



CHARACTERIZATION OF CARBONATED STEELMAKING SLAG AND ITS POTENTIAL APPLICATION IN CONSTRUCTION

Tran Anh Tu, Tran Gia Huan, Nguyen Ngoc Tri Huynh, Nguyen Khanh Son *

Dept. of Silicate Materials, Faculty of Materials Technology, Ho Chi Minh City University of Technology (VNU HCM), 268 Ly Thuong Kiet, District 10, Ho Chi Minh city

*Email: ksnguyen@hcmut.edu.vn

Received: 31 July 2019; Accepted for publication: 26 August 2019

Abstract. In the south of Viet Nam, steelmaking slag is commonly considered a normal category of solid waste. And they exist the fact that slag occupies the ground for dumping and may lead to serious environmental issues due to their high content of heavy metal and fine dust. In this paper, we aim to analyze the influence of the accelerated carbonation condition in the laboratory on the physio-chemical properties of carbonated steel slag. Materials composition was characterized by using different analysis techniques of XRD, SEM, TG and others measurements of the physio-properties (density, loss on ignition L.O.I.) were also realized with regard to the requirement of national standard TCVN 7570:2006 for concrete aggregate. In conclusion, we will discuss on the effect of reaction condition and on the feasibility of implementing this specific treatment method on the industrial scale.

Keywords: steelmaking slag, solid waste, CO₂ sequestration, accelerated carbonation, concrete aggregate.

Classification numbers: 2.9.4, 3.2.2, 3.3.3.

1. INTRODUCTION

Steel slag, generated from a converter furnace, is a by-product of the process of steelmaking through smelting pig iron and/or steel-scrap. The molten liquid is a complex solution of silicates and oxides that solidifies after cooling phase [1]. As an estimation, 15 % by weight of the steel product is slag by-product. That means each ton of final steel product goes together with 150 kg of the solid waste of slag. Depending on the type of converter furnace, the named the generated slag as follows: EAF steel slag, BOF steel slag or Ladle steel slag [2]. The technology of Electrical Arc Furnace (EAF) is often used to refine steel scrap. Iron scrap is also the primary feedstock of almost steel plant in South of Vietnam due to a shortage of iron ore from mines. In Ba Ria - Vung Tau province, they estimate that the annual production a total of 13 steelmaking plants is around 3.75 million tons [3]. In one hand, they meet the local needs in the current context of the rapid growth of urbanization in this region and in the others hand, the contribution of steel production is one of the main export products. But, as a consequence, they discharge a huge amount of 412.000-562.500 tons of slag and a high volume of CO₂ emission. Both of them cause serious environmental issues that relate to soil, groundwater and air. As we

know, CO₂ emission is now considered as the main cause of climate change in the world. In practice, slag dumpsites are now expanding over the year at steel plant's site due to the fact that they exist no strategic plan for recycling this solid waste [3]. Also, as mentioned in the reference [3], they exist somewhere the information about the successful application of steel slag as material for leveling, soil improvement, coarse aggregate for asphalt and/or cement concrete, etc. But at the same time, they also exist much fearfulness considering environmental impact and/or toxicity of steel slag due to heavy metal and/or other existing impurities. In terms of technology, the issue of volumetric instability due to the high content of CaO, MgO in slag composition and the remaining steel scrap due to the smelting process of electrical arc furnace equipment. The remaining steel scrap might lead to potential corrosion and increasing temperature while exposed to weathering conditions. Slag potential expansiveness might lead to the destruction of the coarse aggregate of concrete and global damage of the concrete structure. Seen as a whole, these contradictory arguments limit the feasibility of slag aggregate in the practical application of construction works. Despite the fact that the re-utilization of steel slag in civil works guarantees several benefits related to the environmental safeguard in terms of natural resources preservation (avoiding onerous quarrying processes) and waste disposal reduction.

In principle, the phenomenon of mineral sequestration consists of the capture reaction of CO₂ gas of Ca and Mg silicate mineral-bearing rock and/or hydroxide compound to transform those materials to stable and solid forms of carbonates mineral [4]. As reported by Huijgen *et al.*, the fundamental concept behind the mineral sequestration is the classical principle of natural rock weathering. But, in general, the carbonation reaction in nature is very slow and could only be achieved after many years. It has been identified as one of the major challenges for large-scale mineralization of CO₂ [5]. Although, researchers and industry agree together that this is the most effective and eco-friendly process of CO₂ capture and storage. Research on further enhancement of the mineral carbonation reaction may contribute to the development of cost-effective CO₂ sequestration on a large scale of on-site mineral sequestration. As analyzed in the first paragraph, CO₂ emission and potential expansiveness are two key points that we must take into account a viable way of recycling steel slag [6,7]. To combine those two factors in a mature technology of mineral sequestration is challenging and becoming an intensive business under the circumstance of economic demand and environment impact. Huijgen *et al.* [5] were the first to conduct a systematic study of the reaction mechanisms of CO₂ sequestration by carbonation of steelmaking slag through an alkaline solid. From that, many types of research in literature present various acceleration approaches to overcome the kinetics barrier of the carbonation reaction of steel slag.

In the next paragraph, we will investigate the influence of the accelerated carbonation condition on the physio-chemical properties of carbonated steel slag. This study is remaining at the laboratory demonstration scale before putting the concept into practice. We aim to take into consideration the factor of particle size of slag gravel by maintaining the reaction condition at the same CO₂ content and relative humidity. The reaction temperature was maintained at room temperature conditions (approx. $30 \pm 2^\circ\text{C}$). The results of materials analysis both in terms of mineralogical composition and intrinsic character will be discussed. In the end, we aim to highlight the effect of the reaction condition on the carbonation of steel slag and also to anticipate the feasibility of implementing this specific treatment method in practice.

2. MATERIALS AND EXPERIMENT IN CARBONATION CHAMBER

2.1. Preparation of slag aggregate

Rough gravel of slag (particle size > 800 μm) was collected from the dumpsite of Vietnam steel plant in Ba Ria – Vung Tau province. We used laboratory jaw crusher to reduce the particle size of slag grain and at the same time used a permanent magnet for iron removing. After that, slag gravels were sized by using two sieves 4.75 and 37.5 μm . The last means we obtained 2 categories of particle sizes as given in Figure 1: coarse slag aggregate 20-40 mm and fine slag aggregate 2.5-5 mm as usually distinguished in the concrete aggregate component. Those two categories will be placed in the carbonation chamber in the next step to investigate the effect of particle size on the reaction rate.



Figure 1. Preparation of two categories of steel slag aggregate: coarse slag 20-40 mm and fine slag 2.5-5 mm.

We attempt to measure density, water absorption and loss on ignition of slag with regard to the criteria values of the national standard for concrete coarse aggregate such as the case of calcite. The averaged result of a specific density was 3.51 g/cm^3 , showing a higher density (3.51 g/cm^3 vs. 2.65 g/cm^3) than natural calcite. The last is probably due to the presence of remaining iron scrap in slag. The result of water absorption was $1.7 \pm 0.5 \text{ \%wt}$ that is slightly higher than 0.5 \%wt of calcite aggregate. But considering the intrinsic porous microstructure of the slag aggregate, the obtained result of water absorption could be much more important. In addition, the porous microstructure of slag might make an impact on the mechanical strength of the slag aggregate. The measured value of a loss on ignition was 6.5 \%wt , that could be linked to different thermal decomposition of mineral composition of slag. This statement was clarified with the result of XRD analysis (D8 ADVANCE, Bruker-Belgium) that revealed main mineral components of steel slag including calcite, free lime, alite and portlandite, etc.

2.2. Accelerated carbonation chamber and saturated salt solution

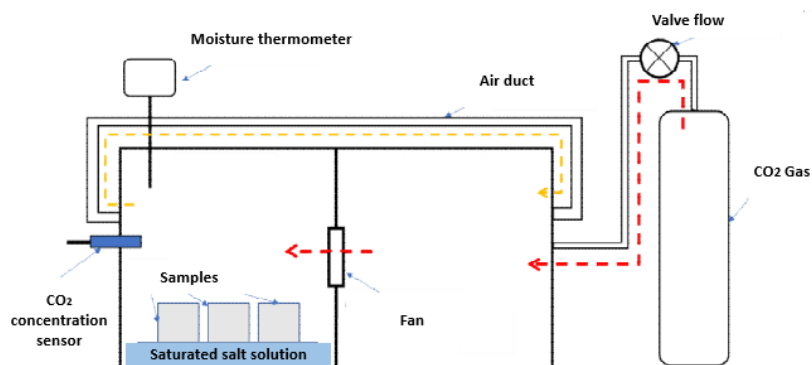


Figure 2. Design schematic of the accelerated carbonation chamber in the laboratory.

The accelerated carbonation chamber was previously designed and implemented in the laboratory [8]. As given in Figure 2, the chamber contains two units: the left one serves for

sample storage and the right one serves for air mixing. A ventilation fan and air duct permit the easy circulation of mixing air between the left and right unit. CO₂ gases are supplied from compressed air tank into the mixing unit using controlled flow valve. The CO₂ sensor is installed to control the changing value of gas concentration. Value of relative humidity inside the chamber also is recorded continuously thanks to the installation of a digital humidity meter. Besides that, the temperature inside the chamber is also a normal room temperature condition (approx. 30 ± 2 °C) and is showed by the digital meter. It is noted that humidity is one of the controlled factors of the carbonation reaction of slag aggregate inside the chamber. In this study, we used a saturated salt solution for stabilizing the moisture content. Those solutions were placed in a number of pans next to the trays of slag gravel in the left unit (Figure 2). The high surface area of salt solutions stored in those pans allows its either absorb or desorb water in order to maintain the equilibrium relative humidity (RH). According to Young, by using a saturated salt solution of sodium chloride (NaCl) and barium chloride di-hydrate (BaCl₂.2H₂O), we could respectively stabilize the moisture content 80 ± 2 % and 97 ± 2 %. In addition, to combine the use of the two saturated salts solutions, we could stabilize the moisture content 90 ± 2 % at room temperature [9].

2.3. Operation of accelerated carbonation chamber

We first carried out the process of operating in idle mode the carbonation chamber in laboratory condition. The variation of moisture content and CO₂ concentration were investigated. Figure 3 shows the obtained results during one week. As given in Figure 3 (left), measured values of the moisture content were stabilized at 80 %, 90 %, 99 % thanks to the use of the saturated salt solution. The variations of CO₂ content were also slightly small around the medium value of 7 %. It seems that such variations depend on the moisture condition due to possible dilution of gaseous in the salt solutions. From the results of the operation in idle mode, we can point out the good performance of the developed chamber for experimental study of slag carbonation. In this step, two categories of slag aggregate (coarse and fine grain) were introduced into the chamber for accelerated reaction under three above moisture conditions. After 3 weeks, we carried out different characterization tests for those carbonated slag samples.

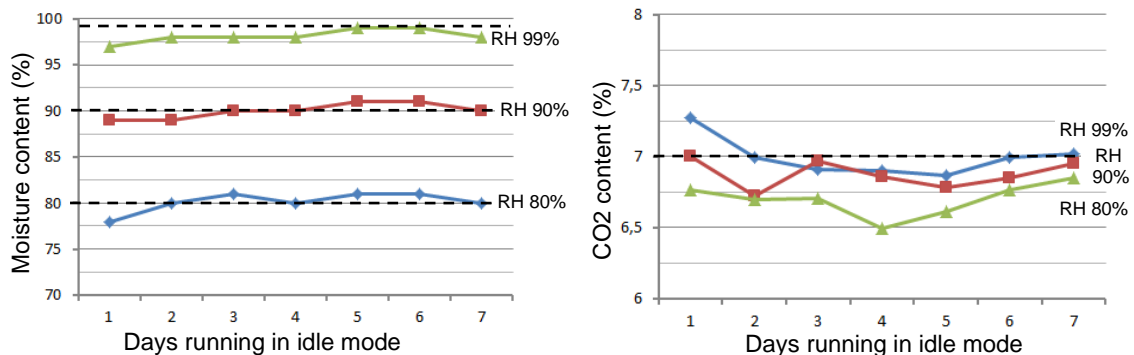


Figure 3. Variation of moisture content (%) and CO₂ concentration (%) of carbonation chamber running in idle mode for one week.

3. RESULTS AND DISCUSSION

3.1. Materials analyzing of carbonated steel slag

We conducted a study of the evolution of the material composition of the carbonated slag by using XRD (D8 ADVANCE, Bruker-Belgium), SEM (S-4800, Hitachi-Japan) and TG (LABSYS evo STA, Setaram-France) analysis. To minimize the number of analysis, only slag samples prepared under 6 % of CO₂ content and 97 % relative humidity were investigated. Figure 4 reveals the results of the mineral composition of steel slag (coarse and fine particle) compared to the controlled sample of slag before the carbonation reaction. We highlight the peak of calcite (N^o1) and lime (N^o8) in the pattern of the results of XRD analysis. The intensity of calcite peaks was relatively prominent with regards to background noise linked to amorphous glassy phase. Other phases of minor minerals including alite, wuestite, etc. were also recognized but with low intensity peaks. To compare with XRD pattern of the controlled sample, we could not recognize the peak of calcite but they existed the peaks of hydrated lime. The last mean thanks to the carbonation reaction hydrated lime transformed into calcite mineral by uptaking CO₂ of the chamber. But the reaction was not complete after 3 weeks due to the presence of hydrated lime in the final product.

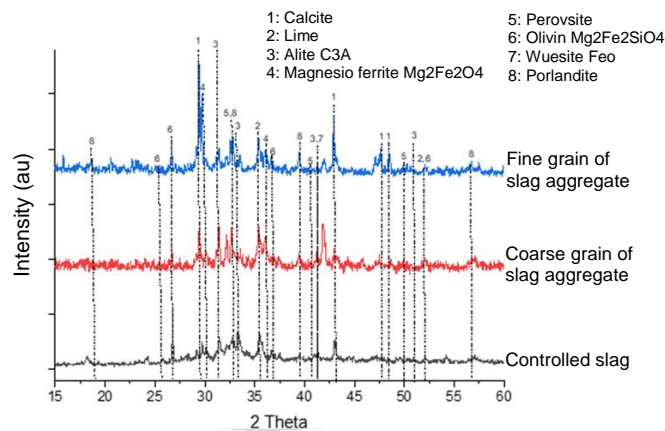


Figure 4. XRD patterns of carbonated steel slag and controlled sample of slag before carbonation reaction.

Figure 5 shows SEM photos of steel slag samples before and after carbonation. They reported a significant change in the microstructure of steel slag sample after 21 days under the accelerated carbonation condition. In the photo on the right hand side, the morphology of calcite crystal in rods could be found abundantly thanks to carbonation reaction. The result also confirmed the peaks of calcite mineral in the above XRD patterns.

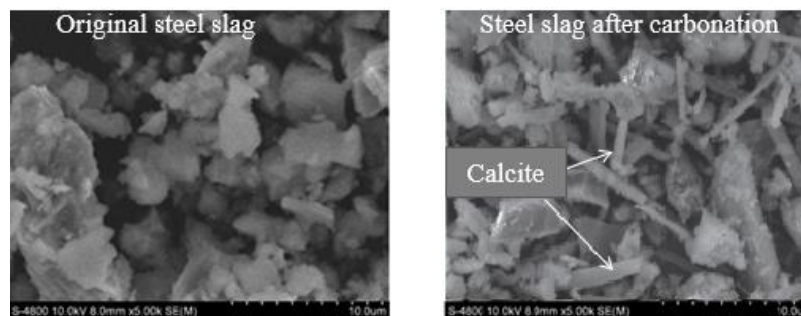


Figure 5. SEM photos of steel slag samples before and after carbonation.

Figure 6 shows the results of TG analysis of steel slag samples before and after 21 days under accelerated carbonation condition (99 % relative humidity, room temperature, 6 % of CO₂ content). In general, we noted a significant difference in total mass loss of these two sample series. They were respectively 5 % wt and 15 % wt in the range of temperature between 30-900 °C. As given in the TG curve, we can distinguish into 3 main stages of mass loss. The first stage is in the range of temperature between 30 and 105 °C which corresponds to water evaporation. The second stage is in the range of temperature between 150 and 600 °C which corresponds to different dehydration reaction of mineral phases (hydrated C-S-H, hydroxide Ca(OH)₂...) and/or transition of iron oxide compound. The third stage is in the range of temperature between 600 and 900 °C which corresponds mainly to decomposition reaction of CaCO₃. Therefore, except the first stage that is usually the same value for two series of controlled slag sample and carbonated slag sample, results of mass loss of second and third stage of carbonated slag sample were clearly higher than those of controlled slag sample due to the contribution of different calcite mineral phase in two sample series.

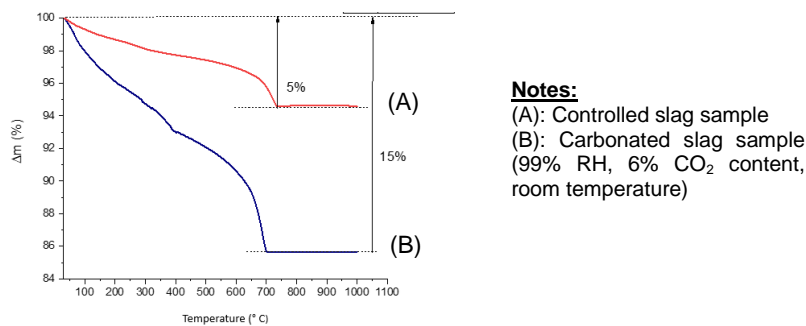


Figure 6. TG curve of two sample series controlled slag and carbonated slag sample.

3.2. Material properties of carbonated steel slag

After carbonating 21 days in the chamber, we conducted a study on material properties such as measurement of loss on ignition and density for both coarse and fine slag aggregate. It should be noted that besides the influence of particle size of steel slag, different humidity has also been studied to discuss possible impacts.

Figure 7 reveals the evolution of the measured value of density over 21 days time of accelerated carbonation for two categories (coarse and fine aggregate) of steel slag. Measurement of density was realized respecting to the instruction of Vietnamese standard TCVN 7570-4:2006 (for concrete aggregate). Typically, the value of density increased in function with time and reached the average value of 3.64; 3.68 or 3.71 g/cm³ depending on the humidity condition. It should be noted that the initial value of the density of the slag was 3.51 g/cm³ as reported in section 3.1. Compare two categories of steel slag sample, it seems that the fine particle of slag aggregate revealed slightly higher density and also the earlier rate of conversion. With regards to the obtained result of materials analysis in section 3.1, such an evolution of density could be absolutely linked to the phenomenon of carbonation. Fine grain of steel slag seems to be easier uptaking CO₂ gaseous in order to transform hydrate lime into calcite. We can explain this result by considering the evidence that high surface area of fine slag aggregate provides better contact solid-gaseous reaction than the low surface area of coarse slag aggregate. Furthermore, the effect of high humidity condition on the reaction rate was clearly

shown in Figure 7. The optimal condition for carbonation of coarse and fine aggregate of steel slag was under 99 % moisture content and room temperature.

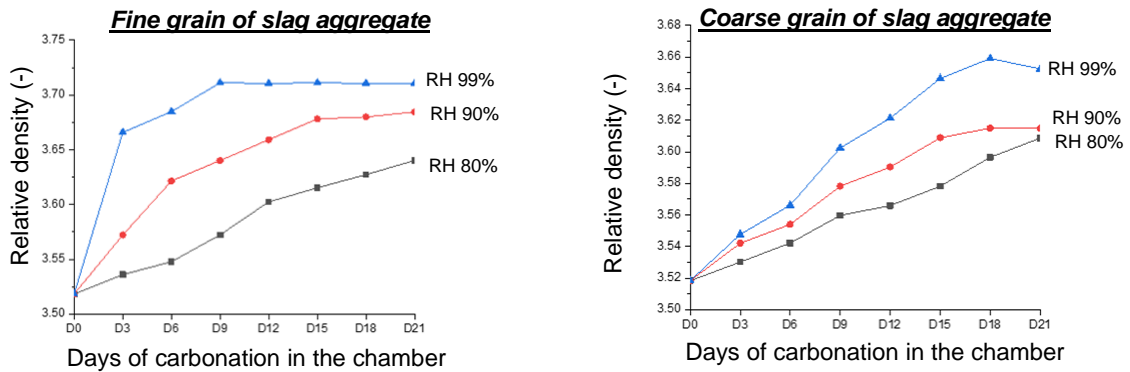


Figure 7. Evolution of specific density of two categories of steel slag aggregate (fine and coarse grain).

In Figure 8, we can see the measured values of loss on ignition of carbonated slag which was distinguished by two categories of coarse and fine aggregate. The test of loss on ignition L.O.I was realized with slag powder according to the instruction of Vietnamese standard TCVN 7570-7:2006 (for concrete aggregate). As previous results of specific density, those values of loss on ignition evolve over time of placing in the carbonation chamber. That means due to the progress of the carbonation process, an amount of hydrate lime converted into calcite mineral and make increasing the final mass loss. Compare two categories of steel slag sample, L.O.I of the fine grain of slag aggregate on the left hand figure showed more important than L.O.I of the coarse grain of slag aggregate on the right hand figure. The last means that the rate of carbonation reaction is more important in the case of the fine slag aggregate. However, after 21 days, it seems that the results of L.O.I of coarse slag aggregate keep increasing trend. Such tendency could be explained by the uncompleted reaction of carbonation of steel slag. We did not identify the same phenomenon in the case of fine slag aggregate. With regards to the effect of humidity condition, we obtained the same result as the result of specific density. That means 99 % moisture content was the optimal condition for the carbonation reaction of steel slag for both of coarse and fine grain. The reaction rate was also slightly high at the beginning period and achieve early the final state of carbonation with a small variation of L.O.I between 12 and 21 days.

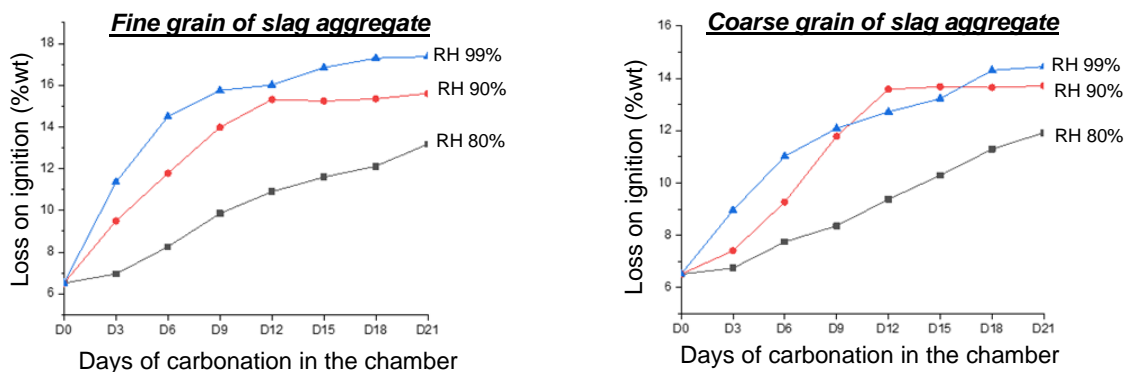


Figure 8. Evolution of measured L.O.I of two categories of steel slag aggregate (fine and coarse grain).

4. CONCLUSIONS

To conclude, the use of the acceleration carbonation chamber in the laboratory is necessary to optimize the reaction condition of steel slag before putting the concept of technology into practice. The result of materials analysis such as XRD, SEM, TG confirmed the presence of abundant calcite in the carbonated steel slag in the accelerated condition. The effect of relative humidity (99 %) on the carbonation reaction of slag must be also taken into account. The carbonation process took place more intensely during 3 weeks placing in the chamber thanks to the honeycomb structure of steel slag aggregate. The effect of different particle size of slag aggregate on the carbonation progress was also clarified. The fact that higher the surface area of fine slag aggregate provides better contact conditions for the carbonation reaction than low surface area of coarse slag aggregate. Thus, the progress of carbonation reaction in the accelerated carbonation chamber helps us decrease free lime in slag and convert into stable calcite mineral. By adopting this technique, the potential expansiveness of steel slag could be achieved before using concrete. In the future study, we could investigate on the physio-mechanical properties of carbonated slag aggregate for potential application as aggregate for cement or bituminous concrete.

Acknowledgments. The research is funded by Ho Chi Minh city University of Technology, VNU-HCM under grant number T-CNVL-2019-25.

REFERENCES

1. Shi C. - Steel slag – its production, processing, characteristics, and cementitious properties, *Journal of Materials in Civil Engineering* **16** (3) (2004) 230-236.
2. Yildirim I. Z., and Monica P. - Chemical, mineralogical, and morphological properties of steel slag, *Advances in Civil Engineering Volume 2011* (2011), Article ID 463638, 13 pages (doi:10.1155/2011/463638).
3. Ecoslag company, Steel slag – green material for future, Technical report, (2012) p.85.
4. Huijgen W. J. J., Geert-Jan W., and Rob N. J. C.- Mechanisms of aqueous wollastonite carbonation as a possible CO₂ sequestration process, *Chemical Engineering Science* **61** (13) (2006) 4242-4251.
5. Huijgen W. J. J., Geert-Jan W., and Rob N. J. C. - Mineral CO₂ sequestration by steel slag carbonation, *Environmental science & technology* **39** (24) (2005) 9676-9682.
6. Pan S. Y., Chang E. E., and Pen-Chi C. - CO₂ capture by accelerated carbonation of alkaline wastes: a review on its principles and applications, *Aerosol Air Qual Res* **12** (5) (2012) 770-791.
7. Ukwattage N. L., Ranjith P. G. and Li X. - Steel-making slag for mineral sequestration of carbon dioxide by accelerated carbonation, *Meas. J. Int. Meas. Confed.* **97** (2017) 15–22.
8. Son N. K., Huynh N. N. T., and Tu T. A. - Experimental study and characterization of bio-based aggregate concrete under accelerated carbonation condition, *Journal of Building Science and Technology - IBST* **4** (2017) 48–54.
9. Young J. F. - Humidity control in the laboratory using salt solutions—a review, *Journal of Applied Chemistry* **17** (9) (1967) 241-245.