

DEPENDENCE BETWEEN THE COMPOSITION OF PORE SOLUTION AND THE EXPANSION OF MORTAR CONTAINING REACTIVE AGGREGATE

ZDZISŁAWA OWSIAK

Technical University of Kielce, Al.1000-lecia P.P.7, 25-314 Kielce, Poland

E-mail: owsiak@tu.kielce.pl

Submitted July 9, 2004; accepted November 23, 2004

Keywords: Alkali-silica reaction, Mortar, Pore solution, Expansion measurement

The study deals with the investigation of changes of sodium and potassium hydroxide concentrations in the mortar pore solution and related material expansion. The experiments following the alkali-silica reaction were carried out on a model mixture of opal as reactive aggregate component and cements having different alkali content. The pore solution was obtained by extraction of the crushed mortar with hot water. The molar sodium-potassium hydroxides ratio in the mortar pore solution is similar to the sodium-potassium ratio in cement. The decrease of alkali concentration in the solution with time and the increase of mortar expansion are proportional. Mortar expansion increases as a result of expansion pressure generated by products of the alkali-silica reaction. The time change of the alkali concentration in the solution is not affected by C_3A content in cement.

INTRODUCTION

The interaction between aggregate and cement paste significantly influences the functional properties and durability of concrete. On the other hand, products of the chemical reaction of paste with aggregate can be the cause of destructive changes of concrete. For several decades there have been many reports about the harmful chemical reaction of aggregate with the surrounding cement paste in concrete, especially with the concrete pore solution [1]. Of greatest significance for these processes are sodium and potassium ions occurring in the concrete pore solution. The alkali reaction with aggregate in concrete is connected with both the occurrence of reactive aggregate and the alkali content in concrete, the content of sodium and potassium oxides in cement having the greatest effect. Different components of cement and concrete, e.g. mineral additions as well as aggregates containing considerable amounts of active alkali and alkali from the external environment can also increase the alkali content.

The alkali-aggregate reaction between the mortar or concrete pore solution and certain kinds of aggregate leads to concrete expansion and causes its cracking and destruction. The mentioned problems of alkali reaction with aggregate are not fully explained and a very complex course of these processes requires further research. This reaction is very slow and its outcome can be revealed after many years. For the course of alkali-silica reaction the composition of the pore solution in con-

crete is important, particularly - active alkali content in concrete and also aggregate reactivity. The concentration of ions presented in the concrete pore solution changes with the formation of reaction products; hence the onset and the course of reaction can be predicted on the basis of the composition of pore solution.

The investigation of the alkali-silica reaction was carried out on model arrangements containing opal as an aggregate component reactive with alkali as well as cements of different alkali content. The investigation concerned changes of concentrations of sodium and potassium hydroxides in the mortar pore solution and the related expansion.

The alkali content in the pore solution

Earlier investigations concerned the estimation of changes occurring in pore solution of cement paste in the initial stage of cement hydration, and samples of the solution obtained by filtering the cement paste prior to bonding were analysed [2]. A considerable progress in the study of the composition of solution in pores of cement paste is due to the use of devices for pressing the solution out from mature cement pastes, mortars or concretes, using pressures of a few hundred MPa [3]. The volume of expressed pore solution typically obtained represents only a small fraction of the total solution residing within hydrated cement paste. This is one of reservations, which imply that the analysed composition

cannot be representative. It is very probable that the height and duration of the applied pressure may have some effect on the composition of the exuded solution. However, this method is recognised as sufficient for the analysis of pore solution from a mature cement paste [4].

Pressing the solution under high pressure out from the pores of hardened concrete is very difficult. Therefore, an alternative way is used for determining the alkali content in concrete pore solution through their extraction from ground concrete with hot water. Determining the alkali content in pore solution and the content the pore solution in concrete (the volume of pore solution in concrete), the content of active alkali in 1m^3 of concrete is also calculated [5]. The method of alkali extraction with hot water was applied in Canada for the determination of the content of alkali in concrete pore solution (alkali soluble in water, alkali active in concrete) as opposed to the total alkali content, frequently assumed as alkali contained in cement. In concretes a considerable part of alkali remains built in products of cement hydration, and in the presence of the alkali-silica reaction, silica is also built in the products of this reaction [5]. Earlier investigations [6], [7] show that hydrates of Portland cement contain 0.4-0.5 % of Na_2O_e , which approximates the determined content 0.37 % [5]. The results of Diamond [8], Duchesne and Berube [7] also show that the alkali content included in cement hydrates is proportional to alkali in cement. According to this, it is most frequently assumed that about 40 % of the total alkali from cement is included in hydration products. This leads to accepting a safe border of the active alkali content in concrete at the quantity of 1.8 kg/m^3 , at the total alkali content equal to 3 kg/m^3 .

In many investigations considerable changes in the composition of the pore solution have been reported in concretes in which the alkali-silica reaction occurred in comparison with pore solutions from identical concretes but without reactive aggregate [5], [9], [10], [11]. Basing on the results of the above investigation it is possible to assume that during extraction with hot water only alkali present in the concrete pore solution are washed out, whereas alkali included in the products of cement hydration as well as products of alkali reaction with silica remain in the material.

Taylor [12] calculated the predicted concentration of sodium and potassium ions in the cement paste pore solution, assuming that all alkalis from cement pass to solution. He stated that only 42 % of alkali occurs in the solution in pores, and the remaining quantity is bonded with hydration products. In turn, Berube et al. [13] showed that when hydration is completed about 40 % of alkali are found in hydration products and that is why they cannot take part in a reaction with aggregate. Divergences in the observed concentrations result from

the fact that in concretes the concentration of sodium and potassium hydroxides in the pore solution depends on many factors, first of all on the alkali content in the cement used, cement content in concrete and on the W/C ratio in concrete mix. With time and with a greater part of hydrated cement phases, the volume of pore solution is reduced and an increased alkali concentration can be observed. Moreover, drying can cause that some part of the concrete forms local concentrations higher than average ones [9].

EXPERIMENTAL

For the course and scope of reaction it is essential to know the composition of the concrete pore solution. It is also important to know the change of alkali ion concentrations during the alkali-silica reaction as well as the dependence between the compositions of the concrete pore solution and linear changes of concrete, which are the outcome of expansion.

The experimental part of this study was based on the investigation of the reaction alkali-silica in a model arrangement. Standard sand with a known addition of opal was used as aggregate, and cements had a diverse content of alkali and tricalcium aluminate.

The investigation included:

- change of mortar bars according to ASTM C227 [14];
- analysis of the composition of solution in mortar pores during the alkali-silica reaction.

In the investigation Portland cements CEM I were applied. They were obtained by grinding industrial clinkers to the value $370\text{ m}^2/\text{kg}$. The chemical and mineral composition of clinkers is shown in table 1. Selected cement clinkers had a varied content of tricalcium aluminate from 2 %, through average 7 % to a high content equal to 12 %. Increase of the alkali content was achieved by adding K_2SO_4 to particular cements. The total SO_3 content in cements was 3.0 %, the alkali content, expressed as Na_2O_e , was 0.35%, 0.7%, 1.1%, and 1.5% in cements A and B; and 0.94%, 1.1% and 1.5% in cement C.

Opal was used as a model reactive aggregate. Opal grain size distribution and its amount in aggregate affect the size of expansion [6]. In the experiment there was used opal of grain size distribution 0.5 to 1 mm in the quantity of 4% in relation to the mass of standard quartz sand.

The investigation of the expansion of mortar bars was carried out in accordance with ASTM C 227 [14]. The pore solution was obtained by applying extraction of the solution from crushed mortar with hot water [5]. All samples were crushed to grain-size distribution below $160\text{ }\mu\text{m}$. Two samples of 10 g of crushed mortar

were boiled for 10 minutes in 100 ml of distilled water; next the samples were left for one day at room temperature. After this time the suspension was filtered and the remaining solid parts were washed with distilled water replenishing filtrate to 100 ml. Concentrations of Na and K in the solution were determined by the method of atomic absorption spectrometry.

Table 1. Chemical and mineral composition of clinkers used in the investigation, (%).

Compositions	Cement samples		
	A	B	C
Loss on ignition	0.20	0.38	0.20
Insoluble parts	0.00	0.20	0.10
SiO ₂	22.41	23.25	21.20
Al ₂ O ₃	4.26	4.67	6.40
Fe ₂ O ₃	5.46	3.45	2.80
CaO	66.68	66.61	66.29
MgO	0.82	0.91	2.70
SO ₃	0.31	0.12	0.10
CaO _w	0.33	1.59	0.69
Na ₂ O	0.26	0.1	0.15
K ₂ O	0.14	0.38	1.20
Na ₂ O _e	0.35	0.35	0.94
C ₃ S	60	52	59
βC ₂ S	19	28	16
C ₃ A	2	7	12
C ₄ AF	17	11	9

RESULTS AND DISCUSSION

The results of the investigation of composition of the mortar pore solution after 1, 4, 12 and 26 weeks are represented in figure 1. The change in time of sodium and potassium hydroxides content in the mortar pore solution with reactive aggregate depends mostly on the alkali content in cement. At a small alkali content in cement up to 0.35% Na₂O_e, the sum concentration of sodium and potassium hydroxides in the mortar pore solution changes slowly. However, with the increasing alkali content in cement, the concentration of sodium and potassium hydroxides in the solution decreases with curing time. For the alkali content 1.5% it decreases by over 40% between the first and the 26th week of concrete curing. In the solution in mortar pores, already with the content of Na₂O_e of 0.7% in cement, after 26 weeks the concentration of sodium and potassium hydroxides is still so high that the reaction may continue. The alkali border concentration in the mortar pore solution below 0.250 mol/litre [15], recognized as safe, occurs only in mortar from cement containing 0.35 % of Na₂O_e (see table 2). The sodium and potassium hydroxides content ratio in the pore solution in mortars with reactive aggregate after each period of time was similar to the sodium-potassium ratio in cement, which proves that sodium and potassium are bonded by the products of alkali-silica reaction in proportions reflecting their content in cement. This regularity does not occur only in the case of the cement A-0.35, which contained more sodium (0.26%) than potassium (0.14%), whereas in the pore solution in mortar the sodium and potassium contents are approximately equal.

Table 2. Alkali content in mortar pore solution.

Sample	After 12 weeks					Initial alkali content in mortar	
	NaOH (mol/dm ³)	KOH (mol/dm ³)	Na ₂ O _e (mol/dm ³)	NaOH/KOH in solution	Na ₂ O _e (kg/m ³)	Na ₂ O _e (kg/m ³)	Na ₂ O/K ₂ O in cement
A-0.35	0.112	0.121	0.192	0.92	1.32	2.07	1.86
A-0.7	0.131	0.352	0.362	0.37	2.51	4.14	0.39
A-1.1	0.104	0.520	0.446	0.20	3.24	6.45	0.20
A-1.5	0.118	0.649	0.545	0.18	3.96	8.80	0.14
B-0.35	0.046	0.192	0.173	0.24	1.15	2.25	0.24
B-0.7	0.054	0.434	0.340	0.12	2.38	4.14	0.11
B-1.1	0.052	0.794	0.574	0.06	4.37	6.45	0.07
B-1.5	0.048	0.893	0.635	0.05	4.84	8.80	0.05
C-0.94	0.056	0.776	0.567	0.07	3.77	5.75	0.07
C-1.1	0.085	0.634	0.502	0.13	3.65	6.45	0.10
C-1.5	0.089	0.875	0.665	0.10	4.83	8.80	0.07

Composition of the pore solution in mortar in the presence of reactive aggregate

In all mortars with reactive aggregate (quartz sand with addition of opal) there was observed a decrease of the concentration of sodium and potassium hydroxides in the pore solution as a function of duration of the alkali-silica reaction. The change in concentration of sodium and potassium hydroxides in the pore solution in mortar with reactive aggregate depending on time has a similar development regardless of the mineral composition of the cement used (without regard to a different C₃A content in cement) (see figure 2).

Decrease in the concentration of sodium and potassium hydroxides in the pore solution clearly depends on the alkali content in cement. Between the first and the twenty-sixth week the concentration changes by 0.072 mol/dm³ in the case of cement containing 0.35%

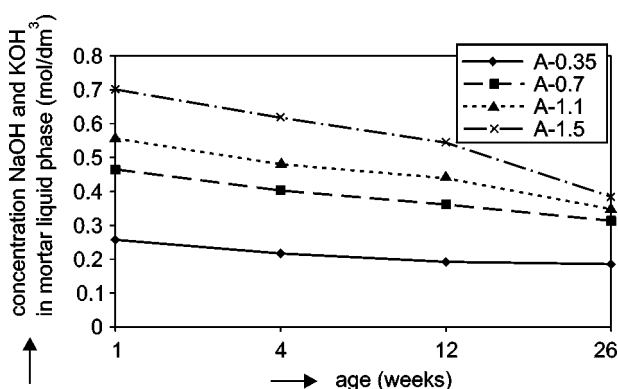


Figure 1. The sum of sodium and potassium hydroxide concentrations in mortar pore solution from cement A with a different alkali content vs. time.

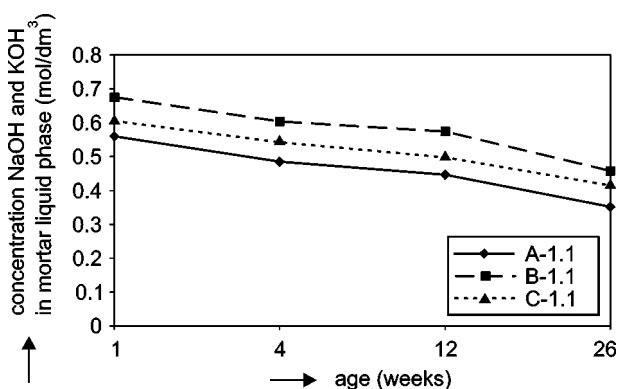


Figure 2. The concentration of sodium and potassium hydroxides in mortar pore solution from reactive aggregate and with different cement content C₃A vs. time.

Na₂O_e, and by 0,317 mol/dm³ for cement containing 1.5% Na₂O_e, (see figure 1). This is connected with a faster course of reaction with a higher alkali content, the result of which is the formation of reaction products and the decrease in concentration of alkalis in the pore solution. The decrease in the alkali content and hydroxyl ions shows that the alkali-silica reaction has occurred. The change in the composition of the pore solution recorded in the studied mortars is similar to that published in the literature for reactive aggregates [5], [9], [16].

The diagram (see figure 3) of the alkali content in the pore solution of the analysed mortars after twelve weeks shows that in mortars with cements containing only 0.3 % of Na₂O_e, the alkali content in the pore solution is lower than the limit content (1.8 kg/m³). However, in all the remaining mortars the alkali content is still so high that the alkali-aggregate reaction may continue. This is reflected by the size of the measured expansion of mortar samples. The more alkalis there were in cement, the higher was the use of alkalis in the reaction, and the course of the reaction was faster, which is proved by the volume of expansion (see figures 4 to 6).

Dependence between the composition of the pore solution and the mortar expansion

The properties of expanding mortar caused by a progressive alkali-silica reaction depend on the concentration of sodium and potassium ions and hydroxide ion in the pore solution. This is confirmed by the investigation of the dependence of mortar expansion caused by the alkali-silica reaction on the concentration of alkali ions and hydroxide ions in the pore solution carried out

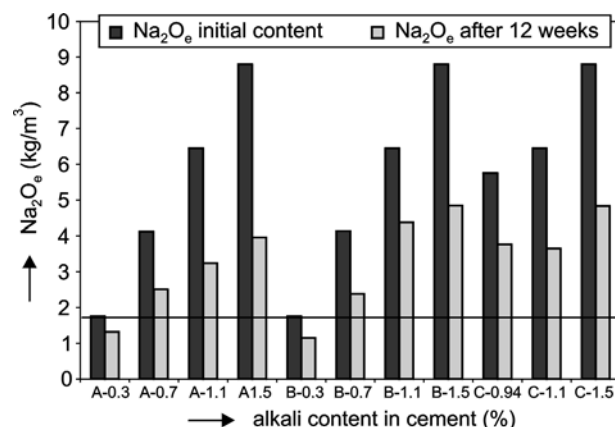


Figure 3. Alkali content in mortar pore solution with reactive aggregate vs. alkali content in cement.

by Diamond and others [17], or the later investigation of Seno [18]. The results of the investigations of linear changes of mortar with time and the concurrent changes of the concentration of sodium and potassium hydroxides in the mortar pore solution presented in figures 4 to 6 show that in this reaction alkali are bonded by reaction products and as a result of this process the phenomenon of mortar expansion is observed. In the initial period expansion pressure is relatively low but later it increases gradually, and even after 6 months it still increases, whereas decrease in the content of sodium and potassium ions is considerable after 4 weeks, and it is the higher, the higher was the total alkalis content in cement. Initial decrease in the content of sodium and potassium ions in the pore solution corresponds to the first stage according to Diamond [8], in which sodium-potassium silicate gel is formed in order to bond sodium and potassium ions in its structure. The pressure increase in this stage results from the formation of the product of alkali-silica reaction in a space limited by hardened cement paste. In the second stage change in the pressure of expansion is connected with water absorption by the gel.

Cement containing more sodium and potassium produces more reaction products, which is confirmed by greater expansion and a more reduced concentration of sodium and potassium hydroxides in the mortar pore solution. These dependences are in accordance with the observations of Seno [18]. Determination of changes in the concentration of alkali ions in the pore solution can be used for the estimation of aggregate reactivity and the degree of mortar expansion.

When considering the effect of the composition of the concrete pore solution on expansion generated by the alkali-silica reaction, it is necessary to take into account the role of water. It is generally believed that in the alkali-silica reaction, the degree of concrete moisture plays an essential role and it is often observed that concrete destruction occurs when moisture is high enough. However, there are different opinions as on the content of free water, the level of which depends on the total alkali content. The critical content of free water below which reaction and concrete expansion are stopped due to the shortage of water has not yet been determined. However, these processes can be quickly resumed when free water appears in the system [19], [20]. Therefore, expansion inhibition can be achieved by controlling the moisture content in concrete [21]. On the other hand, the development of expansion by providing water from outside to concrete cores cut out from the structure in which the alkali-silica reaction occurs can be helpful for the estimation of the remaining potential expansion in moisture inflow from the external environment.

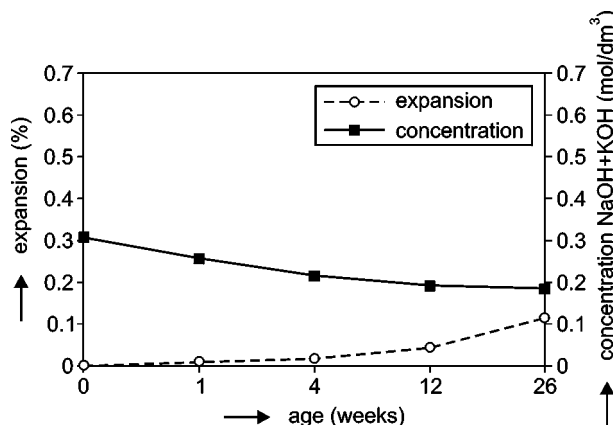


Figure 4. The concentration of sodium and potassium hydroxides in pore solution and mortar expansion ($\text{Na}_2\text{O}_e = 0.3 \%$) vs. time.

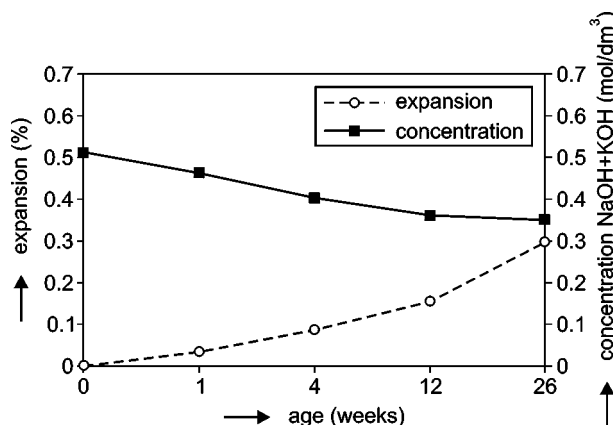


Figure 5. The concentration of sodium and potassium hydroxides in pore solution and mortar expansion ($\text{Na}_2\text{O}_e = 0.7 \%$) vs. time.

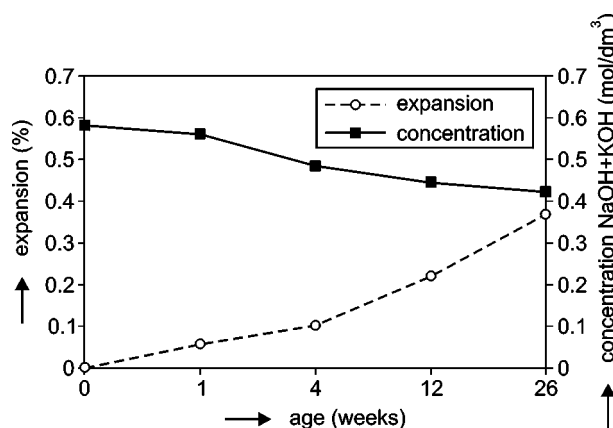


Figure 6. The concentration of sodium and potassium hydroxides in pore solution and mortar expansion ($\text{Na}_2\text{O}_e = 1.1 \%$) vs. time.

CONCLUSIONS

The following conclusions can be formulated from the results of the reported investigation of alkali reaction with silica aggregate:

- The decrease in the content of sodium and potassium ions in the mortar pore solution depends on the alkali content in cement.
- The time change of the concentration of sodium and potassium hydroxides in the pore solution in mortar with reactive aggregate has a similar course, which is not affected by C_3A content in cement.
- The molar sodium-potassium hydroxides ratio in the pore solution in mortar with reactive aggregate was similar to the same ratio in cement. This fact indicates that sodium and potassium are bonded by products of the alkali-silica reaction in proportions reflecting their content in the cement.
- The decrease of sodium and potassium hydroxide concentration in mortar pore solution and the increase of mortar expansion are proportional. Mortar expansion increases as a result of expansion pressure generated by products of the alkali-silica reaction.
- The determination of the content of potassium and sodium ions in the concrete pore solution followed by the comparison with limiting content $1.8 \text{ kg/m}^3 \text{ Na}_2\text{O}_e$ makes possible to predict whether the alkali-silica reaction will continue.

Acknowledgement

The presented work was part of the research project financially supported by the State Committee for Scientific Research under grant No 8 TO7E 026 20.

References

1. Nixon P. J., Page C. L. in: *Concrete Durability*, SP 100, 2, p. 1833-1869, Ed. J. M. Scanlon, American Concrete Institute, 1987.
2. Bailey J. E., Hampson C. J.: *Cem.Concr.Res.* 12, 227 (1982).
3. Loguet P., Burglen L., Zelwer A.: *Rev.Mat.Constr.* 676, 35 (1973).
4. Rogers C. A., Hooton R. D.: *Cem.Concr.Aggr.* 13, 42 (1993).
5. Berube M. A., Frenette J., Rivest M., Vezina D. in: *Alkali-Aggregate Reaction in Concrete*, pp.159-168, Ed. Berube M. A., Fournier B., Durand B., Laval Universities, Quebec 2000.
6. Taylor H. F. W.: *Cement chemistry*, Academic Press Ltd., London 1990.
7. Duchesne J., Berube M. A.: *Advanced Cement Based Materials* 2, 1 (1994).
8. Diamond S. in: *Alkali-Aggregate Reaction* p.83-89, Ed. Okada K., Nishibayashi S., Kawamura M., The Society of Materials Science, Kyoto 1989.
9. Diamond S. in: *Alkalies in Concrete*, p.155-166, Ed. G. M. Idorn, Technical University of Denmark, Copenhagen 1983.
10. Owsiak Z.: *Cement Wapno Beton* 4, 151 (2001).
11. Owsiak Z.: *Cement Wapno Beton* 2, 67 (2001).
12. Taylor H. F. W.: *Advances in Cement Research* 1, 5 (1987).
13. Berube M. A., Frenette J., Pedneault. A., Rivest M. in: *Alkali-Aggregate Reaction in Concrete*, p.821-830, Ed. Berube M. A., Fournier B., Durand B., Laval Universities, Quebec 2000.
14. ASTM C 227. Standard Test Method for Potential Alkali Reactivity of Cement-Aggregate Combinations. Annual Book of ASTM Standards, Section 4, vol. 04.02. (Mortar-Bar Method) 1997.
15. Kagimoto H., Sato M., Kawamura M. in: *Alkali-Aggregate Reaction in Concrete*, p.859-868, Ed. Berube M. A., Fournier B., Durand B., Laval Universities, Quebec 2000.
16. Berube M. A., Dorion J. F., Rivest M. in: *Alkali-Aggregate Reaction in Concrete*, p.139-148, Ed. Berube M. A., Fournier B., Durand B., Laval Universities, Quebec 2000.
17. Diamond S., Barneyback R. S., Struble L. L. in: *Alkali-Aggregate Reaction in Concrete*, p. 1, Cape Town, Paper S252/22, 1981.
18. Seno Y., Kobayashi K. in: *Alkali-Aggregate Reaction* p.141-146, Ed. Okada K., Nishibayashi S., Kawamura M., The Society of Materials Science, Kyoto 1989.
19. Larive C., Laplaud A. in: *Alkali-Aggregate Reaction in Concrete*, p. 61-70, Ed. Berube M. A., Fournier B., Durand B., Laval Universities, Quebec 2000.
20. Tomosawa F., Tamura K., Abe M. in: *Alkali-Aggregate Reaction* p.881-885, Ed. Okada K., Nishibayashi S., Kawamura M., The Society of Materials Science, Kyoto 1989.
21. Olafsson H. in: *Concrete Alkali-Aggregate Reactions*, p. 461-465, Noyes Publications, New Jersey 1986.

ZÁVISLOST MEZI SLOŽENÍM ROZTOKU V PÓRECH A EXPANZÍ MALTY OBSAHUJÍCÍ REAKTIVNÍ PLNIVO

ZDZISŁAWA OWSIAK

*Technical University of Kielce,
Al.1000-lecia P.P.7, 25-314 Kielce, Poland*

Studie se zabývá sledováním změn koncentrace hydroxidu sodného a draselného v pórech malty ve vztahu k expanzi materiálu. Experimenty zkoumající reakci alkálií s SiO_2 byly prováděny v modelové směsi opálu jako reaktivního plniva a cementů s odlišným obsahem alkálií. Roztok z pórů malty byl získán extrakcí rozdrčené malty horkou vodou. Molární poměr hydroxidu sodného a draselného v roztoku v pórech je podobný tomuto poměru v cementu. Pokles koncentrace alkálií v roztoku s časem a expanze malty jsou si navzájem úměrné. Expanze malty roste následkem růstu tlaku vytvářeného produkty reakce alkálií s SiO_2 . Časová změna koncentrace alkálií v roztoku není ovlivněna obsahem C_3A v cementu.