

ALKALI-SILICA REACTION AUTOGENOUS DEFORMATIONS AND PRESSURE DEVELOPMENT IN A MODEL SYSTEM

Andreas Leemann ^{1*}

¹Empa, Dübendorf, Switzerland

Abstract

Pressure development during alkali-silica reaction (ASR) is attributed to the water uptake of the reaction products. However, autogenous deformations during their formation could have an effect on pressure as well. A model system consisting of micro silica, portlandite and NaOH solution is used to investigate autogenous deformation under unrestrained conditions and pressure development in a cylinder at constant volume. Portlandite content is systematically varied. Depending on the portlandite content, the samples either show autogenous shrinkage or autogenous expansion. The autogenous deformation generally correlates with the pressure development during the reaction. Comparison with heat flow and pore solution data from a previous study conducted with the same model system indicates that the pressure increase goes together with the formation of calcium-silicate-hydrates with a low Ca/Si-ratio and the formation of alkali-silicate-hydrates.

Keywords: alkali silica reaction, model system, autogenous deformation, pressure

1 INTRODUCTION

Although alkali-silica reaction (ASR) is in the focus of concrete research since decades [eg. 1-10], the reaction is not yet fully understood. Some problems encountered while studying the reaction mechanisms depend on the heterogeneity and complexity of mortar and concrete, which make the localisation and characterisation of the reaction products difficult. Expansion and pressure generated by reacting aggregates of various sizes are usually measured on mortar and concrete, making analysis of the reacting component more complicated. Therefore, model systems have been used to study specific aspects of ASR [eg. 2,4,11-15]. Generally, the expansion in the alkali-silica reaction is attributed to the water uptake of the reaction products either by osmosis or by capillary forces. However, there are no data about the autogenous volume changes caused by the formation of the reaction products and the possible implications for the development of expansive pressure. If autogenous shrinkage takes place it reduces the pressure generated by the water uptake of the reaction products. The contrary applies if there is the formation of the reaction products goes along with autogenous swelling. Even if the expansion of sealed concrete specimens with reactive aggregates would be tested, transport of moisture from the cement paste to the aggregates would be possible. As such, the local conditions at the reactions sites would be not autogenous for the silica gel.

In this study, a model system consisting of micro silica, portlandite and alkaline solution is used to measure the autogenous deformation during alkali-silica reaction. The pressure development caused by the autogenous deformation is determined by restraining the sample during the reaction to a constant volume. Furthermore, compressive strength of selected mixtures is determined. The same model system has already

* Correspondence to: andreas.leemann@empa.ch

been used to determine the influence of calcium on silica dissolution and the formation of the reaction products [15]. Data from this previous study will be used to discuss the results of this paper.

2 MATERIALS AND METHODS

2.1 General

For the discussion of the results of this study data from a previous project are used [15]. In this project the same model system was investigated using calorimetry, X-ray diffraction, nuclear magnetic resonance, pore solution analysis and desorption experiments.

2.2 Materials and mixture proportions

The composition of the commercially-available micro silica is given in Table 1. Portlandite ($\text{Ca}(\text{OH})_2$ > 96.0 mass-%, CaCO_3 < 3.0 mass-%) and NaOH (NaOH > 97 mass-%) with a high degree of purity were used.

The samples for the autogenous shrinkage and pressure measurements had a solid to liquid-ratio 1/1.8. The concentration of NaOH was 1M. Portlandite concentration ranged from 2.5-40 mass-% (see Table 2). Additional samples were prepared for the pressure measurements. In these samples the amount of NaOH was kept constant but the amount of liquid was reduced resulting in solutions of higher molarity (Table 2).

The samples were produced in a vacuum mixer (Renfert Twister evolution). Portlandite and micro silica were first mix for 1 minute. Then the NaOH solution was added. In the first minute 150 rotations per minute were used, followed by four minutes of 450 rotations per minute. The mix design of the samples used for pressure measurements is given in Table 2.

Compressive strength was determined on samples of MS10, MS20 and MS40 mixed with 1M NaOH (solid/liquid-ratio = 1.0/1.8).

2.3 Methods for assessment and analysis

Autogenous deformation (volumetric measurements)

The autogenous strain was determined using Archimedes' principle. An elastic membrane (condom made of polyisoprene) preventing moisture loss was used to fill in the test sample which was hung from a balance in a temperature-controlled buoyancy liquid (silicone oil). Changes in the volume of the sample cause a change of buoyancy and with it a change in the weight recorded by the balance in intervals of 60 seconds. The volume changes can be calculated based on the weight changes. The linear length change is calculated by dividing the volume change by a factor 3, assuming isotropic deformation. The method is described in detail in [16]. The measurements were started 10 minutes after the production of the slurries. Due to restraints in measuring time the autogenous shrinkage measurements were ended after 144 hours.

Pressure

The setup for the pressure measurements is shown in Figure 1. The main housing was turned upside down to fill in about 80 g of slurry. The movable piston was inserted. Trapped air could escape through a 2 mm-hole in the piston (not shown in Figure 1) while it was moved down. As soon as the slurry extruded from the hole, it was sealed with a screw and a sealing ring. The bottom housing was screwed on the main housing. With it the piston is pressed down applying pressure on the sample. An initial pressure of 0.5 MPa was applied. Like that not only an expansion could be recorded but shrinkage resulting in a pressure decrease as well. Then the sample was turned to normal position. During the measurement the volume of the sample compartment was kept constant. Therefore, any autogenous deformations had to result in a pressure change.

With a set of four pressure cells, two different samples were measured at the same time (two cells per sample). The measurements were started 20 minutes after production of the slurries. The pressure was usually measured for two weeks.

Compressive strength and E-modulus

Compressive strength was determined on prisms $25 \times 25 \times 100$ mm³ according to European standard EN 1926.

3 RESULTS

Autogenous strain

All samples show shrinkage during the first 12 hours (Figure 2). While samples MS and MS 2.5 continue to shrink after that point in time, the other samples start to expand between 18 and 36 hours. Sample MS10 shows the highest expansion after 144 hours followed by samples MS20, MS5 and MS40.

Pressure

The pressure of all samples decreases immediately (Figure 3). However, all of them start to expand after reaching a minimum value of pressure. This reversal takes place after 3.5 and 7.0 hours for the samples MS, MS2.5, MS5 and MS10. The samples MS20 and MS40 first reach a period of approximately constant pressure, before the pressure starts to increase considerably after 3 and 7 days respectively. In contrast to the other samples, these two samples display a pressure decrease after reaching a maximum value at 4.5 and 11 days respectively.

When the amount of alkaline solution is decreased but the amount of NaOH is kept constant, a pressure increase results in the samples MS10 and MS20 while a decrease is observed in sample MS40 (Figure 4 and Table 3).

Compressive strength and E-modulus

Sample MS40 shows the highest increase of compressive after 7 days and reaches the highest values after 28 days (Figure 5). The opposite applies to sample MS10 with the values of sample MS 20 lying between the other two. The gradient of compressive strength increase is larger for all samples between 2 and 7 days compared to 7 and 28 days.

4 DISCUSSION

The amount of autogenous strain is reflected in the pressure measurements. When the values are compared after 144 hours, both parameters show the same dependence on portlandite content (Figure 6). However, to calculate an elastic deformation and assess the degree of relaxation, E-modulus of the samples would have to be determined. The measurements of compressive strength show that the values increase with increasing portlandite content and the elastic modulus is expected to follow a similar trend. Therefore, it can be assumed that the degree of relaxation decreases with increasing portlandite content. As such, similar autogenous expansion of samples with low and with high portlandite contents would result in higher pressure for the latter. However, the differences in pressure between the samples seem to be surprisingly small, especially if the amount of reacted micro silica is taken into account; it increases from sample MS with 11.2 mol-% to sample MS40 with 93.9 mol-% [15].

The increase of pressure with the reduction of alkaline solution and constant amount of alkalis can be attributed to the lower porosity and therefore higher E-modulus of the samples. Why this applies to the samples MS10 and MS20 but not to the sample MS40 is not clear.

The total heat flow of the samples increases with increasing portlandite content as the formation of calcium-silicate hydrates (C-S-H) is the main cause for the heat release [15]. The comparison of pressure and heat flow change with time shows that the main pressure increase does not go together with the maximum heat release. (Figures 7 and 8). In sample MS10 pressure starts to increase shortly before the maximum heat flow is reached. However, the main pressure increase is observed at decreasing heat flow. The pressure increase in sample MS20 takes place after about 70 hours when heat flow has already decreased to relative low values.

Additionally, the pressure developed can be compared to the change of pore solution chemistry with time (Figure 9). The pressure starts to increase shortly after the silicon concentration starts to rise. Silicon concentration and pressure increase together until the solution gets saturated in silicon and the hydroxide concentration decreases. This can be translated into the type of reaction products formed. In the period of decreasing pressure, micro silica is dissolved and C-S-H is formed. As the sample is likely still fluid in the first phase of the reaction, the pressure decrease could be caused by chemical shrinkage. At a certain point in time, there is a transition from a slurry to a viscoelastic solid enabling the registration of expansion by a pressure increase. When portlandite is depleted, the composition of the reaction products should shift from C-S-H with a relatively high Ca/Si-ratio towards C-S-H with a relatively low Ca/Si-ratio (and possibly high alkali content) and towards alkali-silicate-hydrates (A-S-H). The formation of A-S-H is indicated as well by the decrease of the sodium concentration in the pore solution. This state of the reaction goes together with the pressure increase. The composition of these reaction products is comparable to reaction products in concrete aggregates; they typically have a low Ca/Si-ratio and relatively high alkali content [17-21]. The pressure in the samples MS20 and MS40 increases later compared to sample MS10 because it takes longer for calcium depletion to occur. On the other side, an earlier pressure increase is observed in the samples MS, MS2.5 and MS5 as portlandite is absent or present in only small amounts.

The formation of C-S-H results mainly in Q_1, Q_2 -sites while the formation of A-S-H mainly results in Q_3 -sites [12,15]. Garcia [22] observed an increase of porosity during the formation of Q_3 -sites in a system with amorphous SiO_2 and alkaline solutions. Consequently, it can be expected that the observed pressure increase goes together with the formation of Q_3 -sites. However, the composition of the reaction products during the entire reaction has to be confirmed by data from nuclear magnetic resonance measurements (NMR).

All samples MS to MS40 show about the same amount of Q_3 -sites [15]. If mainly the formation of C-S-H with a low Ca/Si-ratio and A-S-H containing a high amount of Q_3 -sites is responsible for the pressure increase, the relatively small difference in pressure of the different samples (after 14 days) seems reasonable. The differences in pressure are then mainly caused by the differences in their elastic properties, as discussed above.

The observed deformations and pressure changes apply to autogenous conditions. In an open system where a transport of water to the reaction site is possible, the differences in volume and pressure between the studied samples may change significantly.

5 CONCLUSIONS

A model system with micro silica, portlandite and alkaline solution was used to measure autogenous strain and pressure development under restrained conditions. The results were compared with the ones of a previous study in which the same model system was used.

- Autogenous deformations result in pressure changes shown by the same dependence of these two parameters on portlandite content after a reaction time of 144 hours.

- The amount of reacted micro silica and amount of C-S-H formed at the end of the reaction have no major influence on the resulting pressure. Their effect on pressure is likely based on the E-modulus that can be expected to increase with increasing portlandite content.
- Pressure starts to develop after the main hydration occurred, as shown by the comparison with heat flow.
- Pore solution composition indicates that the pressure increases after the system is depleted in calcium. Therefore, the pressure increase seems to go together with the formation of C-S-H with low Ca/Si-ratio and A-S-H.
- NMR measurements are needed to verify the hypothesis of pressure increase as a result of the formation of Q₃-sites typical for A-S-H.

6 ACKNOWLEDGEMENT

The author would like to thank P. Lura for fruitful discussions and valuable input to this study.

7 REFERENCES

- [1] Stanton, TE (1940): Expansion of concrete through reaction between cement and aggregate. *Proceedings of the American Society of Civil Engineers* (66): 1781–1811.
- [2] Vivian, HE (1950): The reaction products of alkalis and opal. *Studies in Cement-Aggregate reaction*. Commonwealth Scientific and Industrial Research Organization, Australia, CSIRO Bulletin (256): 60-81.
- [3] Powers, TC, and Steinmour, HH (1955): An interpretation of some published researches on the alkali-aggregate reaction. Part I: The chemical reaction and mechanism of expansion. *Journal of the American Concrete Institute* (26): 497-516.
- [4] Glasser LSD, and Kataoka, N (1982): On the role of calcium in the alkali-aggregate reaction. *Cement and Concrete Research* (12): 321-31.
- [5] Diamond, S (1989): ASR - another look at mechanisms. In: Okada, K, Nishibayashi, SN, and Kawamura M: *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction in Concrete*. Elsevier Applied Science, Kyoto, Japan: 83-94.
- [6] Wang, H, and Gillott, JE (1991): Mechanism of alkali-silica reaction and the significance of calcium hydroxide. *Cement and Concrete Research* (21): 647-54.
- [7] Helmuth, R, Stark, D, Diamond, S, and Moranville-Regourd M (1993): Alkali-silica reactivity: An overview of research. *Strategic Highway Research Program, National Research Council, Washington DC*.
- [8] Cong, XD, Kirkpatrick, RJ, and Diamond S (1993): 29Si MAS NMR spectroscopic investigation of alkali silica reaction product gels. *Cement and Concrete Research* (23): 811-23.
- [9] Wieker, W, Hubert, C, Heidemann, D, and Ebert, R (1998): Alkali-aggregate reaction- a problem of the insufficient fundamental knowledge of its chemical base. In: Cohen, M, Mindess, S, and Skalny, J (editors): *Proceedings of the Sidney Diamond Symposium on Materials Science and Engineering of Concrete and Cementitious based Composites*. Materials Science of Concrete, American Ceramic Society, Westerville, OH: 395–408.
- [10] Thomas, MDA (2001): The role of calcium hydroxide in alkali recycling in concrete. In: Skalny, J (editor): *Proceedings of the Workshop on the Role of Calcium Hydroxide in Concrete*. Materials Science of Concrete, American Ceramic Society, Westerville, OH: 225–236.
- [10] Struble, LJ, and Diamond, S (1981): Swelling Properties of Synthetic Alkali Silica Gels. *Journal of American Ceramic Society* (64): 652-655.
- [11] Hou, X, Struble, LJ, and Kirkpatrick, RJ (2004): Formation of ASR gel and the roles of C-S-H and portlandite. *Cement and Concrete Research* (34): 1683-1696.

- [13] Kirkpatrick, RJ, Kalinichev, AG, Hou, X, and Struble, L (2005): Experimental and molecular dynamics modeling studies of interlayer swelling: water incorporation in kanemite and ASR gel. *Materials and Structures* (38): 449-458.
- [14] Mansfeld, T (2008): Das Quellverhalten von Alkalisilikatgelen unter Beachtung ihrer Zusammensetzung (Expansion behaviour of alkali silicate gels considering their composition), Doctoral Thesis, Bauhaus-Universität Weimar, Germany.
- [15] Leemann, A, Le Saout, G, Winnefeld, F, Rentsch, D, and Lothenbach B (2011): Alkali-silica reaction: the influence of calcium on silica dissolution and the formation of reaction products. *Journal of the American Ceramic Society* (94) 1243-1249.
- [16] Lura, P, and Jensen, OM (2007): Measuring techniques for autogenous strain of cement paste. *Materials and Structures* (40): 431-440.
- [17] Knudsen, T, and Taulow, N (1975): Quantitative microanalyses of alkali-silica gel in concrete. *Cement and Concrete Research* (5): 443-454.
- [18] Thaulow, N, Jakobson, UH, and Clark, B (1996): Composition of alkali silica gel and ettringite in concrete railroad ties: SEM-EDX and X-ray diffraction analysis. *Cement and Concrete Research* (26): 309-318.
- [19] Kawamura, M, and Iwahori, K (2004): ASR gel composition and expansive pressure in mortars under restrained conditions. *Cement and Concrete Composites* (26): 47-56.
- [20] Katayama, T (2008): ASR gel in concrete subject to freeze-thaw cycles - comparison between laboratory and field concretes from Newfoundland, Canada. In: *Proceedings of the 13th International Conference on Alkali-Aggregate Reaction in Concrete*, Trondheim, Norway.
- [21] Leemann, A, and Merz, C. (2012): An attempt to validate the concrete performance test with the degree of AAR-induced damage observed in concrete structures. Submitted to the 14th ICAAR.
- [22] Garcia-Diaz, E, Riche, J, Bulteel, D, and Vernet, C (2006): Mechanism of damage for the alkali-silica reaction. *Cement and Concrete Research* (36): 395-400.

TABLE 1: Composition of MS (L.O.I. = loss on ignition).

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	Mn ₂ O ₃	P ₂ O ₅	Cl	F	SrO	L.O.I.
92.8	0.94	0.13	0.36	0.74	0.54	1.09	0.39	0.01	0.03	0.05	0.12	0.07	0.01	2.66

TABLE 2: Mixtures for pressure measurements.

parts of NaOH solution per part of solid and molarity of the solution	MS	MS 2.5	MS5	MS10	MS20	MS40
1.8p 1.0M	x ¹	x ¹	x ¹	x ^{1,2}	x ^{1,2}	x ^{1,2}
1.4p 1.3M	-	-	-	x	x	x
1.1p 1.65M	-	-	-	x	x	x

¹: samples used for measurements of autogenous shrinkage
²: samples used for measurement of compressive strength

TABLE 3: Pressure after 14 days.

parts of NaOH solution per part of solid and molarity of the NaOH solution	pressure [MPa]					
	MS	MS	MS5	MS10	MS20	MS40

		2.5				
1.8p 1.0M	0.31	0.41	0.42	0.55	0.47	0.62
1.4p 1.3M	-	-	-	0.63	0.78	0.37
1.1p 1.65M	-	-	-	0.69	0.84	0.40

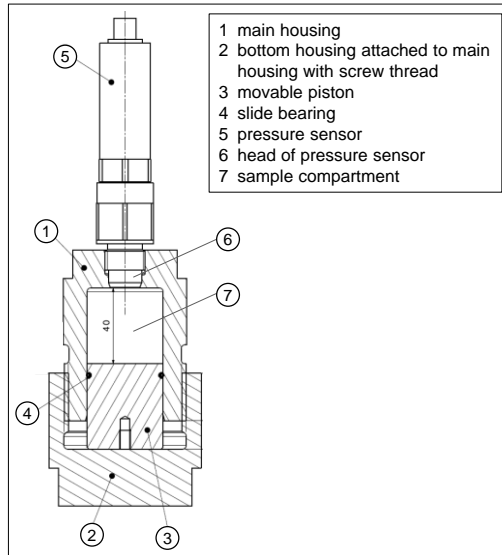


FIGURE 1: Pressure cell (height of sample compartment given in millimeters).

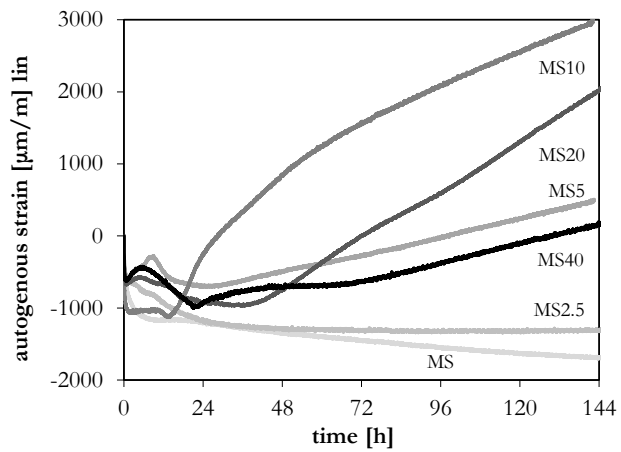


FIGURE 2: Autogenous strain of MS, MS2.5, MS5, MS10, MS20 and MS 40 as a function of time.

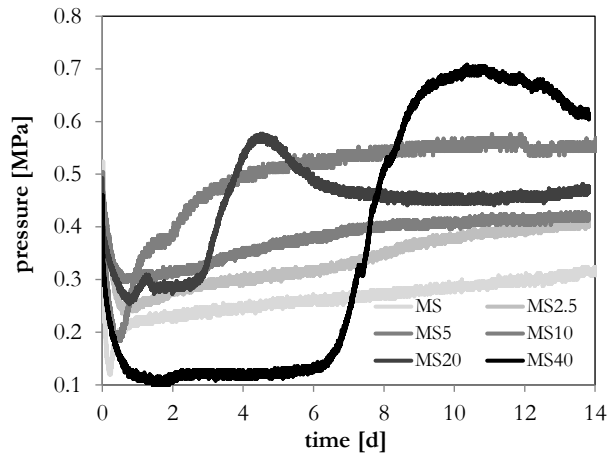


FIGURE 3: Pressure of MS, MS2.5, MS5, MS10, MS20 and MS 40 as a function of time.

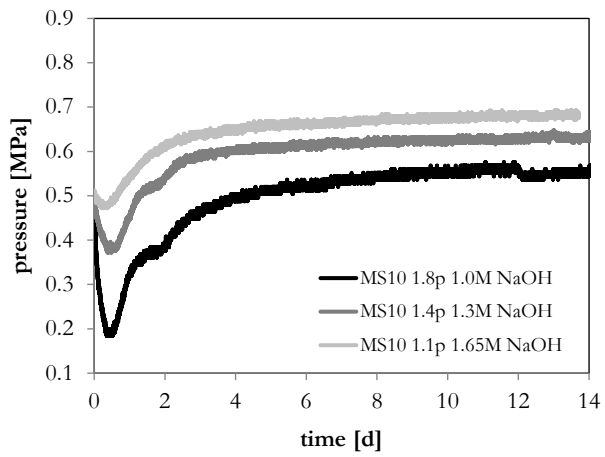


FIGURE 4: Pressure as a function of time of MS10 in NaOH.

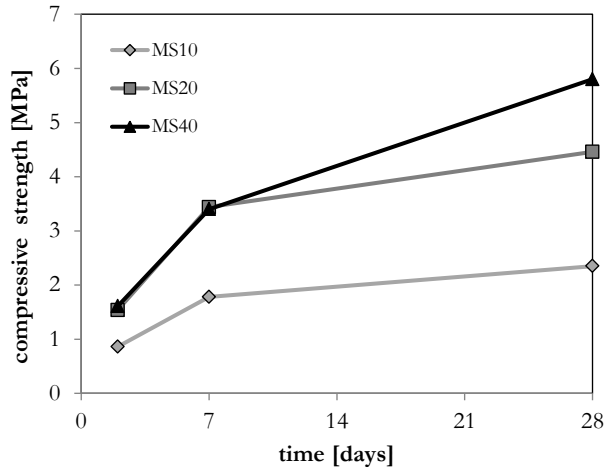


FIGURE 5: Compressive strength of samples MS10, MS20 and MS40 as a function of time.

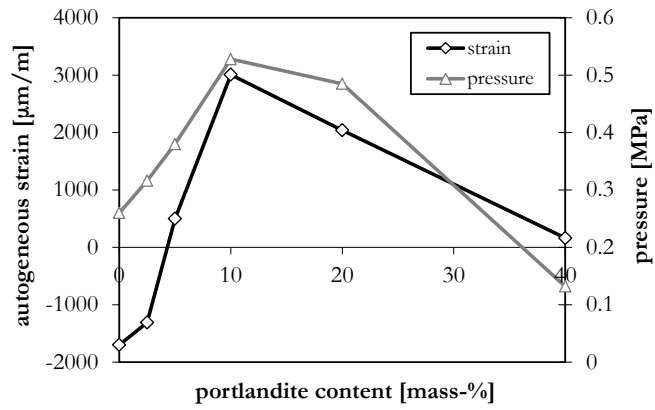


FIGURE 6: Autogenous strain and pressure after a reaction time of 144 h as function of portlandite content (samples MS-MS40, mass-ratio solid:NaOH (1M) = 1:1.8).

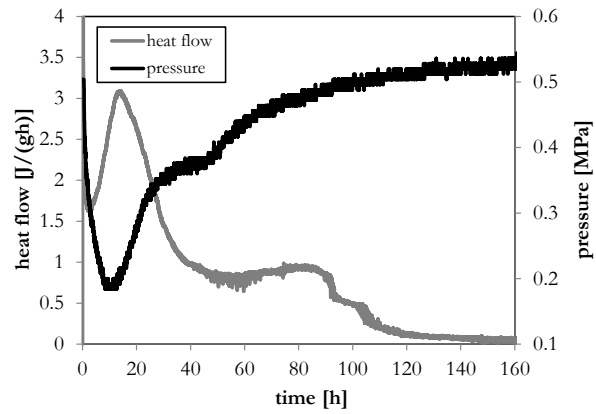


FIGURE 7: Heat flow and pressure as a function of time of MS10 in 1M NaOH (mass-ratio solid:liquid = 1:1.8).

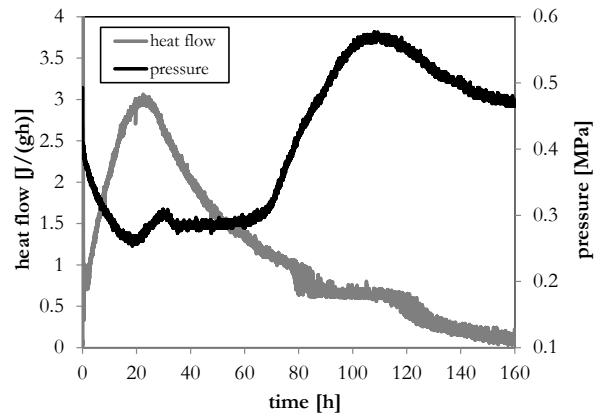


FIGURE 8: Heat flow and pressure as a function of time of MS10 in 1M NaOH (mass-ratio solid:liquid = 1:1.8).

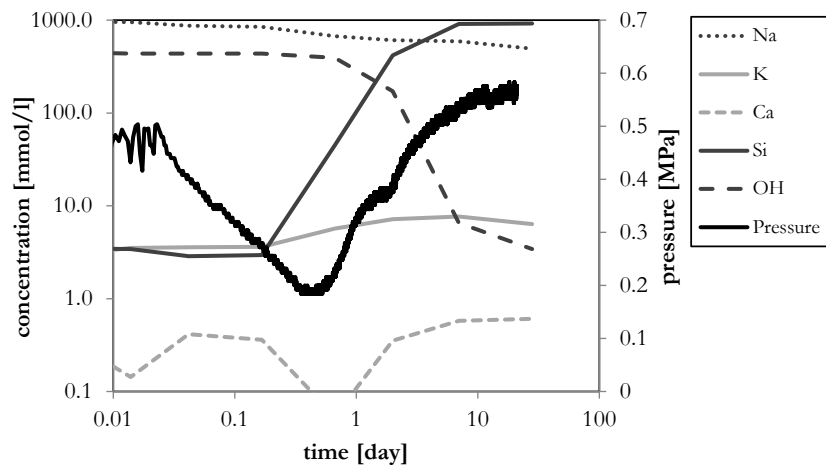


FIGURE 9: Composition of the pore solution and pressure as a function of time (MS10 in 1M NaOH, mass-ratio solid:liquid = 1:1.8).