

# Influence of alkali-activated materials placement during curing on their dynamic parameters

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**Abstract.** The production of Portland cement has a considerable environmental impact. Its replacement with alkali-activated binders can contribute to reducing the environmental burden of building production. The paper presents partial results from our experimental research carried out on test specimens made of alkali-activated slag mortar (activated by sodium carbonate). The specimens of dimensions 40×40×160 mm differed in the manner of placement after 28 days of curing in water. The samples were tested by non-destructive methods at different ages. We observed the effect of sample storage on ultrasonic pulse velocity, dominant frequency shifts and dynamic modulus of elasticity as well as changes of these parameters over time.

## 1 Introduction

The production of Portland cement is a very energy-intensive process that also generates a significant amount of CO<sub>2</sub>. During production of Portland cement, there is approximately one tonne of carbon dioxide per tonne of Portland cement. An alternative to Portland cement binder are alkali-activated materials. These can be materials that are made from secondary raw materials (granulated blast furnace slag, fluid and high temperature fly ash, etc.). For hydration, they need water and a highly alkaline environment created by the activator (sodium hydroxide, sodium carbonate, water glass, etc.). Some characteristics are similar to Portland cement and in some aspects exhibit better properties (better resistance to aggressive environments and elevated temperatures). Their known disadvantages are the formation of efflorescence on the surface, material shrinkage, slower strength development and inconsistent properties due to the different origin of the blast furnace slag and the type of activator.

## 2 Alkali-activated systems

Depending on the CaO content, alkali-activated materials are divided into low CaO materials (power fly ash, metakaolin), where N-(A)-S-H gel is the main hydration product, and high

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CaO materials (blast furnace slag), which have C-(A)-S-H gel as the main hydration product. Currently, the most commonly used materials for alkaline activation are: blast furnace and steelmaking slag, high temperature and fluid fly ash and metakaolins. In general, alkali-activated materials have a higher incidence of efflorescence due to the reaction of alkali metal ions with airborne CO<sub>2</sub> and usually have greater shrinkage than Portland cement-based materials, which can lead to the formation of micro-cracks (mainly observed on blast furnace slag activated by water glass) [1].

Various additives (accelerating, water-reducing and set controlling, air-entraining, plasticizing) are commonly used to obtain the desired properties of Portland cement-based materials, but they generally do not work in alkali-activated systems. Due to the high pH, most types of superplasticizers exhibit structural changes, making them unable to perform their function [2].

We used granular blast furnace slag activated by sodium carbonate in the experiments published in this paper.

## 2.1 Granular blast furnace slag in alkali-activated systems

Granular blast furnace slag is a latent hydraulic binder. It is manufactured as a by-product in the production of pig iron. It consists predominantly of silicates, aluminosilicates and calcium-alumino-silicates. Depending on the type and speed of cooling we can obtain slags with different properties. Granulated blast furnace slag is produced by rapid water cooling of hot slag below 800 °C. By rapid cooling we obtain highly amorphous granules up to 5 mm in size with an amorphous phase content above 90%. This product is then ground very finely to increase the initial reactivity of the slag [3]. The chemical composition depends on the raw materials used in the iron production process. Higher CaO content results in an increase of slag basicity and in an increase of the binder material strength [4].

Activation of blast furnace slag is a highly heterogeneous process. The first step is to dissolve amorphous slag particles at high pH. Ca-O, Mg-O, Si-O-Si, Al-O-Al and Al-O-Si bonds are disrupted. The Ca-O and Mg-O bonds are significantly weaker than the other bonds, therefore more calcium and magnesium ions are released at the start of the reaction, and the slag grains are surrounded by a silicon and aluminium rich layer. The first structural units of Si(OH)<sup>4-</sup> and Al(OH)<sup>4-</sup> are formed, which then react with OH<sup>-</sup> ions present in the solution to form more complex precursors. As the glass phase dissolves, the concentration of precursors increases until the solution is saturated. Then the pH gradually begins to decrease. As the pH decreases, the C-S-H gel precipitates in the free space between the slag particles. Slag composition, type and concentration of activator have a significant effect on the mechanism and products of hydration and microstructure of alkali activated slag [5-7].

The main hydration product formed during the alkaline activation of blast furnace slag is a low crystalline calcium silicate hydrate (C-S-H gel), very similar to the gel formed by the reaction of Portland cement with water, as also a substituted C-A-S-H gel. [8]. Crystalline CaCO<sub>3</sub> calcite is often present in the alkali-activated system structure. Hydration by-products vary depending on the input raw materials and alkaline activator used [9].

At Na<sub>2</sub>CO<sub>3</sub> activation, the strengths are higher than at NaOH activation, but lower than at water glass activation. Gaylussit Na<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O occurs as a minor product [10]. Sodium carbonate, when mixed with blast furnace slag, releases a small amount of heat (probably precipitation of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>) and the hydration occurs after several hours. Therefore sodium carbonate activated matrices can be demoulded after two or three days [11].

## 2.2 Sodium carbonate as activator in alkali-activated systems

Sodium carbonate  $\text{Na}_2\text{CO}_3$  is the sodium salt of carbonic acid. It dissolves easily in water, releasing hydration heat. The aqueous solution is strongly basic and at 5 wt. % (25 °C) has a pH of 11.6. A very common phenomenon when activated with sodium carbonate is an extended setting time. It hardens after a few days, so sodium carbonate is not a very popular activator [12].

Alkaline activation with sodium carbonate also has its advantages. The matrices achieve higher strength after 28 days than using NaOH as activator and is comparable to Portland cement. To dissolve the precursors and precipitate the C-S-H gel, we need to have a solution pH greater than 9.5. Because  $\text{Na}_2\text{CO}_3$  has a lower pH than NaOH, the matrices are better mechanically resistant. In addition, at the start of activation, the  $\text{Ca}^{2+}$  ion concentration in the solution will be low due to the presence of  $\text{CO}_3^{2-}$  in the early stages of the reaction, which also limits the formation of the C-S-H gel [11].

The initial  $\text{Na}_2\text{CO}_3$  reaction can be accelerated by increasing the concentration of the activator, mixing with NaOH or water glass, adding reactive admixture such as MgO or  $\text{Ca}(\text{OH})_2$ . With the addition of accelerators, initial reactions can be accelerated, but at the cost of side effects [13]. Alkali-activated materials tend to have higher shrinkage, but when are activated by  $\text{Na}_2\text{CO}_3$ , shrinkage is similar or lower than the Portland cement systems.

## 3 Dynamic material parameters and testing methods

Dynamic material tests used sinusoidal load to a sample and record the response to this load. The ratio of the stress amplitude to the strain amplitude is the dynamic modulus.

The velocity of ultrasound wave propagation in solids is a function of material properties, it depends on the dynamic modulus of tensile and shear elasticity, density, Poisson number and adiabatic compressibility [14]. For a given material and type of wave, the ultrasound propagation rate is constant [15].

### 3.1 Ultrasonic Pulse Method

In Ultrasonic Pulse Method is the time for which the elastic wave (impulse) spreads from one point to another in the test mass directly measured. This method (unlike the resonance methods) is not bound to test samples, it can be used *in situ* [16]. Repeated ultrasonic pulses (ultrasonic wave beams) are transmitted to the test mass by a transducer. The receiving probe (sensor) receives pulses passed through the material and the apparatus records the time required for the front of the ultrasonic wave beam to pass from the exciter to the sensor. The speed of ultrasonic wave propagation depends on the physical and mechanical properties of the material and on the presence of failures. From ultrasonic measurements it is possible to determine the velocity of ultrasound wave propagation and elastic characteristics of the material such as dynamic modulus of elasticity. During ultrasonic measurements, it is necessary to ensure a good acoustic bond between the concrete surface and the contact surfaces of the probes. Ultrasound is virtually completely reflected at the solid-gas interface. Even a very thin gap between the probe and the test surface makes it impossible to pass ultrasound. Various media called “acoustic bonding” are used to fill this gap. The acoustic bond may be formed by a thin layer of a suitable binder. [17] We used plasticine as a binding agent for our measurements. The time of passage through the layer of acoustic bonding material and the through the probe is called dead time. It is necessary to determine this time and adjust the resulting data by this value. Dead time is determined on a standard with the known time characteristic. We calculated dynamic elastic modulus  $E_D$  from ultrasonic wave velocity and concrete density according to the formula:

$$E_D = \rho \cdot v_L^2 \cdot \frac{(1+\nu) \cdot (1-2\nu)}{1-\nu} \quad (1)$$

where  $\rho$  is concrete density,  $v_L$  is pulse velocity and  $\nu$  is Poisson's ratio. This ultrasonic measurement was performed by PUNDIT Plus Ultrasonic Pulse Analyser.

### 3.2 Impact-echo method

In principle, this method is historically one of the oldest NDT methods, when the "spectral analysis" performed by the ear was used by potters, bell makers and many other professions. But it is a fact that such testing is (to a certain extent) subjective and little sensitive to small defects. Therefore, with the advancement of technology and especially computers, it was switched to discrete Fourier spectral analysis. It eliminated subjectivity and increased the frequency resolution and thus the theoretical sensitivity [18].

The impact-echo method is based on the phenomenon of wave propagation in a solid body, which is caused by short pulse initiated by mechanical impact [19]. The theoretical basis of the impact-echo method is the principle that the propagation of elastic mechanical waves in a solid body occurs only when the force acting on the body causes only elastic deformations in it, and the impulse causing these deformations is as short as possible and rapid [20]. The mechanical pulse generates longitudinal flat waves (P), transverse waves (S) and Rayleigh surface waves (R), which propagate on the surface. P and S waves are used to locate defects hidden inside the element, as well as to determine its thickness [21].

The waves are repeatedly reflected from other surfaces of the element, as well as from structural defects having different acoustic impedances. The frequency of the P wave reaching the transducer is determined by converting the signal from the time signal into a frequency domain using mathematical signal analysis [19]. We use fast Fourier transform for signal processing. The frequencies corresponding to the peak amplitude of the whole spectrum are the dominant frequencies.

## 4 Testing specimens and experiment description

An alkali-activated slag mortar was manufactured for the experiments. Grounded granular blast furnace slag was activated by sodium carbonate  $\text{Na}_2\text{CO}_3$ . The aggregate was quartz sand with particle size up to 2 mm (containing fractions according to EN 196-1). Beams with dimensions  $40 \times 40 \times 160$  mm were made from this mortar. Composition of alkaline activated mortar was:

- weight ratio water to slag: 0.43,
- dose of sodium carbonate (expressed as slag weight): 6%,
- ratio of aggregate (quartz sand) to binder: 3:1.

All alkali-activated samples were left in water for 28 days. Then the samples were divided into three groups. This is time 0 on the graphs. The first group was left in the laboratory under normal laboratory conditions (30% RH, 20 °C), the second group was placed back to water and the third was stored in a  $\text{CO}_2$  chamber. Relative humidity inside the chamber was maintained at 60% RH, the carbon dioxide concentration was 1% throughout the experiment. All three groups were tested before and after 28, 56 and 84 days of the sample depositing.

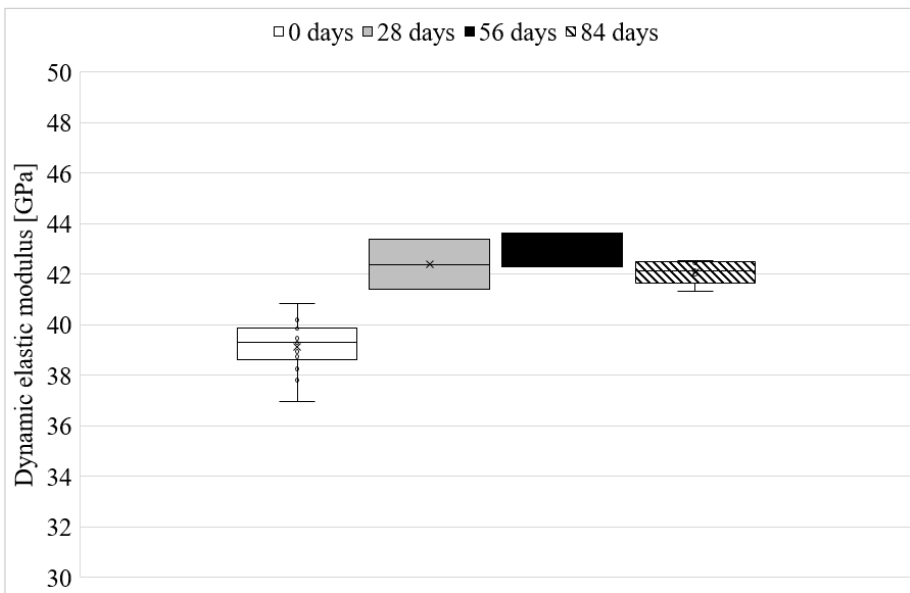
## 5 Results and discussion

The PUNDIT Plus Ultrasonic Pulse Analyser was used to measure the time required for the front of the ultrasonic wave beam to pass from the exciter to the sensor. From the times and

the known dimensions of the samples were ultrasonic signal speeds calculated. The samples were 40×40×160 mm and the velocity was measured through the longer side of the beam. Velocity was then calculated from the average of the three measured times. In all graphs, zero is taking samples out of the water (i.e. 28 days after mixing). The presented numbers are always the arithmetic means of more samples.

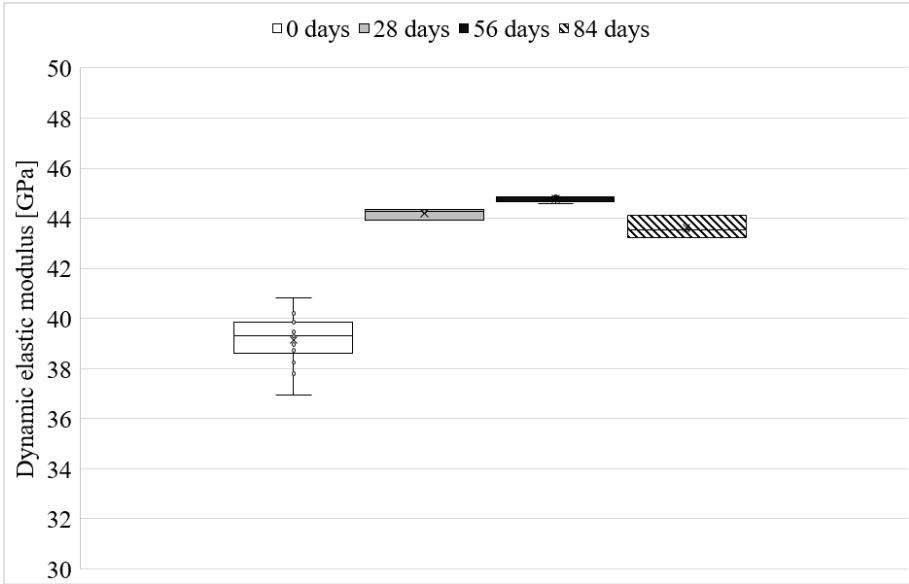
The average ultrasonic pulse velocity 28 days after mixing (zero in the graphs) was 4190 m/s. Until this time all samples were stored in water. Subsequently, the samples were placed to different environments. After 84 days in the CO<sub>2</sub> rich atmosphere (1% CO<sub>2</sub>, 60% RH) the average ultrasonic pulse velocity changed to 4340 m/s, after 84 days in the water changed to 4420 m/s, after 84 days in the laboratory (30% RH, 20 °C) changed to 2890 m/s. The sample density ranged from 2190 to 2290 kg/m<sup>3</sup>.

The graph in Fig. 1 shows the dynamic modulus of elasticity calculated value evolution for the samples in the CO<sub>2</sub> chamber. The relative humidity in the CO<sub>2</sub> chamber was maintained at 60%. After 28 days of storage in this environment, the dynamic modulus of elasticity of these samples increased. Furthermore, its value changed very little (after 56 and 84 days).



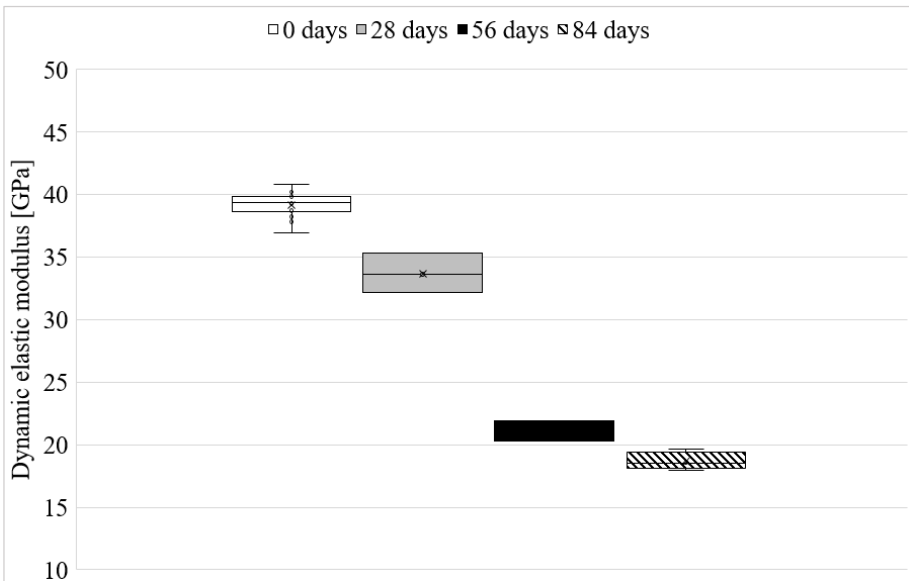
**Fig. 1.** Dynamic modulus of elasticity for the samples in the CO<sub>2</sub> chamber (1% CO<sub>2</sub>, 60% RH).

Samples stored in water (Fig. 2) showed a similar development of the dynamic modulus. The increase in modulus was slightly higher.



**Fig. 2.** Dynamic modulus of elasticity for the samples in water.

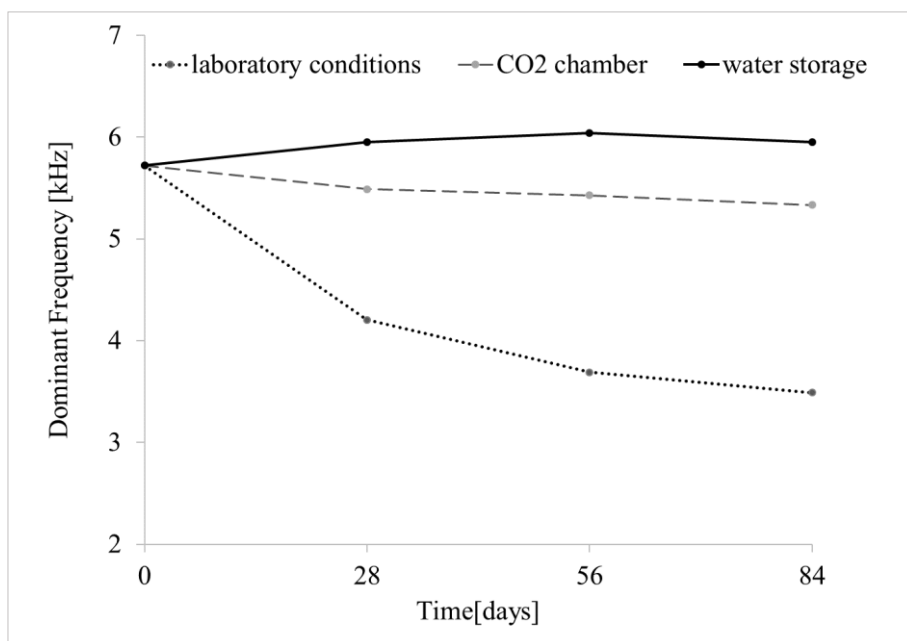
However, there was a total different development of dynamic elastic modulus for samples stored in the laboratory (Fig. 3). The relative humidity in this environment was about 30% and temperature was 20 °C. The modulus in this environment is constantly declining, even after 84 days.



**Fig. 3.** Dynamic modulus of elasticity for the samples in the laboratory (30% RH, 20 °C).

Fig. 4 shows shifts of dominant frequency versus number of days in the environment obtained by Impact-Echo method. Steel hammer was used as an impactor. The hammer was equipped by a sensor, to judge the consistency of strokes. At the beginning of sample

placement, the average dominant frequency was 5719 Hz. Frequency shift to higher values indicate improvement in the properties of the material. Dominant frequencies obtained by the impact-echo have a relatively similar course as the dynamic elastic modules calculated from the ultrasonic measurements (for water and laboratory condition storage). The dominant frequency increased in samples stored in water. Samples stored in CO<sub>2</sub> rich atmosphere at 60% relative humidity showed a very slight decrease in dynamic parameters. A significant decrease occurred in the dominant frequency of samples stored in the laboratory at 30% humidity, which confirms the significant decrease of their mechanical properties.



**Fig. 4.** Impact-Echo - dominant frequency shifts versus number of days in the environment.

Please note that all beams were cured in water for 28 days after their production - the values measured after this are indicated by zero in the graphs. From the measured values it is therefore seen that the alkali-activated slag mortar activated by sodium carbonate curing occurs even after this time. Some inconsistency of values obtained by different NDT methods for CO<sub>2</sub> atmosphere samples can be explained by the high sensitivity of the impact-echo method to the presence of micro-cracks that may have occurred (also to a much lesser extent than in 30% RH) in these samples.

The relationship between physical and chemical changes of alkali-activated systems dried at various RH conditions were described in [22], which may also cause changes in dynamic modulus of elasticity. However, this work is for another type of activator (sodium hydroxide).

## 6 Conclusions

This paper presents results from the measurements carried out on test specimens made of sodium carbonate alkali-activated slag mortar. The mortar beams (40×40×160 mm) differ in the way they are stored after 28 days of curing in water.

The best mechanical properties had samples stored in water or at least stored in sufficient humidity (60% RH). Beams stored in the laboratory at 30% RH showed a significant decrease in properties even though that they cured 28 days in the water. The exact reasons for this will

be the subject of further research. We will also focus on whether this decrease occurs when using other activators. Maintaining such a high humidity for a considerable period of time is rather problematic under normal building production conditions and would greatly limit the use of alkali-activated slag mortar activated by sodium carbonate in practice. Influence of CO<sub>2</sub> rich atmosphere, in contrast, seems to be less important. Samples exposed to a 1% CO<sub>2</sub> atmosphere maintained or even improved their mechanical properties (depending on which non-destructive method we take into account).

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