

# ALKALI-ACTIVATION OF VITRIFIED BAUXITE RESIDUE: THE EFFECT OF MgO

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## Introduction

To reduce the global carbon dioxide emissions, there is a strong driving force for research on alternative and sustainable types of binder which can compete with the established binders on the market, such as ordinary Portland cement (OPC). One of the alternative binders is the group of inorganic polymers (IP), which can be produced by alkaline activation of (calcium-)aluminosilicates.<sup>1</sup> Also Fe-rich (alumino-)silicates, for instance, metallurgical residues, can be used for the synthesis of an IP. One possible Fe-aluminosilicate is bauxite residue (BR) after a high temperature treatment.<sup>2</sup> BR is generated from the alumina industry, during the digestion of bauxite ore in the Bayer cycle. BR is produced at a rate of 150 Mt/y and the estimated amount of landfilled BR is above 3 billion ton worldwide.<sup>3</sup> A high temperature treatment was introduced as an option to achieve a reactive precursor to increase the solubility of Si and Al.<sup>2</sup> The addition of SiO<sub>2</sub> and C in the heat treatment increased the amount of melt formation at high temperature which transformed into reactive glass after quenching.<sup>2</sup> Compressive strengths up to 40 MPa were reported, but the durability of these binders remains unclear. On work performed on GGBFS, addition of Mg was found to have a positive impact on the durability of IP due to the formation of hydrotalcite after alkali activation. This increased the resistance to carbonation and Cl<sup>-</sup> intrusion due to CO<sub>2</sub> uptake and Cl<sup>-</sup> surface adsorption.<sup>4,5</sup> Mg is an interesting element to add in the high temperature treatment due to the availability of dolomite or Mg containing mining residues. In this paper, the potential of increasing the MgO content in the glass and 28 d strength of the resulting IP were investigated.

## Materials and methods

The BR in this study originated from the mud slurry pumping system to the BR disposal area at Aughinish (Rusal) alumina plant. The BR was dried at 105°C for 24 h. After drying, the residue was milled below 100 µm using a rotary disk mill. The chemical composition of the BR was quantified using a Bruker S8 Tiger X-ray fluorescence spectrometer (XRF). Loss on Ignition (LOI) was determined in triplicates using thermal analysis (TGA). The XRF and TGA data were used to calculate with FactSage 7.0 the highest amount of glass to be produced, using SiO<sub>2</sub>, C and MgO as

additives. A temperature of 1200°C, as well as an addition of 10 wt% SiO<sub>2</sub> and 2 wt% C to the dried BR, were chosen as the starting conditions in obtaining a significant melt (> 70 wt%). In total, four different glasses were synthesised by adding 0, 1, 3 and 5 wt% of MgO to the optimal mix design, named as TBR(0, 1, 3 or 5)MgO. After melting and quenching, the treated bauxite residue (TBR), was milled using a disk mill and a vibratory ring mill until a Blaine specific surface area of 4400 ± 200 cm<sup>2</sup>/g according to EN 196-6. After milling, paste samples were prepared by mixing the TBR with an alkali activating solution (H<sub>2</sub>O = 65 wt%, SiO<sub>2</sub>/Na<sub>2</sub>O = 2.0 molar ratio) using an Ika RW20 mixer for 4 min with a L/S of 0.4. The paste was subsequently cast in cubes with 20 mm lateral length and cylindrical mould of 35 mm diameter and cured at 20 ± 2°C for 28 d in a closed box. An OPC-based binder using a L/S of 0.4 was added as reference and cured according to EN 196-1. Cubes were tested in quadruplicates after 28 d with an Instron 5985 testing machine using a 250 kN load cell and a crosshead speed of 2 mm/min. 28 d cylindrical specimens were put at 22°C, 65% H<sub>2</sub>O, 0.03% CO<sub>2</sub> for 3 d and were then placed in a CO<sub>2</sub> chamber with 1% CO<sub>2</sub>, 65% H<sub>2</sub>O and 22°C for 3 months to accelerate the carbonation rate. The mineralogical compositions of TBR was assessed using a D2 Phaser diffractometer (Bruker). The quantification was done by adding 10 wt% zincite as an internal standard, which was wet-milled with the sample in a micronising mill. The software Diffraction EVA V4.1 (structures from PDF2 database) and TOPAS-Academic V5 (structures from ICSD database) were used for qualitative and quantitative analysis, respectively. The TBR samples were further investigated by scanning electron microscopy (SEM - Philips XL30 FEG). Samples were embedded in a resin, polished and coated with carbon or platinum. Energy-dispersive X-ray spectroscopy (EDX), using 30 kV, was performed for micro-chemical analysis.

## Results and Discussion

Table 1 shows that Na<sub>2</sub>O is decreased compared to the initial level before firing, most probably due to its volatile behaviour. The predicted amorphous content using FactSage was > 70 wt%. Due to a lower cooling rate and possibly a higher pO<sub>2</sub> during the experiment compared to the thermodynamic calculations, a higher amount of titanomagnetite and spinels was formed, Table 2.

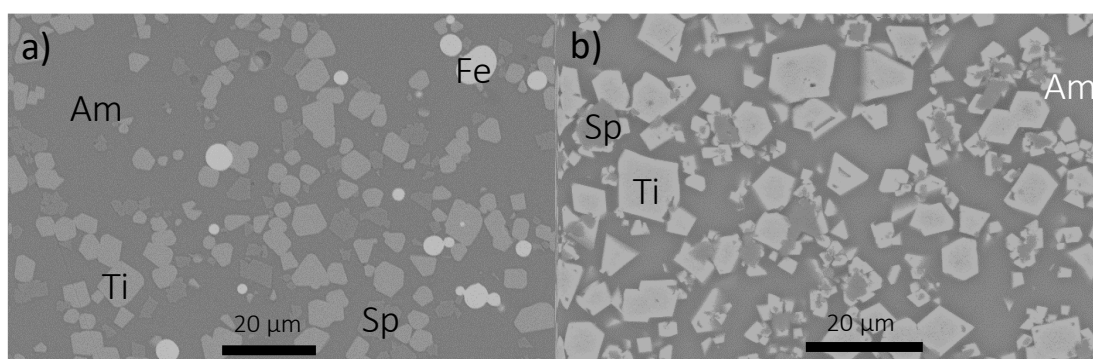
**Table 1:** Chemical composition of the BR and TBR using different additions of MgO (estimated relative error is 10%)

|         | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | Na <sub>2</sub> O | CaO | MgO | Other |
|---------|--------------------------------|------------------|--------------------------------|------------------|-------------------|-----|-----|-------|
| BR      | 48.3                           | 9.8              | 17.1                           | 8.6              | 8.2               | 6.0 | 0.1 | 1.8   |
| TBR0MgO | 46.7                           | 16.8             | 14.2                           | 8.3              | 6.6               | 5.7 | 0.1 | 1.6   |
| TBR1MgO | 47.2                           | 16.4             | 14.0                           | 8.4              | 6.3               | 5.7 | 0.8 | 1.3   |
| TBR3MgO | 46.3                           | 16.3             | 13.7                           | 8.2              | 5.9               | 5.6 | 2.6 | 1.4   |
| TBR5MgO | 45.8                           | 16.0             | 13.4                           | 8.1              | 5.9               | 5.5 | 3.9 | 1.4   |

**Table 2:** Mineralogical composition of the TBR

|                 | TBR0MgO    | TBR1MgO    | TBR3MgO    | TBR5MgO    |
|-----------------|------------|------------|------------|------------|
| Amorphous       | 49.7 ± 1.1 | 48.6 ± 6.4 | 53.6 ± 3.5 | 45.0 ± 0.8 |
| Titanomagnetite | 35.6 ± 0.8 | 36.4 ± 4.3 | 28.2 ± 1.9 | 31.9 ± 0.8 |
| Iron            | 2.0 ± 0.2  | 0.6 ± 0.1  | 0.9 ± 0.1  | 0.8 ± 0.0  |
| Spinel          | 7.6 ± 0.3  | 9.1 ± 2.2  | 13.0 ± 1.1 | 16.5 ± 1.1 |
| Nepheline       | 3.2 ± 0.2  | 2.4 ± 1.0  | -          | -          |
| Wüstite         | 1.7 ± 0.1  | 2.9 ± 0.7  | 4.3 ± 0.4  | 5.7 ± 0.6  |
| Quartz          | 0.2 ± 0.2  | -          | -          | -          |

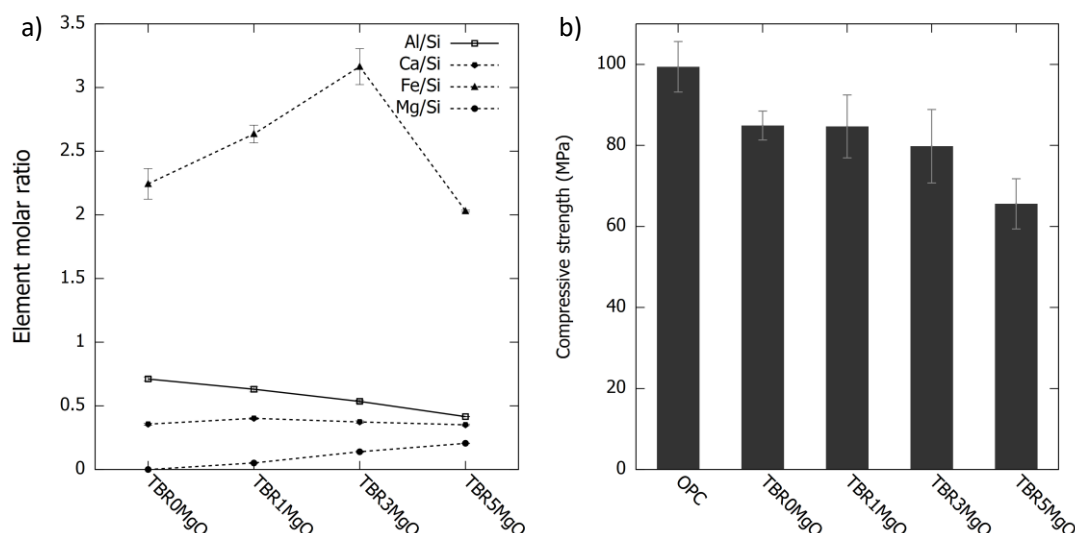
Figure 1 shows SEM images of the resulting TBR. By increasing the amount of Mg in the TBR, a higher quantity of cubic spinel is present. A significantly lower amount of amorphous phase was only visible for TBR5MgO due to the high amount of spinels in a glassy matrix.



**Figure 1:** Microstructure of TBR using BSE imaging for a) TBR0MgO and b) TBR5MgO; Am: amorphous, Fe: iron, Ti: titanomagnetite, Sp: spinel

Figure 2a shows that Mg is incorporated in the glass. By increasing the Mg content, the Al content decreases compared to Si due to increased spinel formation. Only iron does not show a clear evolution, which could be linked to the amount of titanomagnetite type spinel crystallised in the neighbouring glass.

Figure 2b shows that the 28 d compressive strength of the different TBR samples is at least 20% lower compared to the reference OPC paste (CEM I 52.5R, L/S = 0.4). The lowest compressive strength is measured for TBR5MgO and can be linked to the increase in crystalline phases (spinel) and decrease of Al, affecting the final binder chemistry. Ongoing carbonation tests already show that by increasing the Mg content the amount of visual efflorescence is increasing for TBR3MgO and TBR5MgO. This is an indication that less alkalis were reacting towards the final product due to the lower reactivity of the TBR for alkali activation.



**Figure 2:** a) Normalised SEM-EDX data of the glass phase b) 28 d compressive strength data

## Conclusion

In this study, it was shown that BR can be transformed to reactive precursors for IP, after melting with additions of SiO<sub>2</sub>, C and MgO. An increasing amount of MgO increased the amount of Al-bearing spinels whereas the 28 d compressive strength decreased when 5 wt% of MgO was incorporated. It is hypothesised that a MgO addition > 5 wt% decreases reactivity due to the formation of more crystalline phases and due to a decline of the Al concentration in the glass, which affects the final binder chemistry. Currently-running carbonation tests will show if MgO additions can have a positive effect on the carbonation resistance.

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