laboratory test is still conservative for concrete containing fly ash?

Recently, ASR researchers have been confronted with yet another challenge. Conventionally, cement was considered as the main source of alkali in concrete. However, recent studies have indicated that aggregates can also release alkali over time and thereby increase the alkali load in the concrete, which would make it more prone to ASR. Most of the research performed on alkali release from aggregates is done in model systems, where aggregates are leached in an aggressive solution [6]. There is a need to verify whether aggregates do release these alkalis in field or during accelerated performance tests performed on concrete in the laboratory.

The overall goal of the study was two-fold:

I) Assess whether accelerated ASR-performance tests are conservative, i.e. is the aggregate reaction accelerated equally or more by the temperature than the fly ash reaction?

This was assessed by comparing changes in the rate of reaction of aggregate due to increasing curing temperatures (20, 38 and 60 °C) with the changes in the rate of reaction of fly ash with curing temperature. The rate of reaction of aggregates is experimentally determined by expansion testing of concrete. The rate of reaction of fly ash is assumed to be directly correlated to calcium hydroxide (CH; Portlandite) consumption measured by thermogravimetric analysis (TGA).

II) Validation of alkali release by aggregates.

This was done by analyzing the pore solution of mortars containing different potentially releasing aggregates sealed cured at 20, 38 and 60 °C for 4, 13 and 78 weeks. Limestone was used as reference aggregate not releasing alkalis.

2. MATERIALS, MIXES, EXPERIMENTAL MATRIX AND METHODS

2.1 Materials

Two binder types were used: a pure Portland cement (CEM I acc. EN197) which is referred to as “PC”, and a blended cement consisting of 80 wt.% of the same Portland cement and addition of 20 wt.% low CaO siliceous fly ash, which is referred to as “PC+FA”. The Portland cement contains 3.5% limestone and has an alkali content of 1.22 wt.% Na₂O_{eq}, and the fly ash has 2.41 wt.% Na₂O_{eq} (Table 2.1).

Table 2.1: The oxide composition of PC and FA in wt.% determined by XRF.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
PC	61.06	20.06	5.11	3.18	2.51	3.66	1.09	0.50	2.58
FA	3.24	57.56	23.12	5.86	1.84	0.35	2.01	1.08	1.97

Four types of aggregates were used (see Table 2.2). Limestone, provided by Franzefoss Minerals, serves as a non-alkali-reactive and non-releasing reference. Tau, which is a Mylonite, is moderately alkali-reactive with an unknown alkali-release potential. Ottersbo is a Cataclasite, which is highly alkali reactive and has a moderate potential for alkali-release [7]). Finally, New Mexico, which consist of a mixture of rock types, is extremely alkali-reactive with an unknown alkali-release potential.

Table 2.2: Aggregates used in this study (the first three originating from Norway, the latter from US)

Abbrev.	Name	Type	Reactivity	Alkali releaser
Ls	Limestone	Limestone	None	No
Tau	Tau	Mylonite	Moderately	?
Ott	Ottersbo	Cataclasite	High	Moderate
NM	New Mexico	Mixture	Extreme	?

2.2 Concrete mixes

For all the 8 concrete mixes the fine aggregate was a crushed limestone originating from the same quarry as the coarse limestone (Table 2.2). For the coarse aggregates the sources described in Table 2.2 were used. The concrete recipes are presented in Table 2.3. The water-to-binder ratio was 0.50. The concretes were mixed in a 50 l Hobart mixer.

Table 2.3: Concrete recipes in [kg/m³] and measured concrete properties

Binder	PC				PC+FA			
<i>Coarse aggregate</i>	<i>Ls</i>	<i>Tau</i>	<i>Ott</i>	<i>NM</i>	<i>Ls</i>	<i>Tau</i>	<i>Ott</i>	<i>NM</i>
Portland Cement (PC)	443	447	447	436	356	359	359	348
Fly ash (FA)	0.0	0.0	0.0	0.0	89	90	90	87
Free water	221	224	224	218	222	224	224	218
Absorbed water	5.2	2.7	5.3	13.1	5.2	2.7	5.2	12.9
Limestone (Ls) 0/5 mm	505	686	680	832	500	678	670	819
Coarse aggr. 4(5)/16 mm	1175	1028	1017	821	1163	1016	1001	808
Sika ViscoCrete RMC-315	2.13	2.15	3.48	0.44	0.77	1.14	1.57	2.23
Alkali content Na ₂ O _{eq}	5.37	5.37	5.37	5.40	6.42	6.42	6.43	6.45
Slump (mm)	125	115	110	115	130	115	120	120
Air content (%)	2.1	1.8	2.3	2.2	1.8	1.8	2.1	2.3
Compressive strength (MPa), 28d	51.5	59.2	56.7	53.7	44.0	48.0	47.9	45.8

2.3 Mortar mixes

The corresponding 8 mortars were mixed with a nominal water-to-binder ratio (w/b) of 0.60 to obtain sufficient workability without adding any admixtures to avoid introducing any other parameters into the pore water system. The recipes of the mortar mixes are given in Table 2.4. The w/b was re-calculated considering the water absorbed by the aggregate. The measured water absorption of the aggregates is: Ls-0.2 wt.%; Tau-0.2 wt.%, Ott-0.5 wt.%; NM-1.6 wt.%. The re-calculated w/b varied from 0.55-0.59, see Table 2.4. The fixed grading of the fine aggregates used for the mortar is given in Table 2.5.

The mortars were mixed with a Hobart mixer with a capacity of 5 L according the EN196 in batches with a volume of 4.27 L containing 2.2 kg cement, 1.32 kg distilled water, and 6.6 kg aggregate. The mortars were cast in 125 mL plastic bottles, sealed and immediately placed at the curing temperatures (20, 38 or 60°C) until the different test termini. This is in contradiction to the concrete prisms that were kept at ambient temperature in the lab. until demolding the day after casting. A little de-ionized water was added to the bottles during curing. Prior to testing, the bottles were pre-cooled overnight at 20°C.

Table 2.4: Mortar recipes in [kg/m³]

	PC				PC+FA			
<i>Fine aggregate</i>	<i>Ls</i>	<i>Tau</i>	<i>Ott</i>	<i>NM</i>	<i>Ls</i>	<i>Tau</i>	<i>Ott</i>	<i>NM</i>
Portland Cement (PC)	482	491	486	466	381	388	384	369
Fly ash (FA)	0	0	0	0	95	97	96	92
Free water	286	291	284	258	283	288	281	255
Absorbed water	2.9	2.9	7.3	22.4	2.9	2.9	7.2	22.1
Fine aggregate	1445	1472	1457	1398	1428	1455	1441	1383
w/b nominal	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
w/b real (re-calc.)	0.59	0.59	0.58	0.55	0.59	0.59	0.58	0.55
Na ₂ O _{eq} (PC and FA)	5.9	6.0	5.9	5.7	6.9	7.1	7.0	6.7

Table 2.5: Grading of the fine aggregates for the mortar mixes.

Fraction [mm]	2/4	1/2	1/0.5	0.25/0.50	0.125/0.25	<0.125
[wt.%]	10	20	20	25	15	10

2.4 Experimental matrix

The experimental matrix is presented in Table 2.6. The expansion measurements at 20, 38 and 60 °C were performed on concrete (Table 2.3). For the corresponding 24 mortar test series (Table 2.4), the portlandite content was determined using TGA (see section 2.6) at the same temperatures and the pore solution was investigated using PWE and CWE combined with FS and ICP (see section 2.7). For the TGA and CWE analysis, the mortar samples were crushed with a jaw crusher and subsequently milled with a rotating disc to obtain fine powder.

Table 2.6: Experimental matrix - The crosses indicate the samples, curing temperature and time intervals investigated as well as the methods used (for abbreviations see sections 2.6 and 2.7).

				7 days			28 days			13 weeks			26 weeks			1 year			1.5 years			
	Aggr	Temp. (°C)	20	38	60	20	38	60	20	38	60	20	38	60	20	38	60	20	38	60		
Concrete	All	Expansion	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	
Mortar	Ls	PWE_FS+pH				X	X	X	X	X	X											
		CWE_FS				X	X	X											X	X	X	
		CWE_ICP																		X	X	X
		TGA	?*	?*	?*	?*	?*	?*	?*	?*	?*	?*								X	X	X
	Tau	PWE_FS+pH				X	X	X	X	X	X											
		CWE_FS																		X	X	X
		CWE_ICP																		X	X	X
		TGA																				
	Ott	PWE_FS+pH				X	X	X	X	X	X											
		CWE_FS																		X	X	X
		CWE_ICP																		X	X	X
		TGA																				
	NM	PWE_FS+pH				X	X	X	X	X	X											
		CWE_FS																		X	X	X
		CWE_ICP																		X	X	X
		TGA																				

?* TGA samples disappeared during storage.

2.5 Expansion measurements on concrete

For all the 24 test series on concrete (4 aggregates, 2 binders and 3 temperatures), the same prism size was used; 70x70x280 mm³. The prisms were de-molded after 1 day and subsequently placed in the following storage containers;

- as described for ASTM C1293 for the prisms exposed to 20°C and 38°C [2]
- as described for RILEM AAR-4.1 for the prisms exposed to 60°C [8]

The main interest with respect to the expansion testing is the rate and extent of expansion in the first part of the exposure period. Later during the exposure the influence of errors, in particular the rate and extent of alkali leaching, will strongly influence the expansion curves that are expected to level off [5].

All the readings of length were performed at the times described in Table 2.6 without pre-cooling the prisms. Additionally, final readings were recently measured after 2 years of exposure.

2.6 Portlandite content in mortar

Thermogravimetric analysis (TGA) was used to quantify the portlandite content of the mortars. About 100-250 mg of the ground mortar powders were placed in 600 μ L alumina crucibles. The powders were heated from 40 to 900 $^{\circ}$ C at 10 $^{\circ}$ C/min, whilst purging the chamber with N_2 at 50 mL/min. Looking at the derivative (DTG) of the mass loss curve (TG), a characteristic mass loss peak for portlandite occurs in the range of 400-550 $^{\circ}$ C. Integrating this mass loss peak in the DTG curves gives the mass of water lost during heating originating from portlandite. Equation 1 is used to calculate the wt.% of portlandite in the sample.

$$CH = \frac{\Delta m_{400-550\text{ }^{\circ}\text{C}}}{m_{\text{sample}}} \cdot \frac{M_{\text{Ca(OH)}_2}}{M_{\text{H}_2\text{O}}} \quad (1)$$

Here CH is the wt% of portlandite in the mortar, $\Delta m_{400-550\text{ }^{\circ}\text{C}}$ is the integrated mass loss peak in the range of 400-550 $^{\circ}$ C of the DTG-curve, m_{sample} is the mass of mortar placed in the alumina crucible, $M_{\text{Ca(OH)}_2}$ and $M_{\text{H}_2\text{O}}$ are respectively the molar masses of portlandite (74 g/mol) and water (18 g/mol).

2.7 Pore solution analysis on mortar

The pore water from the mortar samples was obtained either by squeezing it out under pressure (PWE) or by extracting it with cold water (CWE). PWE was aimed to be the dominating method, and CWE would only be carried out for the limestone mixes for comparison. However, at later curing ages (e.g. 1.5 years) we had to turn to CWE as we failed to squeeze out water with PWE.

The pore water extraction (PWE) was performed using a steel die method. After stripping the plastic bottles from the cast mortar samples, they fitted perfectly in the hollow steel cylinder. The piston was placed on top and 150 MPa pressure was applied for 10 minutes, before being increased to 275 MPa until sufficient amounts of solution had been expressed. The pore solution was collected in a syringe attached to the tube at the bottom steel plate. The results of PWE are expressed as volume concentrations e.g. mol/L or g/L pore solution.

For the cold water extraction (CWE) procedure based on [9], 20 g of the ground mortar powders were placed in a beaker, after which 20 g deionized water was added. The contents were mixed on a magnetic stirrer for 5 minutes, then transferred to a vacuum filtration unit. When the solids appeared to have dried fully, the filtrate was extracted and placed in a 15 mL centrifuge tube. The results of CWE are expressed as g/g mortar.

The concentration of elements in the solutions were analyzed by two different techniques: Flame atomic absorption spectroscopy (FS) and inductively coupled plasma mass spectrometry (ICP-MS). FS was initially used to determine the concentration of Na and K in the PWE and CWE solutions. The FS instrument used is a SpectrAA-400.

To compare different methods and determine which to use for future studies, ICP-MS was also used to determine the concentration of K, Na, Al and S in the CWE solutions of the 1.5 year old mortars. Samples for ICP-MS were prepared by diluting the CWE solutions 1:10 by volume with deionized water before adding 0.14 mL 32.5% HNO_3 . These diluted and acidified solutions were then analyzed with a Thermo Scientific Element 2 ICP-MS.

The pH of the expressed solution was determined using a 6.0255.100 Profitrode from Metrohm. The electrode was calibrated with buffer solutions of pH 7, 10 and 13.

3. RESULTS AND DISCUSSION

3.1 Expansion results

Figure 3.1 shows the expansion results as a function of time for the 12 concrete test series with PC binder stored at 20, 38 and 60 $^{\circ}$ C, respectively, with the different coarse aggregates: limestone (Ls), Tau, Ottersbo (Ott) and New Mexico (NM). Figure 3.2 shows corresponding results for the 12 concrete test series with PC+FA binder. Note that the vertical axes of Figure 3.1 and Figure 3.2 are different.

The expansion curves tend to level off after a certain time of exposure. This has mainly been attributed to alkali leaching from the prisms, but also to some extent due to consumption of alkali by the ASR-gel. Due to the lack of alkali in the concrete to sustain the ASR, the expansion levels off [5]. This is most pronounced for the highest temperature.

When comparing the expansion levels at the different storage temperatures during the first 26 weeks (before the alkali leaching influences the expansion too much), one can clearly see that the expansion caused by the alkali aggregate reaction is accelerated in time with increasing curing temperature, as expected, and that the effect of the temperature increase is aggregate dependent. At 20 °C, hardly any expansion was measured, except for the NM containing PC concrete that expanded "considerably" (here defined as an expansion of at least 0.025%) already after 26 weeks. At 38 °C, the time to reach an expansion of about 0.025% was 3.5, 7.5 and 16 weeks, respectively, for NM, Ott and Tau. The corresponding times at 60 °C was shortened to 1.5, 2 and 4 weeks, respectively, for NM, Ott and Tau. It appears like the less reactive the aggregate is, the more is it accelerated by temperature.

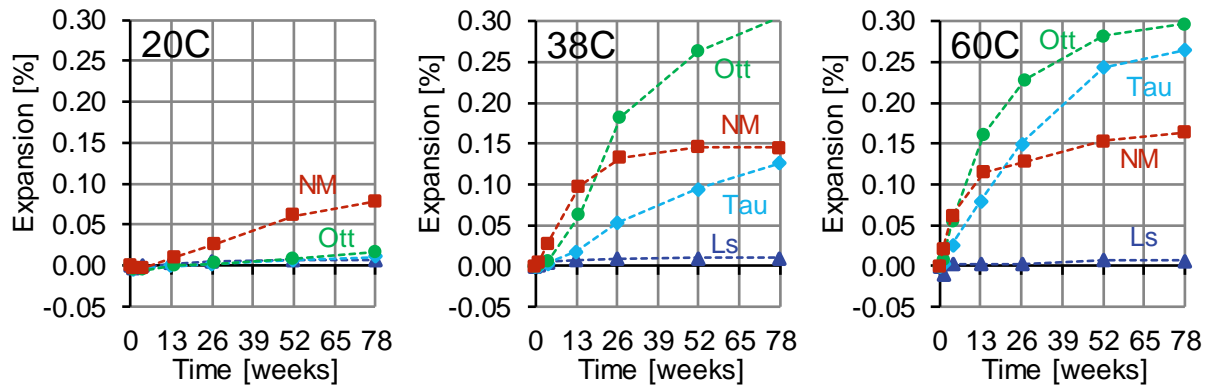


Figure 3.1: Expansion results for the 12 concrete test series with PC binder.

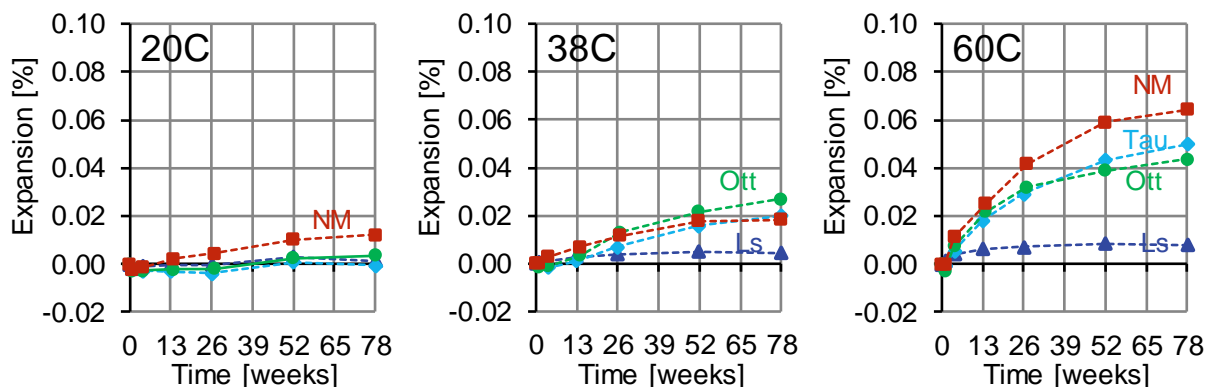


Figure 3.2: Expansion results the 12 concrete test series with PC+FA binder.

When comparing Figure 3.1 and Figure 3.2 it is clear to see that the added fly ash (20 %) in the PC+FA binder is able to reduce the expansion levels considerably compared to the PC binder without fly ash, as expected. The expansion for example for the Ott aggregate is almost an order of magnitude larger for the concrete with PC binder compared to the PC+FA concrete at 38 and 60 °C: after 52 weeks, the expansion is about 0.26-0.28% for the PC concrete (Figure 3.1), whereas the expansion level is about 0.02-0.04% for the PC+FA binder (Figure 3.2). Limestone (Ls) aggregate was selected as the non-alkali-reactive reference aggregate, and as expected it does not expand at any of the exposure temperatures. The New Mexico (NM) aggregate was considered as the most alkali reactive amongst the investigated ones. It is therefore also the aggregate which is the first to cause expansion. The effect is clearest at 20 °C, at which none of the other aggregates cause considerable expansion independent of the binder. At 38 °C, it is also the first aggregate to kick off expansion, however the expansion seems to level off after 26 weeks for the PC binder and after 52 weeks for the PC+FA binder. At 60 °C, the expansion of the NM concrete with the PC binder tends to level off already after 13 weeks (Figure 3.1), whereas the PC+FA concrete with NM (Figure 3.2) tends to level off after 52 weeks. As discussed above, this levelling is most likely caused by exhaustion of the alkali in the system. Another possible, but less likely explanation, or combined explanation, is exhaustion of the silica in the extremely reactive NM aggregate.

The Ottersbo (Ott) aggregate is highly alkali reactive, but slower compared to the NM aggregate. However, even though the expansion kicks off later compared to the NM concretes, the ultimate expansion for Ott at 38 and 60 °C are considerably higher compared to the NM concrete (e.g. for the

PC binder in Figure 3.1 the expansion after 26 weeks is 0.18-0.23% for Ott vs. 0.13% for NM). The expansion of the Ott concretes does not level off as early and to the same extent as the NM concretes. Hence in the case of Ott concrete there does not seem to be a clear exhaustion of alkali in the system or silica from the aggregate. Lack of silica to sustain the ASR has never been observed for any of the known Norwegian reactive aggregates (in which most are moderately reactive).

The Tau aggregate is also alkali reactive, but even slower compared to the Ott aggregate. It needs longer time or higher temperatures for its reaction. As for the Ott concrete, the Tau concrete does not show clear signs of leveling off after 78 weeks of exposure, which means that sufficient alkali and silica are available in the system for the reaction to proceed. Based on the results up to 78 weeks at 60 °C, it seems as if Tau concrete will reach similar expansion levels as the Ott concretes.

3.2 FA reaction after 1.5 year of curing

Figure 3.3 shows the Portlandite content (CH) in the limestone (Ls) mortars with fly ash (Ls_PC+FA) and without fly ash (Ls_PC) after 1.5 years of curing at 20, 38 and 60 °C.

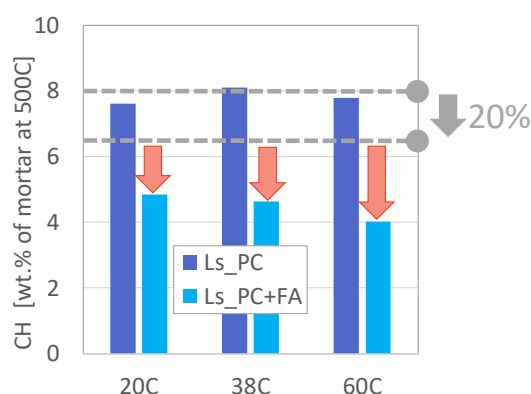


Figure 3.3: Comparison of Portlandite content (CH) in the limestone (Ls) mortars with fly ash (Ls_PC+FA) and without fly ash (Ls_PC) after 1.5 years of curing at 20, 38 and 60 °C

The fly ash will affect the CH content in two ways. Firstly, it dilutes the PC as we replace 20% of it with fly ash. It is the PC which forms the CH during hydration, so for simplicities sake we could reduce the CH content with 20 wt.%. It should be noted that this is not fully correct as the fly ash also has a filler effect which will influence the CH content formed by the PC [10], but we don't consider this for now. Hence, the reduction in CH in the fly ash containing samples beyond the 20% reduction is considered to be caused by the pozzolanic reaction as indicated by the red arrows in Figure 3.3. The CH consumption seems to be slightly enhanced by increasing the curing temperature, as expected.

The aim of the TGA investigations was to have an idea of the rate of reaction of the fly ash compared to the rate of alkali reaction of the aggregates. However, as we only have one time-step for the CH content we are not able to discuss the rate of the fly ash reaction. We should have investigated the changes in the CH content by comparing PC and PC+FA pastes or mortars cured at 20, 38 and 60 °C at earlier time-steps as indicated in the experimental matrix in Table 2.6 with “?”. This was originally planned, but the samples disappeared during storage.

3.3 Comparison PWE and CWE at 4 weeks

As we needed to switch from pore water extraction (PWE) to cold water extraction (CWE) to extract pore solution at later curing ages, we need a comparison of both methods. The results obtained with the two methods are expressed in different units: PWE gives concentrations in mmol/L pore solution, whereas CWE in mmol/g mortar, due to the nature of the two methods. In order to compare results from both methods one has to determine the volume of pore solution in the mortar. In this case we assume 0.10 g pore solution per 1.00 g mortar, which would agree with a water binding capacity of 0.23 g / g PC or PC+FA, a degree of reaction of the PC of 60%, and that the mixing water which is not bound is free and makes out the pore solution.

In Figure 3.4, the K and Na concentrations obtained with PWE and CWE were compared on mortar samples containing limestone (Ls) aggregate sealed cured for 4 weeks at 20, 38 and 60 °C.

We can observe some discrepancy between the two methods, even though Plusquellec et al. [9] has reported a relatively good agreement between the results from both methods. A potential cause of error

is always the assumption of the volume of the pore solution when comparing PWE and CWE results, which introduces a systematic error. In this case, CWE seems to overestimate the free K and Na concentration. However, the difference in the results from both methods is not solely a systematic error as the results of both methods do not follow the same relative differences, especially for the PC+FA_38C and PC+FA_60C samples (Figure 3.4). Further comparison of the two methods is needed in order to validate their results.

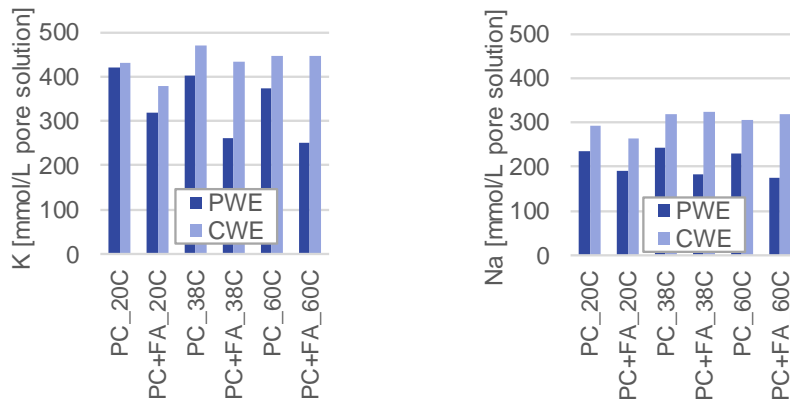


Figure 3.4: Comparison of the K and Na content determined by PWE and CWE results for the limestone (Ls) mortars with fly ash (PC+FA) and without fly ash (PC) after 4 weeks of curing at 20, 38 and 60 °C.

As we were not able to obtain pore solution through PWE on the mortars at the testing intervals later than 13 weeks of curing, the later age results are only obtained through CWE. Based on the comparison presented here, it is clear that one cannot directly compare the CWE and PWE measurements. We will thus focus on relative differences within the test series.

3.4 Pore solution composition by PWE_FS after 4 and 13 weeks

The pH, Na and K concentration of the expressed pore solution was determined on mortar samples sealed cured for 4 and 13 weeks at 20, 38 and 60 °C. The results are presented in Figure 3.5.

As stated previously limestone (Ls) can be considered as the reference, as it neither contributes with alkali nor will produce ASR-gel which can take up alkali.

The effect of the binder type i.e. PC vs. PC+FA can be seen by comparing the darker with the brighter bars for Ls mortar in Figure 3.5. We would expect a slightly lower pH, and lower K and Na concentrations for the PC+FA samples compared to the PC samples due to the pozzolanic reaction of the fly ash. This is the case for most of the samples.

When looking at the impact of the curing temperature on the Ls mortar samples, one can observe a trend of decreasing pH with increasing temperature. We see also a slight decreasing trend in the K concentration with temperature, but for Na we observe a slight increase for two of the aggregates (Tau and Ott) after 13 weeks. The decrease in pH at 60 °C can be due to an increase in the S content in the pore solution caused by instability of ettringite at higher curing temperatures [11]. However, at 4 and 13 weeks (presented in Figure 3.5) only the Na and K concentration was determined using FS and pH with a pH electrode. At later ages, additional elements were determined using ICP-MS which can elucidate the temperature effect (see section 3.5).

The presence of the aggregates in the mortar (0/5 mm grading) can influence the pore solution in two ways. Firstly, aggregates can release alkali metals into the pore solution over time and thereby increase the concentration of Na and/or K, and the pH. Secondly, the alkali reaction of the aggregates might produce alkali-silica-gel which has a high capacity to take up alkali metals and can thereby reduce the alkali concentration in the pore solution. It should be noted that the alkali-uptake of the alkali-silica gel is not permanent as the alkali can over time be exchanged with Ca and thereby be released again into the pore solution [12]. We are not able to distinguish between the alkali release by aggregates and the alkali uptake by the alkali gel, as both processes take place at the same time.

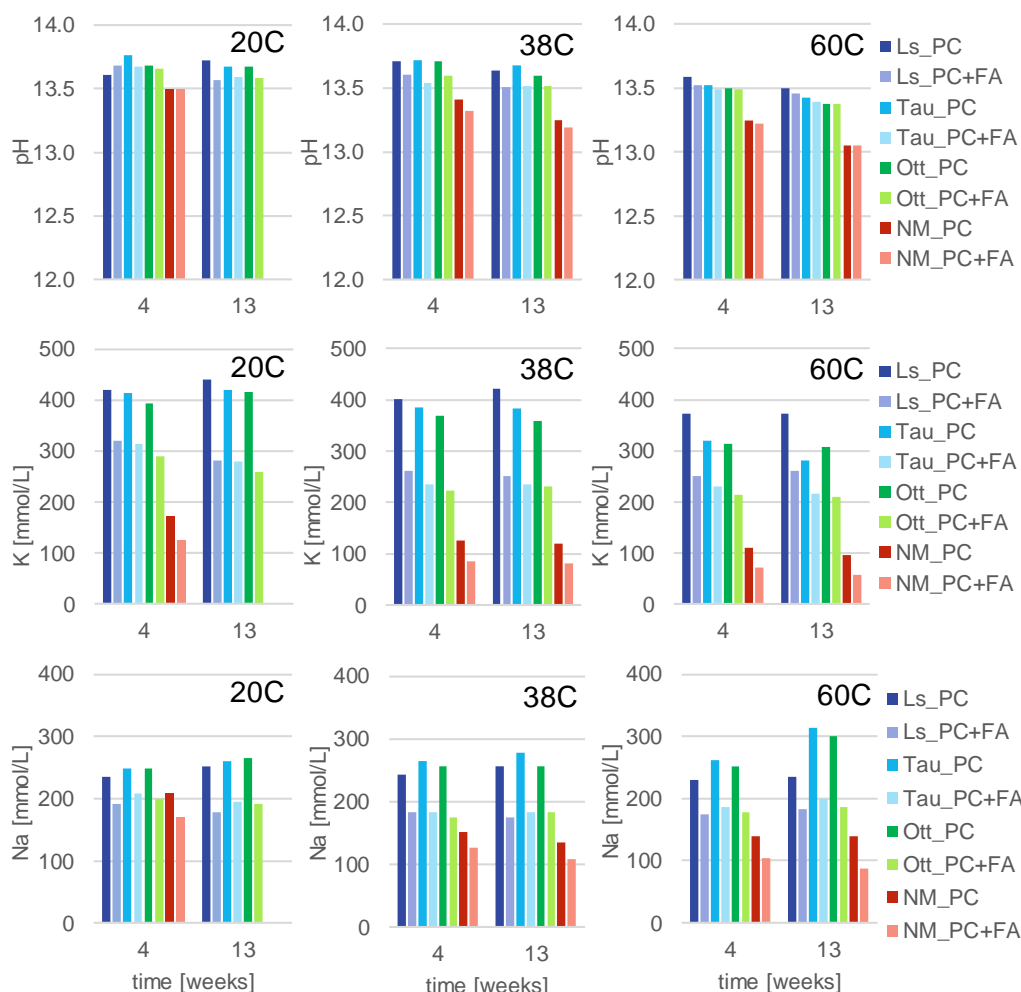


Figure 3.5: pH, K and Na concentration of the expressed pore solution after 4 and 13 weeks.

The mortars with Tau and Ottersbo sand (Ott) have a similar pH and similar K and Na concentrations compared to the Ls mortar, except for at 60 °C at which slightly lower pH levels, lower K and higher Na levels were recorded. The decrease in K could be explained by the uptake of K by alkali-silica gel as the Tau and Ott concrete has started to expand considerable at 60 °C after 13 weeks (see Figure 3.1 and Figure 3.2). The increase in Na might be due to release by the aggregates.

The mortars prepared with New Mexico (NM) show a considerably lower pH, K and Na levels compared to the Ls mortar at all tested curing times and temperatures. The pH and alkali levels seem to decrease with time, indicating that more ASR-gel is being produced between 4 and 13 weeks which takes up more alkali. In the previous section, we briefly discussed possible explanations for the leveling off of the expansion in the case of NM aggregates after 13-26 weeks (Figure 3.1 and Figure 3.2). The considerable decrease in the pH and alkali levels in the NM mortar samples at 4 and 13 weeks shown in Figure 3.5, might indicate a reduction of the alkali level in the pore solution below a level which is required to maintain the alkali-silica reaction.

3.5 Pore solution composition after 1.5 years of curing

Figure 3.6 shows the K, Na, S and Al content determined by ICP-MS in the solutions obtained by CWE from the mortar samples with the different aggregate (Ls, Tau, Ott, NM) cured for 1.5 years (78 weeks) at 20, 38 and 60 °C. At 20 °C only the limestone (Ls) containing mortars were investigated.

When comparing the binders, i.e. PC and PC+FA, for the Ls mortars in Figure 3.6, the PC mortar seems to have slightly higher K concentration compared to the PC+FA mortar which is in line with the results at 4 and 13 weeks (Figure 3.5) and previous studies [10]. However, the Na concentrations of the Ls mortars with PC and PC+FA seem to be similar (Figure 3.6) which is not in agreement with observations at earlier ages (Figure 3.5), nor with previous studies [10]. The reason for this is unknown, but it could be due to inaccuracies of the CWE method. When it comes to the other elements, we can see that the

PC mortar has a slightly lower Al and slightly higher S content in the pore solution compared to the PC+FA mortar. The higher Al content for the PC+FA mortar can be expected as the fly ash contributes with additional Al to the system [10,11]. The lower S content for the PC+FA mortar is due to the fact that the fly ash dilutes the main sulphate containing component namely PC, and the additional Al from the fly ash might lead to more AFm which might also affect the S content in the pore solution [10,11].

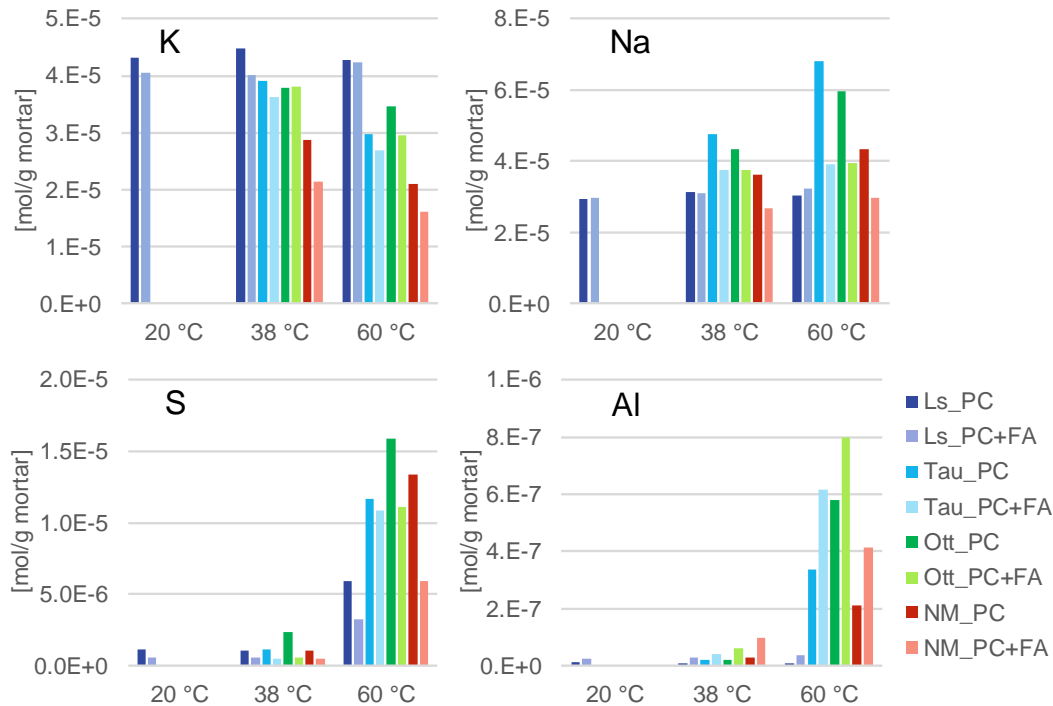


Figure 3.6: K, Na, S, and Al content determined by ICP-MS in solution obtained by CWE from the different mortar samples cured for 1.5 years at 20, 38 and 60 °C.

When looking into the impact of the curing temperature for the Ls mortars in Figure 3.6, we can observe that the K, Na and Al content in the pore solution seems to be more or less independent of the temperature, however, as expected, the S content increases when the mortar is cured at 60 °C. This is most likely due to the instability of ettringite at these temperatures causing a higher S concentration in the pore solution [11]. It should be noted that the higher S content in the pore solution at 60 °C can explain the lower pH measured at that temperature (see Figure 3.4), as for a similar K⁺ and Na⁺ concentration in the solution, a higher S (or SO₃⁻) concentration would mean a reduction in the OH⁻ concentration and thereby a reduction in the pH.

Regarding the impact of the aggregates on the pore solution in Figure 3.6, we can see some general trends for the Tau, Ott and NM aggregates: the K content is reduced, whereas the Na, S and Al content increases at 60 °C compared to 38 °C. The decrease in K and increase in Na is in line with the results after 4 and 13 weeks (Figure 3.5).

The decrease in K in the presence of these aggregates (Figure 3.6) might be due to the uptake by the ASR-gel [12]. When for example looking at the expansion results for Tau after 78 weeks (1.5 years) in Figure 3.1 and Figure 3.2, we can see that Tau expands much more at 60 °C compared to 38 °C independently of the binder, and therefore most likely contains more ASR-gel. At the same time, the uptake of K is also larger at 60 °C compared to 38 °C for Tau (Figure 3.6), indicating that there might be a link between the alkali reaction (ASR-gel formation) and the K uptake in the presence of the reactive aggregate.

In the case of the Na (Figure 3.6), we see instead an increase in the pore solution in the presence of the reactive aggregates, in particular for the PC binder. The increase is largest for Tau, followed by Ott, whereas the impact for NM is less. The increase in Na could be due to alkali release from the aggregates (e.g. sodium rich feldspar), indicating that Tau is potentially the strongest releaser of Na closely followed by Ott, whereas NM is only a moderate Na releaser after 1.5 years of sealed curing. It should always be kept in mind that the release of alkali by the aggregates can be masked by the uptake of alkali in ASR-gel.

The Ottersbo aggregate was part of a preliminary accelerated release test (RILEM AAR-8) [7]. The aggregate contains 4.3 wt.% Na₂O and 1.8 wt.% K₂O. After 52 weeks of exposure at 60 °C it was able to release 0.11±0.04 wt.% Na₂O and 0.06±0.03 wt.% K₂O. Given also the difference in molar mass between Na₂O and K₂O (62 and 94 g/mol, respectively), it is clear to see that the Ott aggregate releases preferentially Na (36 mmol/kg aggregate) compared to K (13 mmol/kg aggregate). This could explain the observed increase in Na and decrease in K in the presence of reactive aggregates. If we calculate the Na release based on the accelerated results for Ott aggregate (0.11 wt.% Na₂O in aggregate * 65 wt.% aggregate in mortar * 2 mol Na / 62 g/mol) we would expect a Na release in the pore solution of approx. 2E-5 mol/g mortar which is approx. the difference in Na we observe between the Ls and Ott mortar at 60 °C (see Figure 3.6), indicating that alkali release might be accounted for in accelerated performance testing. The higher Na contents at 60 °C compared to 38 °C indicates also that the increased curing temperature accelerates the release of Na, as expected. It should be noted that there is a strong influence of the binder on the Na content: The PC binder shows much higher Na levels compared to the PC+FA binder. This might be due to the pozzolanic reaction of the fly ash which results in C-S-H with a lower Ca/Si ratio with a higher capacity to take up alkali, which thereby masks the effect of the reactive and releasing aggregates on the alkali content in the pore solution.

The increase in the S content seems to be enhanced in the presence of the Tau, Ott and NM aggregates (Figure 3.6). These aggregates are not expected to contribute with additional S. Hence the increase in the pore solution must be due to a shift in the AFm/AFt equilibrium, as mentioned earlier. As the S content in the pore solution increases, we also observe an increase in the Al content. This could indicate that at 60 °C, the equilibrium shifts from AFm and AFt phases towards siliceous hydrogarnet, which has been observed to have as a consequence that the Al and S content in the pore solution increases [11]. The reason why this effect is much stronger in the presence of the aggregates is unclear. Potentially the aggregates supply additional Si which shifts the AFm-AFt equilibrium even more towards hydrogarnet. In order to confirm that further research is need. The increase in Al concentration is also of interest, since Chappex and Scrivener [13] claim that increased aluminate in solution protect against ASR.

4. SUMMARY AND CONCLUSIONS

The first question posed in this study is whether accelerating the alkali-silica reactions (ASR) by increasing the testing temperature during performance testing is conservative for binders containing fly ash. Fly ash is known to be able to mitigate ASR. The increase in temperature during testing accelerates both the aggregate reaction and the fly ash reaction. Hence, the test would no longer be conservative if the fly ash reaction is accelerated more than the aggregate reaction.

A selection of 4 different aggregates, and 2 binders were investigated at 20, 38 and 60 °C for up to 1.5 years. The binders were a high alkali Portland cement (PC), and blended binder containing 20 wt.% siliceous fly ash and 80 wt.% PC. Based on the expansion results, we could conclude that with the selection of aggregates, we were able to cover a range from non-reactive (Ls), moderately reactive (Tau), highly reactive (Ott) and extremely alkali-reactive (NM) aggregate. As expected, the aggregate reaction was accelerated by increasing the storage temperature and there was a clear impact on the expansion of the binder composition, or more precisely the fly ash replacement, as the fly ash was able to reduce the expansions with almost an order of magnitude.

By studying the Portlandite consumption caused by the pozzolanic reaction of the fly ash, we could also confirm that the fly ash reaction is accelerated by increasing the temperature, however due to the lack of multiple time-steps we cannot conclude on the kinetics of the fly ash reaction.

The second question raised in this study was the validation of alkali release from aggregates. For this, we focus on the pore solution analysis done on mortar samples containing the different aggregates sealed cured for 1.5 years at 20, 38 and 60 °C. Validation of alkali release from aggregates by looking at the pore solution is complex as a range of phenomena affect the pore solution composition at the same time, such as the uptake of alkali by the ASR-gel produced during the ASR reaction, uptake of alkali by the C-S-H, as well as temperature driven changes in equilibrium between the hydration phases and the pore solution etc.

Increasing the curing temperature from 38 to 60 °C resulted in a strong increase in the S content of the pore solution. This can be related to the instability of ettringite at higher curing temperatures and the formation of siliceous hydrogarnet instead. This could also explain the observed increase in Al in the pore solution at 60 °C, and the lower pH measured at 60 °C.

The pore solution results of the mortars with alkali reactive aggregates showed a decrease in the K content in the pore solution which seems to be related to the alkali uptake by the produced ASR-gel. On

the other hand, they showed an increase in the Na content which might be related to alkali release by the aggregates. In the fly ash containing samples, the potential release of Na by aggregates is masked by the pozzolanic reaction of the fly ash. Both the indicated alkali uptake by ASR-gel and the release of alkali by the aggregates seem to be enhanced with increasing curing temperature. These findings need to be further investigated, however, they are showing the importance of reporting alkali per K and Na, and not as $\text{Na}_2\text{O}_{\text{eq}}$ as this would fully mask these observations.

5. FURTHER RESEARCH

To compare the rate of the pozzolanic reaction of the fly ash with the rate of the aggregate reaction we would need to determine CH consumption by fly ash at different time-steps from early age on as originally planned. In order to verify the link between the observed increase in Na content in the pore solution and release from the aggregates, we need to perform accelerated alkali release tests [7] on the aggregates used in this study, and verify the preferential release of Na. We need also to verify the preferential adsorption of K by the ASR-gel by investigating polished section from the expanded concrete samples with SEM-EDS.

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