

# Effect of Water-binder Ratio and Blaine fineness on the Carbon Dioxide Activation of a Cement-Free Binder

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**Abstract**—The effect of water-binder ratio and Blaine fineness on the carbon dioxide activation of a cement-free binder was studied. An electric-arc furnace slag from the national steel industry in Portugal was used. The slag's chemical composition was determined by energy dispersive spectroscopy analysis, it was rich in calcium oxide, iron oxide and silicon oxide with some minor contents of other oxides. The slag was turned into powder and mixed with water in three different ratios from 0.10, 0.125 and 0.15. Two different sieve ranges of powder were used, 45 $\mu$ m and 125 $\mu$ m, each powder had its own density and Blaine number which were respectively 3.7712g/cm<sup>3</sup> and 529m<sup>2</sup>/kg; and 3.7033g/cm<sup>3</sup> and 136m<sup>2</sup>/kg for the 45 $\mu$ m and the 125 $\mu$ m. The temperature and the gas pressure were controlled aiming to improve its activation. Compressive strength up to 71MPa was achieved on the samples. Thermogravimetric analysis and x-ray diffraction were done to see the formed products, mineralogical phases and compare the activation between the different situations.

**Index Terms**—iron carbonation, cement-free binder, carbon dioxide activation, industrial waste, slag

## I. INTRODUCTION

Global warming has exceeded its limits in 2015, therefore it is compulsory finding efficient methods for reducing greenhouse gases. This temperature anomaly was record also due a high content of carbon dioxide (CO<sub>2</sub>) at the atmosphere [1]. CO<sub>2</sub> emissions and wastes from sources across a spectrum of industrial processes pose negative impacts on human health and the environment and stood at 4,4 billion tons of CO<sub>2</sub>-equivalents in 2014. [2].

The waste from European economic activity and households produced 2.5 billion tons in 2012 the steel industry also produces large amounts of wastes, which are often dumped in landfills resulting in potential soil and water contamination. Wastes from coal combustion also represent a great risk to the environment and only a

fraction of this material is recycled with the rest dumped into landfills, posing serious, long-term environmental and public health problems. Similarly, mining and quarrying activities can cause significant environmental, economic and social impacts. [3]. All this results in accumulation of large amounts of mineral wastes in deposit fields what leads to environmental pollution, serious landscape impacts, affecting the quality of life for local population. Preventive measures typically involve the use of earth/rock dams or lagoons to store the wastes. Unfortunately, potential collapse of such structures could have serious impacts on the environment and human health and safety [4].

Researchers already showed that most mining, quarrying and other industrial wastes can be reused in earthworks and construction as the coarser fractions namely in asphalt, pavements and concrete or even become raw material for industrial applications such of marble and polyester mortar industry [5] or even different applications depending on their mechanical properties [6]. Other research studies have been focused in developing technical-artistic value added and polymer-based composite materials using mining coarse wastes as new polymer-based construction materials in technical-artistic applications [7]. The reuse of mud waste as precursor materials for alkali-activated binders and its applications have also been considered very promising from a technical, environmental and economic point of view [8]. Besides the alkaline activation of aluminosilicate industrial by-products such as blast furnace slag and fly ash is widely known to yield binders whose properties make them comparable to or even stronger and more durable than ordinary Portland cement [9]. Alkali-activated binders also possess interesting inherent properties that enable them to perform multiple functions.

It has been recently demonstrated that metallic iron can react with aqueous CO<sub>2</sub> under controlled conditions to form complex iron carbonates which have binding capabilities and can be a potential viable solution for

concrete applications. CO<sub>2</sub> captured from Ferrybridge Power Station's carbon in the UK was used as a feedstock to synthesize polymers and high value chemicals for composite manufacturing [10]. Other products such as textiles, coatings, adhesives, polycarbonate plastics used in bulletproof glass, spectacle lenses and electronic parts are being synthesised from captured CO<sub>2</sub> [11].

Few studies have reported the production of cement by reacting metals with CO<sub>2</sub> to yield iron carbonate binders which has a great potential to work as a waste and CO<sub>2</sub> storage, besides as being an efficient construction material and ordinary Portland cement replacer for ordinary and high performance applications [12]. Bonenfant et al. already achieved an uptake of 24.7 g CO<sub>2</sub>/100 g of slag used which shows how much of CO<sub>2</sub> can be stored instead of emitting this harmful gas [13]. This system exhibits fracture parameters that are significantly higher when compared to those of the OPC systems in both the unreinforced and glass fiber reinforced states [14]. The metallic iron will react with aqueous CO<sub>2</sub> under controlled conditions to form complex iron carbonates which have binding capabilities. The compressive and flexural strengths of the chosen iron-based binder systems increase with carbonation duration and the specimens carbonated for 4 days exhibit mechanical properties that are comparable to those of companion ordinary Portland cement systems that are most commonly used as the binder in building and infrastructural construction [15]. The carbon dioxide activated binder due to its production procedures is a potential construction material for pre-cast application, once a carbonation chamber is needed and other parameters must be controlled. Moreover, further research is needed on this field once different wastes should be tested, the optimal carbonation conditions should be defined, the industrial production design should be drawn and the cost analysis must be done [16].

## II. EXPERIMENTAL PROGRAM

### A. Materials and Procedures

An electric arc furnace slag was received from the national steel industry at Maia and Aldeia de Paio Pires, Seixal, Portugal. This slag is currently being used in pavement constructions [17], however the CO<sub>2</sub> storage potential has been analysed through this cement-free binder which is a carbonated mixture of slag powder and water. The as-received slag was put in the oven at 60°C for 24 hours for drying, crushed into a small size at a crusher mill and then further pulverized into powder at a ball mill. Two different powders were used selected by two different sieves ranges one of 45 µm and the other one of 125 µm. After sieving, the powders were submitted to a density test which showed a result of 3.7712g/cm<sup>3</sup> and 3.7033g/cm<sup>3</sup> respectively and then to a Blaine test that found the Blaine numbers of 529 and 136 m<sup>2</sup>/kg the two different results was to observe its influence on the reaction and the final material.

The chemical composition of the EAF slag was determined by the energy dispersive spectroscopy (EDS) analysis. Through the analysis was possible to see that the slag is rich in calcium (CaO), iron (Fe<sub>2</sub>O<sub>3</sub>) and silica (SiO<sub>2</sub>) with some other minor oxides on its composition. Chemical composition, density and Blaine number of each powder is shown at Table I.

Eighteen cylindrical samples were compacted into a mold of 20 mm of diameter and 40 mm of height. Three for each water to slag ratio, 0.10, 0.125 and 0.15 of each Blaine number. The samples were subjected to carbonation activation right after casting with a concentration of 100% of CO<sub>2</sub> inside the chamber with 0.5 bar pressure. The CO<sub>2</sub> gas used had 99.9% of purity and was injected to the chamber for 72 hours, being replenished as it was being consumed by the samples. The chamber was inside an oven with 40°C of temperature and 100% of relative humidity. After 72 hours of carbonation the samples were taken from the chamber to dry in an oven for 20 hours at 40°C of temperature and then tested on compressive strength in a rate of 0.5kN/second. The scheme of the research design can be seen through Fig. 1.

### B. Reaction and Analysis

Regarding to measure and analyse the carbonation, a thermogravimetric analysis (TGA) and an X-ray diffraction (XRD) were done. On the TGA the raw slag powder and each of the tested samples were heated up to 1000°C with a heating rate of 20°C/min starting from 20°C. For the tested samples a piece was smashed trying to represent also the surface and the inner part of the carbonated sample and mixed before go through the test. The reaction of the slag powder with the CO<sub>2</sub> could be seen by the thermogravimetric and differential thermogravimetric curves which show respectively the mass loss percentage and its peaks. The TGA analysis was done to characterize the formed products and compare between the w/s ratios which has more formed products. Therefore, the crude and all three w/s ratio powder of higher Blaine number were tested.

On the XRD analysis the powder and sample preparation was the same, however the interpretation was based on the changes of the mineralogical phases before and after carbonating to understand which phases were consumed and produced. For that the XRD analysis was done on the non-carbonated powder with higher Blaine number and on the two 0.1 w/s ratio powders to check which one would react more.

TABLE I. CHEMICAL COMPOSITION AND BLAINE NUMBER

	Oxides (%)		Sieve range	Density (g/cm <sup>3</sup> )	Blaine number (m <sup>2</sup> /kg)
	CaO	SiO <sub>2</sub>			
Slag	30.21	14.18	45 µm	3.7712	529
	12.00				
	5.58				
	29.51		125 µm	3.7033	136

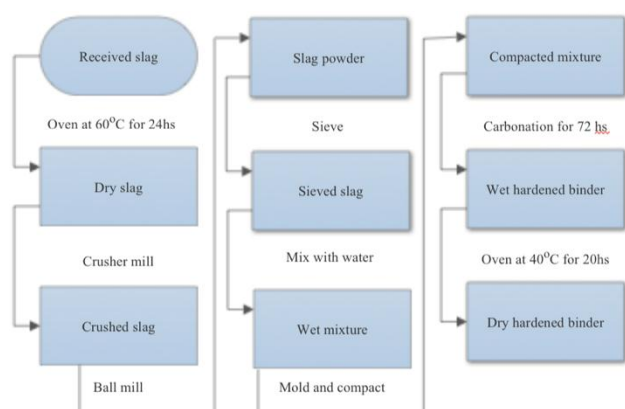


Figure 1. Scheme of the research design.

### III. RESULTS AND DISCUSSION

After taking the samples out from the carbonation chamber, they were all wet due to the high relative humidity inside the chamber and only after 20 hours of drying in an oven the visual aspect could be analyzed. All samples seemed to be hardened, well reacted and homogeneous. However due to its particle size the sample which had 125µm powder was not as same homogeneous and activated as the 45µm one. Moreover, after the compressive strength test on the 125µm it was possible to see that some inner parts were leaving unreacted powder.

#### A. Compressive Strength

The compressive strength of the samples showed that increasing the water-binder ratio implicate on the activation, making it lower when the ration was higher than 10%. Regarding to the samples of higher Blaine number with 0.1, 0.125 and 0.15 had 71.73, 55.73 and 51.97 MPa of compressive strength respectively as shown in Table II. Samples with the water-binder ratio of 0.1 showed the best compressive strength results, however an optimal water-binder ratio couldn't be defined as it was not analysed any ratio under 10%. Successive researches should be carried on with a wider range of water-binder ratios to verify and confirm the optimal ratio.

As expected, due to the reactivity area, the samples of coarse powder had less activation which could be seen through also the compressive strength results that for 0.1, 0.125 and 0.15 was 23.43, 18.33 and 16.73 MPa respectively also shown in Table II. The behaviour of the compressive strength results due to the increase of the water-binder ratio was similar, decreasing the compressive strength results when the water ratio was higher than 10%.

The found results confirm the expected potential for the carbon dioxide activated binder to be used as a construction material to replace Portland cement in pre-cast applications. Furthermore, the found compressive strength assure that the material is suitable for ordinary and high performance applications. Achieving the

optimal water-binder ratio even better mechanical properties can be reached.

TABLE II. COMPRESSIVE STRENGTH

Powder	w/s ratio	Compressive strength (MPa)
45 µm	0.100	71.733
	0.125	55.733
	0.150	51.967
125 µm	0.100	23.433
	0.125	18.333
	0.150	16.733

#### B. X-ray Diffraction Analysis

Through the XRD analysis was possible to see that the non-carbonated slag had mainly four mineralogical phases: gehlenite (C2AS), wusite (FeO), dicalcium silicate (C2S) and tricalcium silicate (C3S), where the two first, rich in aluminium and iron respectively, did not reacted during the carbonation. The main formed products, which were calcium silicate hydroxide (CSH) and calcite (CaCO3), could be also seen through the analysis. Between the two carbonated powders was possible to see that as higher the Blaine number, higher was its activation evidencing more products phases on the XRD analysis, what represent more carbon dioxide consumption. The carbon dioxide activated binder also confirm the potential in storing industrial water and CO2. Fig. 2 show the XRD analysis on the non-carbonated powder with higher Blaine number and on the two 0.1 w/s ratio powders.

#### C. Thermogravimetric Analysis

The thermogravimetric and differential thermogravimetric curves showed no weight loss for the non-carbonated powder during the TGA. This result was expected once the

temperature during the steelmaking process is over 1000oC what makes the crude slag do not change when submitted to temperatures up to 1000oC. Meanwhile between the carbonated samples it was possible to see the difference on the percentage of weight loss which can be associated with the level of activation. All TGA results can be seen at Fig. 3 where the four thermogravimetric and differential thermogravimetric curves are drawn and are also in harmony with the compressive strength results showing that as less water-binder ratio, more activation, therefore, higher mass loss and more formed products. It is also possible to see on Fig. 3 that all carbonated samples have two peaks, one between 165-215oC which represent the first dehydration of the calcium silicate hydrate, and the other between 555-670oC which represent the second

dehydration of the calcium silicate hydrate. Further studies should be carried on with the TGA as it is not possible to see the calcite peak represented on any of the thermogravimetric or differential thermogravimetric curves.

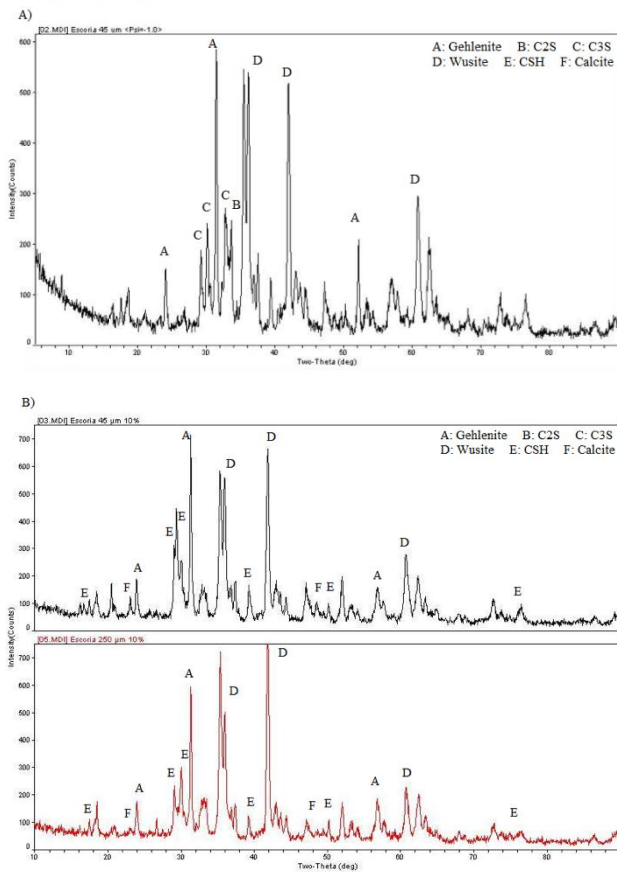


Figure 2. Mineralogical phases through XRD analysis: (A) before carbonating the 45 μm powder, and (B) after carbonating the samples of 0.1 w/s ratio.

#### IV. CONCLUSION

This research article has reported experimental results and analysis on the effect of the water-binder ratio and powder fineness on the carbon dioxide activation of a cement-free binder. The following conclusions can be drawn from this study:

- The studied binder showed great potential to be used as a construction material used to replace Portland cement binders based on the achieved mechanical properties. The binder has a compressive strength which suit for ordinary and high performance applications.
- The study also found that as much higher is the water-binder ratio the compressive strength is lower. This decrease was analyzed for water-binder ratio higher than 10%.
- Another conclusion was related with the slag fineness where was found that it influences on the activation and compressive strength development. As higher the Blaine number, the slag had more activation and higher compressive strength.
- The reaction of the wet slag in a carbon dioxide atmosphere was mainly based on the consumption of the dicalcium silicate and tricalcium silicate and the product formation

of calcite and calcium silicate hydroxide. Two mineralogical phases rich in iron were not reactive which were the gehlenite and wustite.

- Further research is needed to find the optimal water-binder ratio and test wastes with less or no iron phases intending to have a more activated construction material.

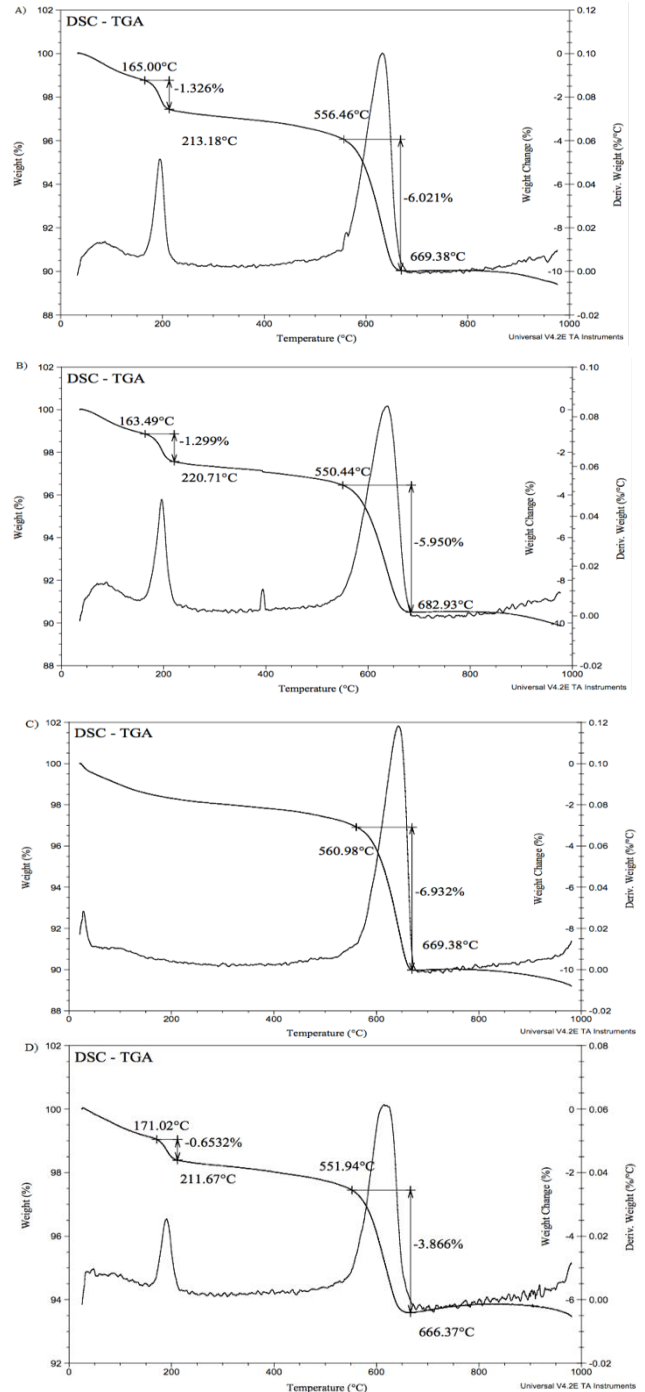


Figure 3. Thermogravimetric and differential thermogravimetric curves of the carbonated samples with temperature and weight loss indicated of: (A) 45 μm and 0.1 w/s ratio, (B) 45 μm and 0.125 w/s ratio, (C) 45 μm and 0.15 w/s ratio, and (D) 125 μm and 0.1 w/s ratio.

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