Autoclaving of alkali-activated materials

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Abstract. Alkali-activated materials are amorphous materials that look like natural stone or a concrete structure. As in the case of concrete, on the surface of alkali-activated materials, a white coating appears in the form of efflorescence. For conventional efflorescent concrete, the reaction between Ca(OH)$_2$ with water and CO$_2$ is generally harmless, except for the discoloration. In the case of alkali-activated materials, efflorescence can be a big problem, especially if they are exposed to moisture or in contact with water. The white efflorescence on the surface of the materials is sodium carbonate heptahydrate $\text{Na}_2\text{CO}_3\cdot7\text{H}_2\text{O}$ [1]. Various chemicals to prevent primary and secondary efflorescence can be used to reduce the appearance of the efflorescence. In the case of alkali-activated materials, this is a more complex process. The following paper proposes the use of hydrothermal processing during alkali-activated materials production. Hydrothermal treatment in an autoclave significantly reduced the appearance of efflorescence on the alkali-activated materials surfaces.

1. Introduction

The use of alkali activated fly ash materials is still low compared to portland cement concrete. One of the reasons is the formation of efflorescence on the surface of the materials. For conventional concrete, efflorescence involves the reaction of Ca(OH)$_2$ with water and CO$_2$ and is generally harmless. The only harmless phenomenon of such a reaction is discoloration. The intensity of carbonisation of concrete freely exposed to the external environment is greater, the greater the porosity of the concrete. the greater its susceptibility to scratches and cracks (the lower the density of the concrete mix, the greater the w/c ratio in the mix, the worse the concrete care) and the CO$_2$ concentration in the ambient air is higher [2, 3, 4, 5].

Polish Standards for concrete products (eg PN-EN 1338: 2005 - “Concrete paving stones. requirements and test methods”) and the required Technical Approvals of the Road and Bridge Research Institute allow for the occurrence of limestone efflorescence as a natural process of concrete maturation.

Commercial products are used in the form of liquid additions to a concrete mix to ensure watertight concrete surfaces. They prevent solids from absorbing capillary water. They do not affect the hydration of the cement and the hardening process of concrete, because they only become active after the setting process is completed. Since the distance between the cement grains coated with blocking preparations is very small, the surface tension of the water particles does not allow it to penetrate into the intermediate spaces. Surface preparations are also used to help to reduce efflorescence. Preparations based on polymer and silicon-lithium compounds with the highest silicate modules, thanks to penetration and hardening of concrete in the molecular structure, enables the production of a high-strength cement matrix with extreme physical and chemical properties. Additional modification
with a selective polymer binder ensures maximum sealing of the concrete by binding the concrete matrix components such that they do not contain free calcium compounds. Preparations based on lithium silicate deeply penetrate the concrete layer, reacting with free calcium hydroxide to create a hard, durable, tight and compact structure.

In the case of relatively modified materials, efflorescence can be a big problem, especially when they are exposed to moisture or contact with water. Treatments aimed at limiting efflorescence on the surface of geopolymers have been developed. These include, for example, the addition of alumina or a hydrothermal cure. The addition of alumina significantly reduces the mobility of alkali. However, reduction of efflorescence by means of hydrothermal curing can be achieved by using a curing temperature above 65°C and increasing the humidity during the process [1, 6].

2. Material and research methods
To reduce the amount of efflorescence on the surface of the elements, samples in the form of cubes were prepared in accordance with the EN 12390-1 standard for concrete. The shape and size of the samples were also selected such that tests on the characteristic compressive strength could be carried out after the hydrothermal treatment of the alkali modified materials.

2.1. The material used to make the samples
Fly ash from the Polish power plant in Skawina was used to prepare the samples. The oxide composition of the fly ash is shown in Table 1 and its morphology in Figure 1.

The mass of the samples was prepared from a mixture of dry ingredients, which included, in addition to volatile dust, sand in a 1: 1 ratio and a liquid component, which was a twelve molar (12M) alkaline solution based on sodium hydroxide and water glass. The mixture consistency was such that the ratio of fly ash to alkali was 0.4.

**Table 1.** Oxide composition of fly ash.

|          | SiO₂ | Al₂O₃ | Na₂O | CaO | Fe₂O₃ | MgO | K₂O | SO₃ | TiO₂ | P₂O₅ | BaO |
|----------|------|-------|------|-----|-------|-----|-----|-----|------|------|-----|
| [% mas]  | 55.89| 23.49 | 0.59 | 2.72| 5.92  | 2.61| 3.55| 0.16| 1.09 | 0.82 | 0.20|

**Figure 1.** Fly ash morphology.

2.2. Sample preparation
The prepared mass was mixed in a mechanical mixer and then placed in moulds that were subjected to a vibrating process on a vibrating table to remove air bubbles and uniformly fill the moulds. The mixing process lasted about 15 minutes, which had a significant impact on the dissolution of the fly dust particles.
Using the above method, three sets of samples were prepared, three samples for each hydrothermal treatment method. The samples were marked as follows: SA, SB, SC.

2.3. Autoclaving
The hydrothermal treatment was carried out in a Parr® pressure chemical reactor (autoclave).

A hydrothermal treatment was carried out in an autoclave for two sets of samples.

The SA sample was subjected to an annealing process in a laboratory dryer at a temperature of about 75°C for 24 hours. The purpose of this treatment was to determine the value limits associated with efflorescence and other parameters of the tested material.

The specimen with the SB determination was, after annealing according to the scheme for SA sample, subjected to hydrothermal treatment in an autoclave. The hydrothermal treatment in the autoclave lasted 6 hours at a temperature of 160°C with a superheated steam pressure of 9 bar.

The SC sample was subjected to an annealing process at a temperature of about 75°C for 3 hours in a laboratory drier and then was subjected to a hydrothermal treatment process in an autoclave for 6 hours at 160°C with a superheated steam pressure of 9 bar.

The hydrothermal treatment process took place at a humidity resulting from the temperature and pressure of the superheated steam. The temperature and time of the process were continuously monitored through software dedicated to the Parr® autoclave.

2.4. Compressive strength test
The compressive strength test was performed on cubic samples of 100 x 100 x 100 mm. The results of compressive strength were interpreted in accordance with PN-EN 13791 [7]. The number of samples in each series did not exceed 4. The value of the characteristic compressive strength is the smaller of the two values, according to formula (1).

\[
f_{ck,is} = \min \{f_{cm(n),is} - k, f_{is,\text{lowest}} + 4\}
\] (1)

2.5. pH test
The leachate pH test was carried out 14 days after the samples were demoulded. For the first 7 days the samples were seasoned, and for the next 7 days they were immersed in distilled water. The pH of the effluent was measured using a CP-105 type pH meter.

2.6. SEM EDS study
Morphology analysis, after geopolymerisation, was performed on a scanning electron microscope of the JEOL JSM-820 company using the EDS microanalyser. Samples for SEM tests were sputtered with a thin layer of gold on a JEOL JEE-4X vacuum sputtering machine.

3. Results

3.1. Change of sample mass
In order to determine the effect of the hydrothermal treatment after the process of alkaline activation of the materials, a measurement of the change in sample mass was carried out, the results of which are presented in Table 2. Based on the results obtained, a slight increase in the mass of samples after hydrothermal treatment can be observed. The increased mass was also maintained after 28 days of ripening at 21°C and humidity of about 50%, which may indicate a reduced porosity of the sample surface and, consequently, a reduced evaporation surface.
Table 2. Analyse sample mass.

| Samples No. | Sample mass [kg] | Geopolymerization 75 [°C] | Autoclaving 160 [°C] | Ripening |
|-------------|------------------|---------------------------|----------------------|----------|
|             |                  | 3 [h]                     | 24 [h]               | 6 [h]    | 28 [days] |
| SA1         |                  | 1.880                     | -                    | -        | 1.878     |
| SA2         |                  | 1.844                     | -                    | -        | 1.838     |
| SA3         |                  | 1.876                     | -                    | -        | 1.868     |
| SB1         |                  | 1.848                     | 1.912                | 1.906    | 1.906     |
| SB2         |                  | 1.850                     | 1.932                | 1.932    | 1.932     |
| SB3         |                  | 1.840                     | 1.928                | 1.928    | 1.927     |
| SC1         | 1.976            | -                         | 1.932                | 1.922    | 1.922     |
| SC2         | 1.948            | -                         | 1.906                | 1.908    | 1.908     |
| SC3         | 1.961            | -                         | 1.923                | 1.920    | 1.920     |

3.2. Compressive strength

Compressive strength tests were performed on standardized cubic samples. Samples were tested after the process of alkaline activation and autoclaving, followed by curing in stable climatic conditions of 50% humidity and 21°C for twenty-eight days. After maturing, tests on the characteristic compressive strength were carried out on a MATEST testing machine. The results of the analysis are presented in Table 3. The value of the characteristic compressive strength does not indicate clear differences between the values. A clear difference occurs in the determined measurement of uncertainty u(x), which indicates that the samples subjected to the autoclave process show a smaller dispersion of compressive strength. This is due to the introduction of the hydrothermal treatment, which significantly affects the course of the activation process, which is confirmed by the morphology presented in the SEM study in section 3.4.

Table 3. Compressive strength after 28 days of ripening.

| Samples No. | Compressive strength [MPa] |
|-------------|----------------------------|
|             | $f_c$ $f_{cm(3),is}$ $\sigma_{fcm(3),is}$ $u(x)$ $f_{ck,is}$ $f_{ck,is,cube}$ |
| SA1         | 54.24                      |
| SA2         | 43.38 49.11 4.452 9.1% 43.11 50.71 |
| SA3         | 49.70                      |
| SB1         | 45.53                      |
| SB2         | 51.36 48.34 2.382 4.9% 42.34 49.81 |
| SB3         | 48.13                      |
| SC1         | 48.03                      |
| SC2         | 47.85 47.93 0.073 0.2% 41.93 49.33 |
| SC3         | 47.92                      |
3.3. pH test

One week after the samples were demolded and seasoned in a laboratory room at a humidity of about 50% and a temperature of about 21°C, the samples were immersed to half their height in distilled water. The samples prepared in this way were soaked for a week, adding water to maintain the set level. After a week of soaking, clear eruptions were found on the SA sample. No efflorescence was found on the autoclaved samples.

After soaking, the leachate pH was tested. The results for individual samples are presented in Table 4. It can be stated that the hydrothermal treatment process slightly influenced the reduction of the effluent pH.

| Table 4. Examination of the effluent pH after soaking of geopolymer samples. |
|----------------------------------|-----------------|-----------------|
| pH                              | SA              | SB              | SC              |
|----------------------------------|-----------------|-----------------|-----------------|
| pH                              | 11.10           | 10.63           | 10.25           |

3.4. SEM EDS

Examination of the morphology of the samples on a scanning electron microscope (Fig. 2) show clear differences between the sample subjected to the process of only alkaline activation and the samples after alkaline activation and autoclaving. The SA material is characterized by a significant amount of crystallized sodium compounds, which is confirmed by the EDS studies. The EDS test result is shown in Figures 3-5.

Analysis of the content of the elements in the EDS study showed that the Al / Si weight ratio in sample SA is 0.5, while the Na / (Al + Si) weight ratio is 1.0. For the SB and SC samples, the Al / Si weight ratio is 0.6 while the Na / (Al + Si) weight ratio is 0.1. The morphology of the SB sample, relative to the SC sample, shows a greater variation, which results from the process of alkaline activation and autoclaving under various conditions, as described in section 2.3.

| Figure 2. Morphology of samples after geopolymerization and autoclaving. |
|----------------------------------|-----------------|-----------------|
| SA                              | SB              | SC              |
| 500X                             | 500X            | 500X            |
Figure 3. The characteristic x-ray spectra obtained for the marked points, sample SA.

Figure 4. The characteristic x-ray spectra obtained for the marked points, sample SB.

Figure 5. The characteristic x-ray spectra obtained for the marked points, sample SC.

3.5. Efflorescence on the surface of samples

Samples after the alkaline activation and autoclaving process were placed in containers with distilled water one week after demolding. The water level reached half the sample height. The soaking process took a week. After a week of soaking, a white efflorescence appeared on the surface of the SA sample that evolved on the surface of the sample over the following weeks. Figure 3 shows the observed efflorescence after 28 days from the start of the soaking process.

No white patches were observed on the SB and SC samples.
4. Conclusions
Carbonate efflorescence on concrete surfaces, also known as limestone, are formed as a result of carbonation of calcium hydroxide - Ca(OH)$_2$. Calcium hydroxide Ca(OH)$_2$, or portlandite, or colloquially "lime", is one of the hydration products of cement (silicate phases of portland clinker). Carbonate efflorescence arises when calcium hydroxide transported through the capillary pore system gets onto the surface of the concrete element.
The rate and intensity of carbonation is affected by both the CO\textsubscript{2} concentration and the ambient humidity. In water-saturated concrete, the carbonation process practically does not occur, while in the case of dried concrete, carbonation occurs very slowly. The best conditions for carbonation occur when a layer of water occurs on the capillary surface, in which the rapidly diffusing CO\textsubscript{2} dissolves and reacts with calcium ions. The maximum carbonation rate is in the range of 50\% to 70\% relative humidity \cite{8}.

A similar mechanism occurs in the case of geopolymers, which are often called geopolymer concrete.

The difference in the composition of the mixture of the alkaline activated materials, in relation to traditional concretes, results in the possibility of the appearance on the surface of elements of sodium carbonate heptahydrate, which is revealed quite quickly under appropriate hydrothermal conditions.

One of the solutions to this problem may be the use of hydrothermal treatment using an autoclave.

The impact of superheated steam, together with the increased pressure, results in the increase of capillary channels on the surface of the samples and causes leaching of the excess of unreacted sodium during hydrothermal treatment.

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