

# The Effect of Curing Medium on the Physico-mechanical Properties of Alkali-activated Slag

M.M. Elwan, H. El-Didamony, S.M. Hafeez

Blast furnace slag is a by-product from the production of pig-iron, which has caused some pollution problems in the area around the *Steel Iron Company* in Helwan/EG. The utilization of this waste product in the production of any product therefore saves money and prevents pollution of the atmosphere. Alkali-activated Slag (AAS) is a binder that can be used as a substitute for Ordinary Portland Cement (OPC) thanks to its ability to resolve most of the problems associated with OPC. AAS can be prepared by the activation of granulated slag by an activator. In this research work the granulated slag is activated with 2, 4, 6 and 8 mass-% NaOH and cured in humidity and under tap water. A comparative study of the physico-mechanical properties in the two curing conditions was investigated. The results revealed that curing in humidity (100 % RH) is better than under tap water as there is no leaching of certain materials.

## 1 Introduction

Granulated slag is a by-product obtained from the production of pig-iron. It is characterized by latent hydraulic properties owing to very weak reactivity with water. Alkali-activated Slag (AAS) is a type of binder that can be used in the production of concrete

based on the use of 100 % slag plus activator, which has been used in Eastern Europe, Scandinavia and China [1, 2]. In recent years, increasing attention has been paid to AAS owing to the numerous influencing factors, as it is an eco-friendly, durable construction material that requires less production energy than Ordinary Portland Cement (OPC) and is associated with low CO<sub>2</sub> emissions, which are the main cause of the "green house effect". CO<sub>2</sub> emissions are one of the obstacles to material recycling of waste products [3]. AAS binder has additional properties compared to OPC such as low heat development during hydration, high and early strength formation, and good durability of concrete against aggressive attack based on AAS [4–8]. Different activators are used for the activation of granulated slag. With the use of very small amounts of OPC, Ca(OH)<sub>2</sub> is liberated during hydration and then reacts with the slag. Calcium hydroxide alone can also be used as an activator [9]. Mixtures of calcium hydroxide with sodium sulphate and calcium carbonate to give sodium hydroxide and calcium

sulphate and calcium carbonate can be used for activation [10]. The most common activators associated with higher physico-mechanical properties are Na<sub>2</sub>SiO<sub>3</sub> (water glass) and NaOH [11]. The significant role of alkali activation is based on the fact that hydroxyl ions (OH<sup>-</sup>) supplied by the alkali activator are known to increase the hydration rate by promoting the dissolution of aluminate in the silicate matrix of the slag. The efficiency of any activator depends on several factors such as the type, dosage, ambient temperature and water-to-slag ratio. A significant factor is also the physico-mechanical nature of the material to be activated. The presence of amorphous phase plays a significant role owing to its considerable reactivity with alkalis. The final microstructure of a hardened AAS system is determined by the raw materials and the curing process [12, 13]. A new type of activator based on the use of silica fume with NaOH was reported in [14–18]. The reaction mechanism of alkali-activated materials can be described in two steps:

- The alkaline pore solution disintegrates the solid matrix to produce reactive silicate and aluminate species with a low molecular weight. The solid is activated with an alkaline solution containing alkali hydroxides, alkali silicates and/or alkali carbonate.
- Pure aluminosilicate materials, e.g. metakaolin and some types of fly ash, pure aluminosilicate materials, e.g. metakaolin and certain types of fly ash, react with condensation, leading to the formation of aluminosilicate polymers [19]. Aluminosilicate polymers typically form three-dimensional structures similar to those of zeolites, but are almost completely amorphous. As shown by several authors [20, 21], the setting of alkali-activated slag and calcium-containing materials can be characterized by both a condensation reaction and a hydration reaction forming CSH (or Al-substituted C–S–H) and C–A–H phases depending on the calcium content and alkalinity.

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Keywords: alkali-activated slag, pig iron

## 2 Experimental

### 2.1 Materials

A ground granulated blast furnace slag, which was provided by *Iron Steel Company* in Helwan/EG, was used in this study. The chemical composition of the material was quantitatively estimated using the modern methods of silicate analysis [22].

The chemical oxide composition of the starting material was:

SiO<sub>2</sub>: 37,48 mass-%, Al<sub>2</sub>O<sub>3</sub>: 12,86 mass-%, Fe<sub>2</sub>O<sub>3</sub>: 0,4 mass-%, CaO: 36,7 mass-%, MgO: 2,45 mass-%, MnO: 2,24 mass-%, Na<sub>2</sub>O: 1,48-mass %, K<sub>2</sub>O: 0,71 mass-%, BaO: 5,31 mass-%, SO<sub>3</sub>: 0,01 mass-% and S: 0,75 mass-%.

### 2.2 Preparation of pastes

The granulated slag (WCS) was first crushed in a jaw crusher to pass in through a 2-mm-diameter sieve. The material was passed over a magnet to remove any contamination of iron melt, then ground in a steel ball mill to reach 4000 + 50 cm<sup>2</sup>/g. A solution of sodium hydroxide at the ratios 2, 4, 6 and 8 % was dissolved in the mixing water (0,24). The slag was placed on a smooth, non-absorbent surface, and then the mixing operation was started with the activator to form the paste. The paste was cast into 2 cm × 2 cm × 2 cm cubic moulds. Specimens were cured in a humidifier (100 % RH) at room temperature for the first 24 h. At the end of the humid curing period, the cubes were demoulded and curing was continued under tap water or in a humidifier (100 % RH)

until the required time of testing was reached, that is 3, 7, 28 and 90 days. This paper aims to study the effect of curing media on the physico-mechanical properties of AAS using 2, 4, 6 and 8 % NaOH as an activator for up to 90 days of hydration.

## 3 Results and discussion

### 3.1 Curing under tap water

The activation of the granulated slag with NaOH cured under tap water for up to 90 days was studied based on the determination of the chemically combined water content, bulk density, total porosity and compressive strength of hardened cement pastes.

#### 3.1.1 Chemically combined water

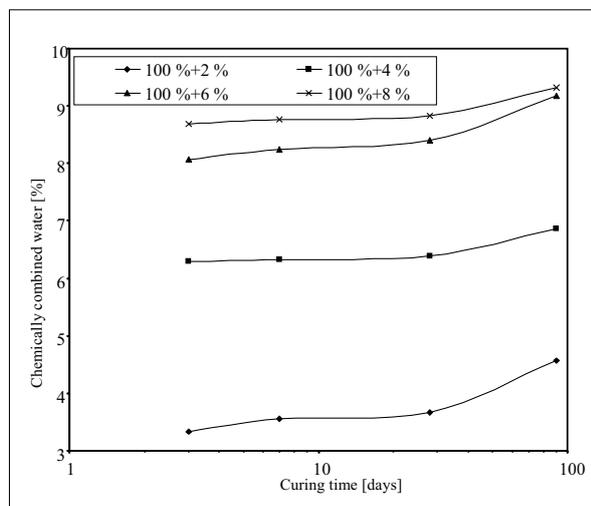
The chemically combined water content of alkali-activated slag as function of the curing time is shown in Fig. 1. The chemically combined water content increases gradually with curing time for all activated pastes. So, as the hydration time progresses, the amount of hydration products increases, and hence the chemically combined water content increases. It was shown that the chemically combined water contents increases with the amount of NaOH. In other words as the concentration of NaOH increases, the activation of the granulated slag is enhanced and the chemically combined water content increases. This is mainly owing to the higher hydraulic properties of granulated slag with the increasing alkaline concentration.

#### 3.1.2 Bulk density

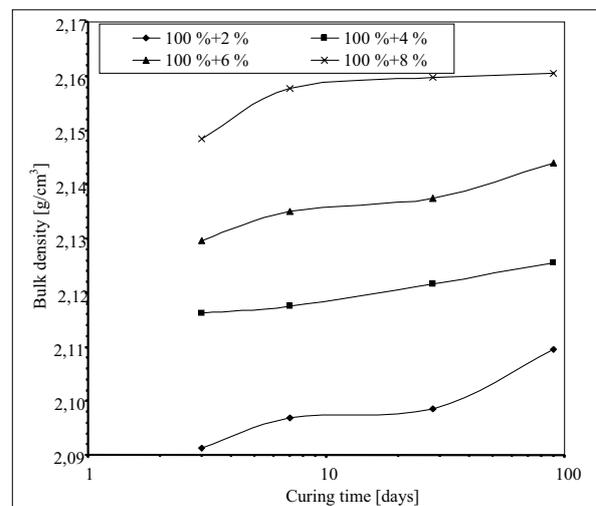
Fig. 2 shows that the bulk density of alkali-activated slag is dependent on the curing time. The bulk density increases with the curing time for all activated slag pastes. This is the result of the continuous precipitation and accumulation of the hydrated products filling up the available pore volume. The increase in the sodium hydroxide concentration tends to increase the bulk density. 8 mass-% NaOH gives the highest values for bulk density, owing to the higher ability on activation to dissolve the slag matrix, liberating active silicates and aluminates and resulting in higher amounts of hydrates and geopolymer.

#### 3.1.3 Total porosity

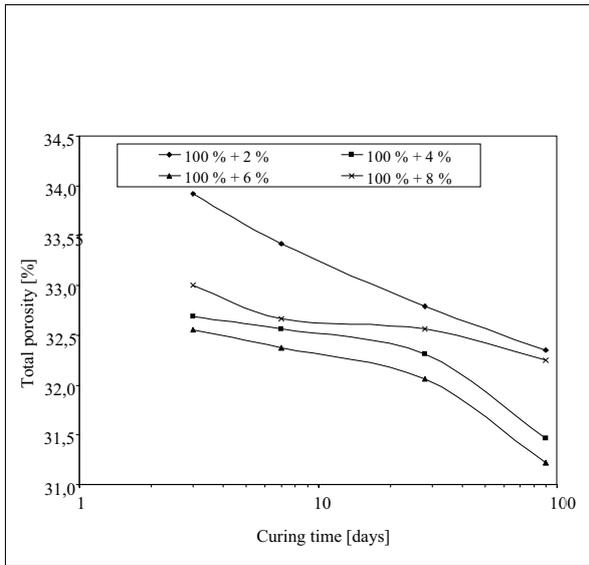
Fig. 3 shows the total porosity of alkali-activated slag cured under tap water as a function of the curing time. The total porosity values for every concentration of NaOH decreases with the curing time. This is due to the continuous activation associated with the formation of hydrated products that fill some of pores until minimum values are reached after 90 days. The total porosity decreases with the amount of NaOH up to 6 mass-% and then increases to 8 mass-%. The sharp decrease in the total porosity of all mixes after 28 days is caused by the higher concentration of hydroxyl ions. 8 mass-% NaOH is characterized by a very high alkaline medium associated with leaching to the surrounding water, leading to an increase in the total porosity. It can be said that 6 % NaOH is the optimum amount for activation.



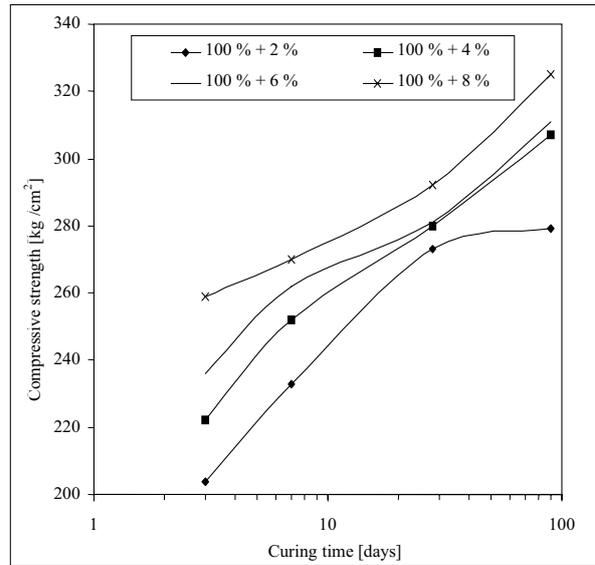
**Fig. 1** Chemically combined water content of alkali-activated slag cured in water as function of the curing time



**Fig. 2** Bulk density of alkali-activated slag cured in water as a function of the curing time



**Fig. 3** Total porosity of alkali-activated slag cured in water as a function of the curing time



**Fig. 4** Compressive strength of alkali-activated slag cured in water as a function of the curing time

### 3.1.4 Compressive strength

The compressive strength of alkali-activated slag as a function of the curing time is shown in Fig. 4. The rate of strength development depends on the degree of hydration of the granulated slag and the rate of geopolymer formation with curing time. It is clear that the compressive strength of all hardened slag pastes increases with curing time up to 90 days. According to *Regound* [23], the formation of  $C_4AH_{13}$  is responsible for the earliest strength. But responsible for strength in the later stages are the hydrates especially C–S–H and the co-existence of geopolymers with C–S–H as well as the reactivity of the interfacial zone between the two phases. The chemical composition suggested that the presence of granulated slag in alkali activation could result in the

formation of two separate phases, namely geopolymers and C–S–H gel.

According to *Yip and Deventer* [24], the simultaneously formed geopolymeric gel and C–S–H gel as well as the reactivity of the calcium precipitates in the interfacial region will determine the durability of such binder from a low-basic alkaline aluminosilicate system. It is also clear that the higher the percentage of NaOH, the more compressive strength values reach maximum at 8 mass-% NaOH in 90 days.

### 3.1.5 XRD analysis

Fig. 5 shows the X-ray diffraction of 100 mass-% granulated slag activated with 6 mass-% NaOH at 90 days. The sample indicates the presence of C–S–H in addition

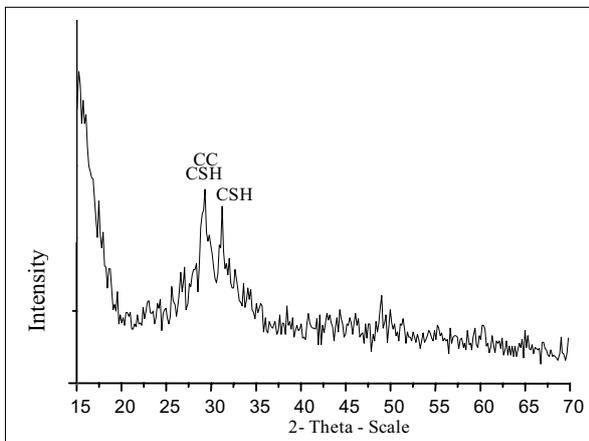
to calcium carbonate. The formation of C–S–H is due to the reaction of active silicates liberated as a result of the dissolution of the slag network with calcium ion, which was present in the granulated slag.

### 3.2 Curing in 100 % humidity

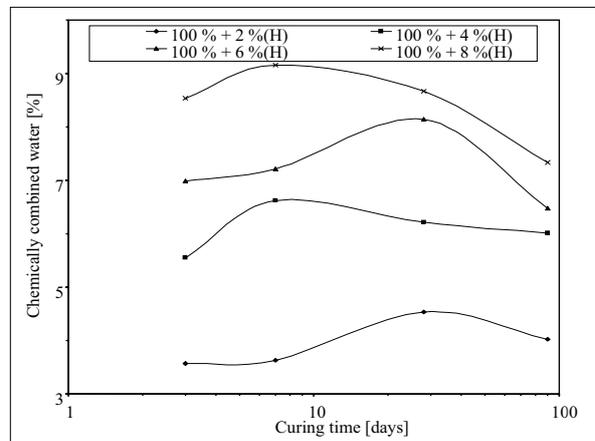
The activation of granulated slag with NaOH cured in 100 % humidity up to 90 days was studied based on the determination of chemically combined water content, bulk density, total porosity and compressive strength of the hardened cement pastes.

#### 3.2.1. Chemically combined water in humidity

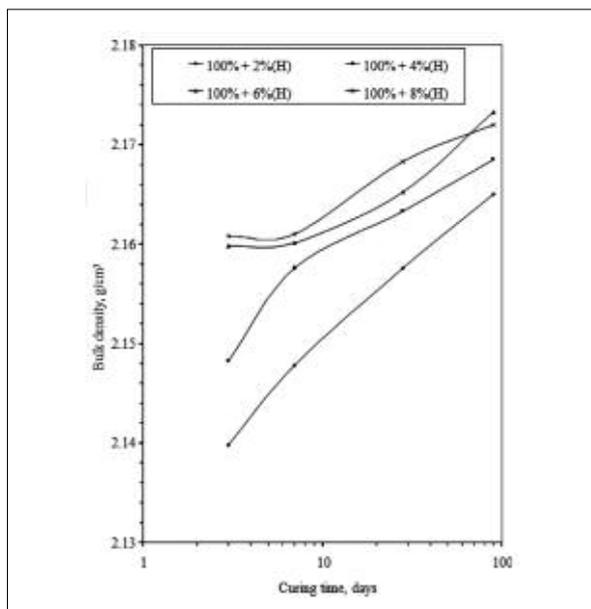
The chemically combined water content of alkali-activated slag as a function of the cur-



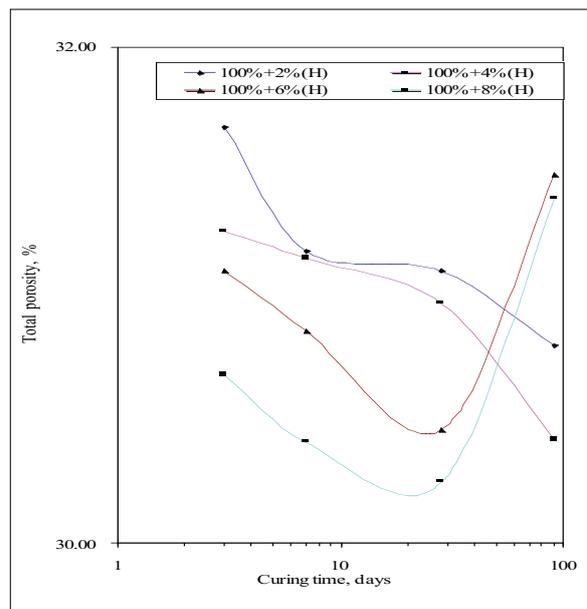
**Fig. 5** XRD spectra of 100 % granulated slag activated with 6 mass-% NaOH after 90 days



**Fig. 6** Chemically combined water content of alkali-activated slag cured in humidity as a function of the curing time



**Fig. 7** Bulk density of alkali-activated slag cured in humidity as a function of the curing time



**Fig. 8** Total porosity of alkali-activated slag cured in humidity as a function of the curing time

ing time is shown in Fig. 6. The chemically combined water content in all pastes increased from 3 to 7 days. This is due to the increase in the hydration rate and the hydration products formed. It is also clear that the more NaOH content formed, the higher the chemically combined water content is at all curing times. Owing to the higher NaOH content, there is greater disintegration of the network to yield active silicates and aluminates able to form more hydration products. All pastes at 90 days have a lower chemically combined water content than at 28 days owing to the continuous presence of NaOH in the paste, which enhances the disintegration of the network to liberate excess active silicates and aluminates that react with C–S–H rich in lime to form low-lime C–S–H, which is characterized by lower chemically combined water than the C–S–H rich in lime. This is also due to the polymerization of C–S–H [25].

### 3.2.2 Bulk density

Fig. 7 shows the bulk density of alkali-activated slag as a function of the curing time. It is clear that the bulk density of pastes cured under tap water is lower than that of pastes cured in humidity owing to the absence of a leaching process and the higher ability on activation than in the case of the pastes cured under tap water. The bulk density of all pastes increases with curing time. This is the result of the increasing liberation of active

silicates and aluminates sharing in hydrates and geopolymer formation. It was found that the higher percentage of NaOH is, the higher bulk density is at all curing times, except that 6 mass-% NaOH gives a higher density than 8 mass-% NaOH at 90 days. This is due to the fact that 8 mass-% NaOH shows greater activation and therefore greater ability to liberate active species, but in case of 6 mass-% at 90 days, this is due to the presence of a lower amount of rich C–S–H able to accept more active species than 8 mass-% NaOH, resulting in the increase in bulk density. The increase in the bulk density of activated slag with 6 mass-% NaOH at 90 days may be due to the low porosity at later ages of activation.

### 3.2.3 Total porosity

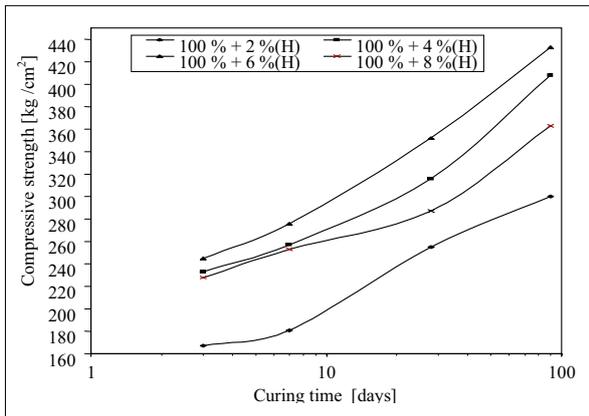
Fig. 7 shows the total porosity of alkali-activated slag cured in humidity up to 90 days. The total porosity of pastes cured under tap water is higher than that of pastes cured in humidity owing to the leaching of some NaOH in the water. The total porosity of all pastes decreased with curing time except at 6 and 8 mass-% NaOH at 90 days owing to the leaching of some NaOH at higher concentrations by the water vapour in the humidity chamber. For a paste with 6 and 8 mass-% NaOH respectively at 90 days, total porosity increases owing to the presence of a high concentration of

NaOH in pastes able to attack a part of the geopolymer again to active species, to increase the total porosity where exchange between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ( $\text{Mg}^{2+}$ ) aids the reformation of NaOH to be used as activator again to liberate active species of some parts from geopolymer dissolution to increase the total porosity at 6 and 8 mass-% NaOH. The cement pastes containing 6 and 8 mass-% NaOH exhibit lower total porosity up to 28 days. This is due to the higher concentration of NaOH, which activates the granulated slag.

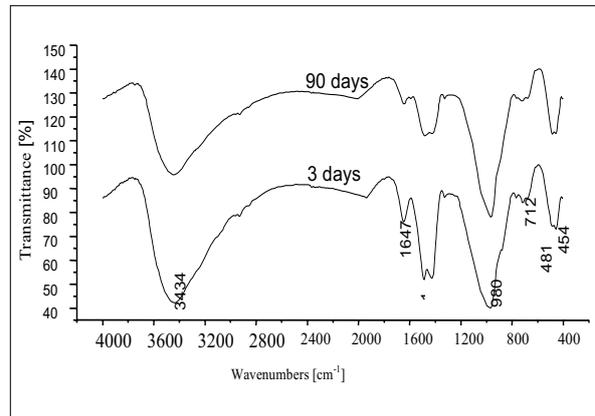
The total porosity of activated slag with 2 and 4 mass-% NaOH decreases with the curing time up to 90 days. This is due to the precipitation of hydration products in some open pores and geopolymer formation. The decrease in porosity after 28 days is due to the lower chance of continuous activation of the slag and regeneration of NaOH.

### 3.2.4 Compressive strength

The compressive strength of alkali-activated slag in humidity up to 90 days is represented in Fig. 9. The compressive strength achieved in three days of all cement pastes with all NaOH additions cured in humidity is lower than the compressive strength of the same pastes cured under tap water. This means that the presence of pastes in tap water accelerates the hydration process to form more C–S–H which is responsible for the strength. In addition, the compressive



**Fig. 9** Compressive strength of alkali activated slag cured in humidity as a function of the curing time



**Fig. 10** IR spectra of activated slag with 6 mass-% NaOH at both 3 and 90 days cured in water

strength at 90 days of all pastes cured in humidity is higher than that of the same pastes cured under tap water. The presence of pastes in humidity at later ages, especially at 90 days, prevents leaching and higher C-S-H will be formed, increasing the compressive strength values. It is clear that the compressive strength of all pastes increases with curing time owing to the increased for-

mation of hydrates and geopolymers responsible for strength. These hydrates are precipitated in some of the open pores to decrease the porosity and increase the strength. As the amount of NaOH increases up to 6 mass-%, the compressive strength of the activated slag increases. On the other hand, granulated slag activated with 8 mass-% NaOH gives lower values for compressive

strength at all curing times. This may be due to the formation of some Na-silicate hydrate, which reduces strength. The compressive strength values with 8 mass-% NaOH are lower than at 4 mass-% and 6 mass-% and higher than with 2 mass-% NaOH at all curing times. There is no leaching with NaOH at a lower concentration, which acts at higher concentration and attacks some parts of

12-13 NOVEMBER 2012

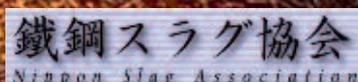
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geopolymer to form active species again like sodium silicate and aluminate, which share in the formation of rich C–S–H as appeared in the chemically combined water.

### 3.3 IR spectra of activated slag with 6 % NaOH cured in water

Fig. 10 shows IR spectra of slag activated with 6 mass-% NaOH at 3 and 90 days cured in water. IR spectra of slag activated with 6 mass-% NaOH at both 3 and 90 days cured in water indicate that the band at  $3434\text{ cm}^{-1}$  is due to the stretching band of the hydroxyl group of activated species as well as Si–OH and Al–OH and also chemically combined water of different hydrates as well as C–S–H, C–A–H and C–A–S–H related by other band, which shows at  $1647\text{ cm}^{-1}$  characteristics for bending vibration of hydroxyl group of activated species and hydrates. The intensity of this band at 90 days is smaller than 3 days owing to the consumption of activated species in geopolymer formation or owing to polymerization to give lower values for combined water. At  $1428\text{ cm}^{-1}$ ,  $\text{CaCO}_3$  is present but the intensity at 3 days is greater owing to the consumption of calcium in the formation of hydrates.

### 4 Conclusions

- Curing in humidity is associated with higher physico-mechanical properties than curing under tap water.
- Curing in humidity prevents leaching so the porosity of pasted cured in humidity decreased compared to that of pastes cured under tap water.
- The higher percentage of NaOH is, the more active species are formed to increase the geopolymer and hydrates responsible for strength.
- The 6 mass-% NaOH gives the highest physico-mechanical properties of cement pastes.

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