Bauxite Residue Valorisation through Reductive Smelting: Production of Inorganic Polymer Fire Resistant Building Materials

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Abstract

In this study thermal treated bauxite residue is used to produce inorganic polymer building material with fire resistant properties. The calcined bauxite residue from the EAF furnace of Mytilineos was mixed with alkaline solution and casted to cure. The inorganic polymer material was tested for its fire resistant properties and pass all criteria of ISO 834 fire temperature curve.

Subject Areas

Material Experiment

Keywords

Inorganic Polymers, Bauxite Residue Thermal Treatment, Fire Resistant Material

1. Introduction

The use of BR in geopolymers, inorganic polymers (IP), alkali activated materials (AAM) and hybrid binders has gained increased attention in recent years. In scientific literature, the terminology used varies greatly depending on the author, but also on whether the nomenclature refers to chemistries or to the structure of final product [1] [2] [3]. In this study we prefer terminology created by Van De Deventer *et al.* [4]. A geopolymer is defined as a mainly amorphous alkalialuminosilicate binder formed by the reaction of a source material consisting almost exclusively of SiO_2 and Al_2O_3 (e.g. metakaolin) and an alkaline solution

(mainly alkali-hydroxide/silicate) [5]. The raw material dissolves in alkaline media releasing Al and Si species that form gels when oversaturation is reached. Further polycondensation and rearrangement lead to the formation of a rigid 3D-network consisting of $Al^{3+}O_4$ and $Si^{4+}O_4$ tetrahedrons connected via oxygen bridges [6]. Alkali cations act as charge balancer of Al^{3+}. IPs can be understood as a superset of geopolymers and have a polymer structure as well; they deviate from the pure aluminosilicate chemistry and include precursors, containing Ca and Fe [7] [8] [9] which are activated using hydroxides, silicates and carbonates, among others. In case of high-Ca precursors, such as ground granulated blast furnace slag, the binder is consisting mainly of C-A-S-H phase [10]). The term IP is also used to refer to binders made from an iron-silicate precursor, for instance, from fayalite slag stemming from non-ferrous metallurgical industry [11]. Recent data demonstrated that the reactions and the structure of Fe-rich IPs are similar to geopolymers with $^{IV}Fe^{3+}$ likely in the silicate network (similar as $^{IV}Al^{3+}$ in geopolymers) [12], and Fe2þ trioctahedral layers [13]. AAM refers to all types of binder formed by the reaction of a solid silicate precursor and an alkali salt, including hydroxides, silicates, carbonates, sulphates, aluminates or oxides [4] [14]. A binder consisting of cement, a silicate source and the addition of an alkali source is often termed as a hybrid alkali-activated binder [2] [15]. In our study we use the term inorganic polymers.

2. Thermal Treatment/Calcination of Bauxite Residue Studies

Thermal modification of BR is an alternative to overcome its low reactivity. The advantage is that the dissolution of relevant elements from the treated residue might be considerably increased in an alkaline solution compared to untreated BR. This potentially decreases the amount of other reactive precursor materials required or even makes an addition redundant. In the study by Ye *et al.* [16], BR (Chalco Co., Zhengzhou, China) was treated at different temperatures from 200°C to 1000°C in order to increase the solubility during alkali-activation. Alkaline leaching tests proved an increase in solubility with increasing treatment temperatures, to a maximum of 800°C, stemming from the dissolution of Na-Al-silicates. For Na-silicate geopolymers produced from a 50/50 mix with GGBFS, no significant differences in compressive strengths were detected up to a BR treatment temperature of 600°C (12 - 20 MPa after 28 d). However, at 700°C and 800°C, an increase in the compressive strength to 36 and 49 MPa, respectively, was reached, while a higher calcination temperature led to a drop below 25 MPa. Geopolymers were subsequently prepared by scanning the whole compositional range from 0 to 100 wt% replacement of calcined BR (800°C) with GGBFS. Significant strength increases were detected with a higher content of GGBFS. About 90 MPa were reached for the 90 wt% GGBFS/10 wt% BR blend and thus slightly higher than the GGBFS reference. Samples prepared solely with calcined BR developed only 5 MPa. Various analytical techniques, such as SEM, FTIR and XRD, verified the formation of a geopolymer binder, next to semi-

crystalline C-(A)-S-H gel and cancrinite. Phases formed after the calcination of BR actively participated in the reactions towards a binder. The results demonstrated, however, that the production of IPs with decent properties solely from this calcined BR is not possible and that another reactive material still needed to be added. Hairi *et al.* [17] used also calcined BR (500°C) with additions of amorphous silica fume (6 - 26 wt%) and amorphous ρ-alumina in the solid mix. The highest compressive strength of 58 MPa (28 d) was reported for a mix of 83 wt% of calcined BR, combined with 17 wt% silica fume and Na-silicate solution (L/S = 0.48). Results of ^{27}Al MAS NMR spectroscopy indicated an increase in the ratio of tetrahedral over octahedral Al, which was interpreted as a higher degree of geopolymerisation. It remained, however, unclear whether the increase in tetrahedral Al was primarily an effect of the calcination of BR (disappearance of gibbsite with octahedral Al and the formation of X-ray amorphous alumina transition phases with octahedral and tetrahedral Al), since the highest tetrahedral to octahedral Al ratios were observed for calcined BR IPs.

3. BR Calcination Campaign at Mytilineos Plant

In a previous study [18] the results of five BR calcination tests at 1600°C - 1700°C in the EAF 1 MVA were presented. The smelting tests utilized Bauxite Residue (BR), metallurgical coke and lime as raw materials, with the aim of producing cast iron and slag suitable for the creation of construction materials. The recipe used adds relative to BR 30% wt and 18%wt Coke. In each test 300 kg of dry KB, 90 kg of CaO, 80 kg of starter slag (from previous test) and 54 kg of coke are melted at 1600°C - 1700°C and 90 kg of pig iron and 300 kg of slag were produced. Five tests were performed during this first campaign. Average furnace energy consumption was 2233 kWh/t BR. A total of 487 kg of cast iron and 1259 kg of slag were produced. The thermally treated BR had the following chemical analysis (Table 1) and mineralogical phases (Table 2 and Figure 1).
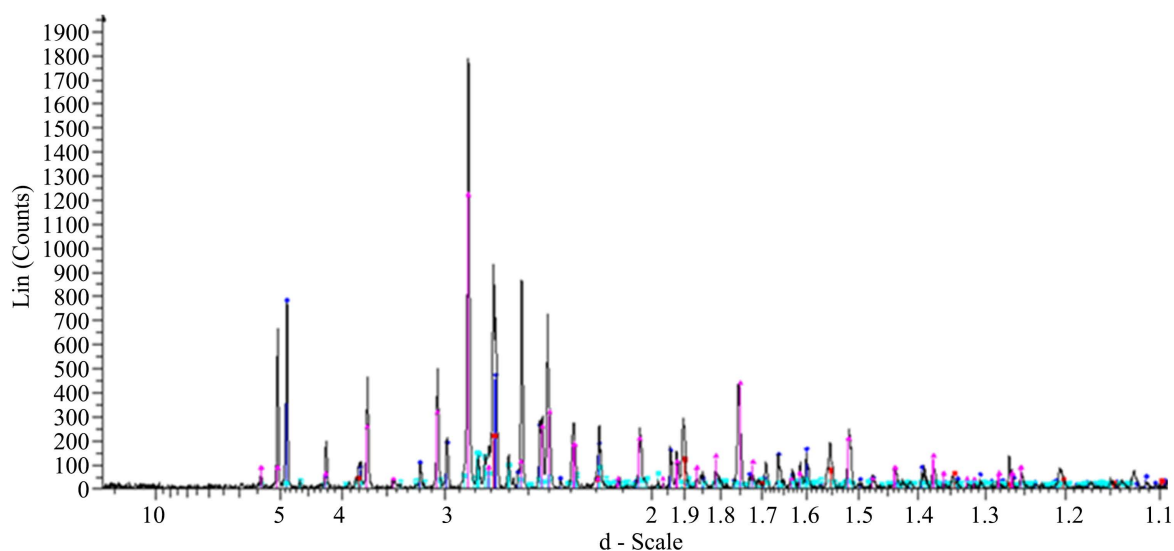
Figure 1. Mineralogical analysis of pyrometallurgical slag of test run #2.

Table 1. Chemical analysis of pyrometallurgical slag produced per run.

TEST % w/wt	#1	#2	#3	#4	#5
Fe_2O_3	1.10	1.14	2.50	1.54	1.34
SiO_2	11.49	14.78	14.24	12.76	11.57
CaO	44.13	40.41	39.26	41.57	44.33
Al_2O_3	30.71	31.09	31.05	30.17	28.22
Cr_2O_3	0.00	ND	0.06	0.06	0.03
TiO_2	7.43	7.21	6.78	7.11	7.18
V_2O_5	0.04	0.03	0.07	0.13	0.10
Na_2O	0.41	0.70	1.48	1.80	1.41
$-SO_3$	0.48	0.45	0.50	0.52	0.55
TOTAL	95.79	95.80	95.94	95.65	94.73
Weight (kg)	248.00	320.00	245.00	191.00	255.00

Pyrometallurgical slag (XRF)

Table 2. Mineralogical phases of pyrometallurgical slag per test run.

XRD samples	$Ca_{12}Al_{14}O_{33}$ Mayenite	Ca_2SiO_4 Calcio Olivine	Ca_2SiO_4 Larnite	$Ca_2Al_2SiO_7$ Gehlenite	$CaAl_2O_4$ Krotite	$CaTiO_3$ Perovskite	H_3BO_3 Sassolite (flux added for XRF pellet)
			Values in wt%				
#1	29.00	20.00	8.00	16.00	15.00	12.00	-
#2	16.00	-	10.00	61.00	-	13.00	-
#3	3.00	-	19.00	65.00	-	12.00	1.00
#4	17.00	-	25.00	33.00	7.00	13.00	5.00
#5	38.00	-	25.00	16.00	-	15.00	6.00

The calcinated BR was first milled to d_{90} = 500 μm and then further milled to d_{90} = 80 μm before used as a precursor for inorganic polymer.

4. Inorganic Polymer from Calcined BR

The synthesis of geopolymers includes 3 stages: 1) The synthesis of the aqueous potassium alkaline phase with defined ratios (water percentage) and molarity but also phase diagrams depending on the desired properties of the final material, 2) the production of the geopolymer paste and 3) the curing of the geopolymer under appropriate temperature/time conditions. The geopolymer paste resulting from mixtures is casted into appropriate moulds and cured in an oven at 60˚C for ninety-six hours. The moulds are then removed from the oven, specimens are removed from the moulds and stored in suitable chamber at ambient temperature until final testing.

The Solid/Liquid ratio needs to be as higher as possible (optimum to have a viscous and castable paste) to minimize the risk of cracks creation during curing and also curing temperature is desirable to be kept low. Following above requirements, the initial sample screening resulted in following synthesis with the highest 28 days compressive strength (Table 3)

Further testing of the developed material, included apart from compressive strength, flexural strength, alkalinity, thermal conductivity and freeze thaw (Table 4).

For the purposes of the research, the under development product, will not bear load or will be force loaded, but will mainly act as a thermal barrier to protect concrete structure from spalling during a fire; so, the compressive strength achieved (17 MPa) is considered high enough [19].

5. Fire Test According to ISO 834

Finally, the developed material was tested based on EFNARC guidelines for fire resistant according to ISO 834 fire temperature curve. The cellulosic curve is applied when fire resistant building materials are tested for their performance under fire. This curve is based on the burning rate of the materials found in general building materials and contents. The temperature development of the Cellulosic fire curve (ISO-8341: Fire-resistance tests—Elements of building construction standard fire curve.) is described by the following equation:

Table 3. Optimum synthesis of pyrometallurgical BR slag inorganic polymer.

Ingredient	Quantity
Pyrometallurgical BR slag (g)	754.00
NaOH [8M] (ml)	83.20
S/L (g/ml)	2.90
Curing conditions (Temperature ˚C/Time h)	60˚C/96h
Density (Kg/m^3)	2196.00

Table 4. Fire resistant pyrometallurgical BR inorganic polymer building material characteristics.

Material characteristics	Value
Compressive strength (MPa)	17.00
Flexural strength (MPa)	4.94
Shore (D, A)	40, 90
Alkalinity	11
λ, thermal conductivity (W/mK)	0.65
Young modulus E (MPa)	5500
Freeze thaw cycles	Cat. 2

$$T = 20 + 345 \times \log(8 \times t + 1) \tag{1}$$

where T stands for temperature (°C) and t stands for time (min) and 20 is the ambient temperature during test.

For the small scale tests a furnace with an adjusted opening from 15 cm × 15 cm to 40 cm × 40 cm was used. This furnace is an electrical furnace working with resistors. The furnace has the ability to simulate all the standard time – temperature curves from ISO 834-1 which reaches a maximum temperature of 1049°C after 2 hours till the RWS curve, which reaches a maximum temperature of 1350°C. (Figure 2) Below there is a description of the several parts of the furnace and the set – up of the furnace:

Controller: the furnace is equipped with time/temperature PL Controller in order to set the desired time/temperature profile according to the selected time-temperature curve.

Furnace temperature: temperature inside the furnace is measured with two thermocouples located in the centre of the chamber. These thermocouples are "S" type (working conditions up to 1600°C with an accuracy of ±1.5°C).

Specimen Temperature: temperature of the specimen is measured in several points (thermocouples mounded inside the specimen) in order to calculate the temperature profile through the concrete specimen within the duration of the test. For these measurements "K" type thermocouples are used (working conditions up to 1260°C with an accuracy of ±1.5°C). The location of these thermocouples during the fire test is installed according to the following figures (Figure 3 and Figure 4).

In the small scale test the thermocouples are placed as follows: three thermocouples located at the protection interface (1, 5, 9), two thermocouples at 25 + 2 mm (4, 6), two thermocouples at 40 + 2 mm (3, 7), two thermocouples at 75 + 2 mm (2, 8) from the front surface of the concrete, plus two thermocouples on the back face (10, 11).
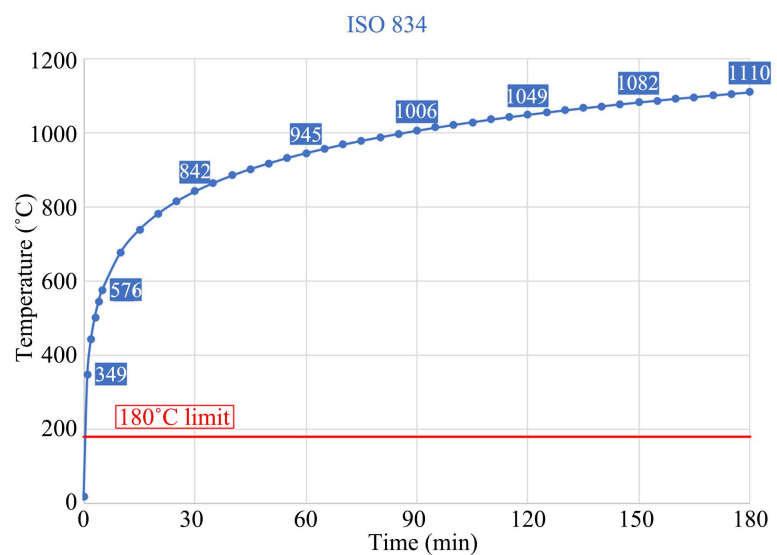
Figure 2. Time temperature evolution in the ISO 834 fire test.

Cross Section of Small Scale Test Slab
With Surface Applied Protection
(Not to scale)

3 thermocouples located at: the protection interface (1, 5, 9),
2 at 25 ± 2 mm (4, 6), 2 at 40 ± 2 mm (3, 7), 2 at 75 ± 2 mm (2, 8), from the front
surface of the concrete, plus 2 on the back face (10, 11).
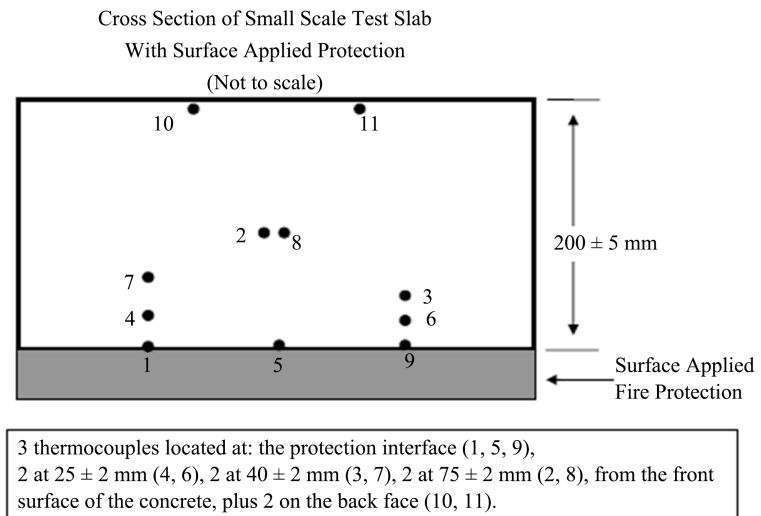
Figure 3. Small scale test for surface applied protection acc. to EFNARC.

Plan View of Small Scale Test Slab
(Not to scale)
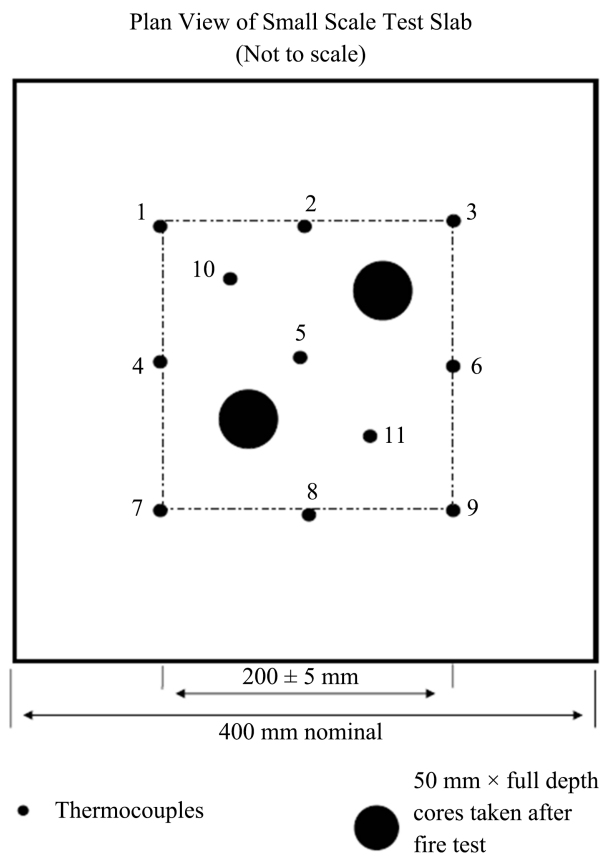
Figure 4. Plan view of small scale test slab.

Concrete Slab: In order to conduct the fire test, concrete slabs were produced. The thickness of the concrete slab was 20 cm. Concrete was manufactured according to the specifications of EFNARC, meaning to achieve an actual cubic strength of 50 to 70 N/mm^2 at 28 days. On the concrete slab, the fire resistant board was fixed using fire resistant anchor nails.

Concrete was manufactured with:

Cement: >350 kg/m^3 CEM ll, 42.5 N grade (EN 197-1)

Water/Concrete < 0.48

Coarse aggregate: crushed limestone with a maximum size D of between 16 and 20 mm.

Plasticizing admixture to give an appropriate W/C and consistence to the mix

Every concrete slab manufactured for the conduction of the test, was measured for compressive strength (three cubes).

Fixing of fire resistant board: The inorganic polymer board is fastened on the concrete slab using Fischer FNA 6 × 30/30 A4 stainless steel anchors. The FNA anchors are installed in combination with a circular washer 30 mm diameter × 1.2 mm thick stainless steel (grade A4) with a hole diameter of 7.5 mm. The fire resistant board have a maximum thickness of 5 cm (resulted to total specimen with the concrete slab at 25 cm).

Results

The ISO 834 fire test on the pyrometallurgical BR slag inorganic polymer was successful, since all criteria were fulfilled. The interface IP/concrete slab reached maximum 120°C, lower than the 180°C limit. Moreover, the concrete slab did not spall or crack and the thermal degradation at the end of the test was 18 mm/°C. The concrete backface temperature reached 77.5°C (Figure 5).

Next steps

The results of the small scale fire test will be re-evaluated in a large scale fire test, in a specimen 1.5 × 1.5 m and five cm thickness.
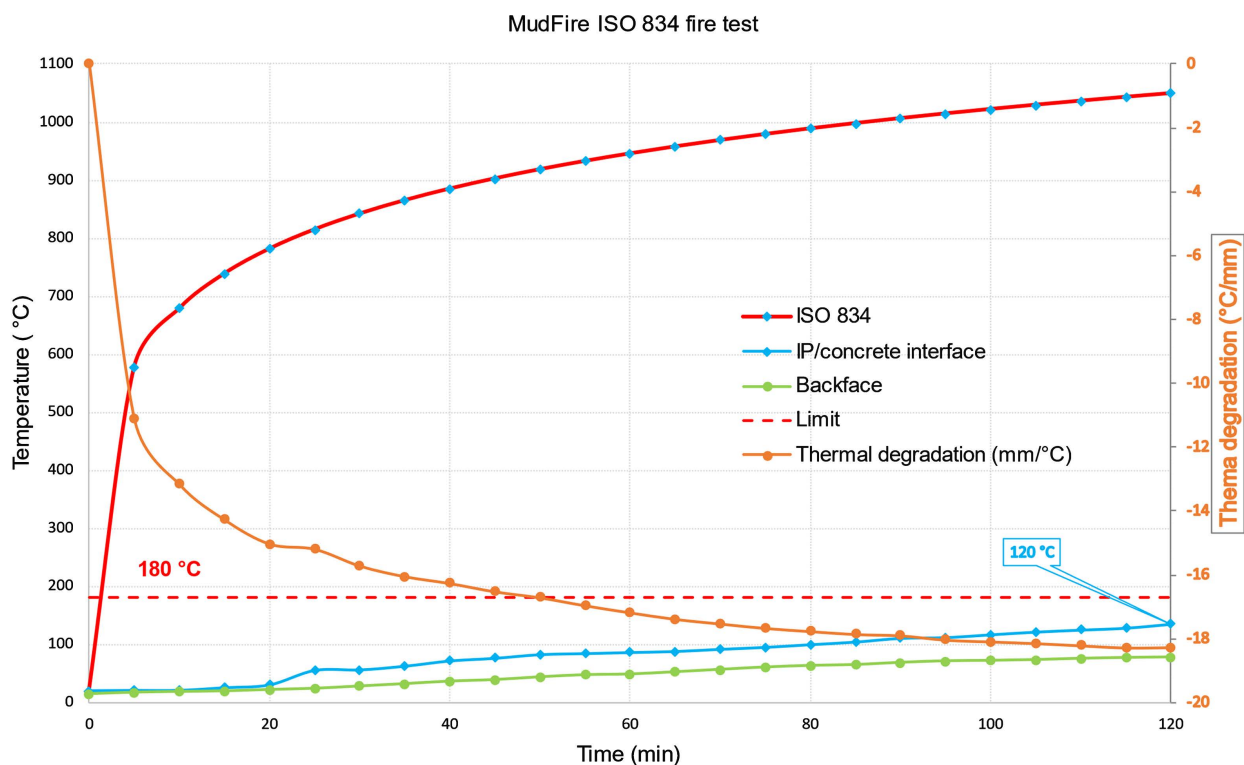

Figure 5. ISO 834 fire test results.

6. Conclusion

In this study we produce fire resistant inorganic polymers from thermally treated bauxite residue with geopolymerization technology. Thermally treated bauxite residue was mixed with alkaline activator to produce a paste which after curing was tested according to ISO 834 fire time-temperature curve. The test was successful since the highest temperature in the inorganic polymer/concrete interface reached a maximum 120°C after two hours and no spalling of concrete occurred. Next step is to repeat the test in large scale ($1.5 \times 1.5 \times 0.05$ m) specimen again with ISO 834 time-temperature fire curve.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest.

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