A PROPOSAL FOR A 100 % USE OF BAUXITE RESIDUE: THE PROCESS, RESULTS ON THE NOVEL Fe-RICH BINDER AND HOW THIS CAN TAKE PLACE WITHIN THE ALUMINA REFINERY

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Abstract

In this work a new pyro-process is presented to transform bauxite residue (BR) into a suitable Fe-rich precursor material for the synthesis of inorganic polymers. Based on thermodynamic calculations, this was achieved by introducing C and firing at 1100 °C, which leads to a carbothermic reduction of iron oxides, present in BR, into ferrous iron, which supports the formation of liquid phase. Addition of silica was also investigated, as it enhances the amount of liquid slag phase. The resulting material after the heat treatment, was mixed with a K-silicate solution and cured at 60 °C for 72h. The final materials are water insoluble and dense, demonstrating compressive strength >40 MPa. These inorganic polymers can find applications in construction, such as pavement or floor tiles. The work is concluding with a presentation on how the process to transform BR can take place within the alumina refinery, by adapting existing installations.

Introduction

Within the Bayer cycle, the alumina/aluminium production from bauxitic raw materials creates substantial amounts of the insoluble to digestion bauxite residue (BR). Per annum >120 Mt of BR is generated, globally considering that one ton of produced alumina results in 1 to 1.5 tons of bauxite residue.[1] Several works are published with ideas of a valorisation of BR. It can be used for instance in construction and chemical applications, like cements, ceramics or catalysis, but also in metallurgy as a source of recovery of metals or minor elements.[2 – 4]

The term geopolymer was first introduced by Davidovits in 1970s. They are defined as Al- and Si-rich cementitious, amorphous binders which are formed by polymerisation of an alkali activated solid aluminosilicate precursor[5]. They consist of chains or a 3D framework of linked AlO_4^{5-} and SiO_4^{4-} tetrahedra. The more general

term Inorganic Polymer (IP) defines a supergroup with a deviation from the tetrahedral coordination of Al and Si and the aluminosilicate chemistry.[6] Several properties such as high flexural and compressive strength, a high resistance against acidic solutions and high thermal stability turn inorganic polymers into promising alternative binders to common building materials like ordinary Portland cements (OPC).[7] Besides aluminosilicates, inorganic polymers can be synthesised from Fe-silicate precursors such as copper,[8] lead[9] or ferro-nickel slags.[10,11] Characteristics of Fe-rich precursor for IP include among others a partially vitrified structure and ferrous iron.[12] The chemical compositions of these non-ferrous slags, e.g. copper slag does not differ considerably from BR, apart from the mineralogical assemblage and the oxidation state of iron. This leads to the question if it is possible to transform BR into such a non-ferrous slag precursor for IP. The first milestone in this trajectory is to create a precursor with a substantial amount of liquid phase at room temperature, assuming that this would be prone to dissolution by alkalis. If that would be possible, the downstream use towards applications would become straight-forward.

The answer to the question posed above is most likely yes. It has been already demonstrated in the past in ceramics made of BR that reducing conditions promote liquid phase formation.[4] This takes place preferentially in the interface between BR and quartz grains,[13] in view of the locally established eutectics. The chemistry of BR is in fact located in the FeO-Al_2O_3-CaO-SiO_2 domain and semi-vitreous precursors can be formed from such compositions, that give eventually inorganic polymers.[12,14] Modification of BR by adding a carbon source followed by thermal treatment can be used to carbothermically reduce ferric iron into ferrous iron and thus promote the formation of liquid phase. Additionally, a silica source can be used to increase the formation of liquid phase. A fast cooling is needed in order to prevent crystal precipitation during cooling and result eventually to a semi-vitreous material.

Experimental Methods

Bauxite residue, provided by Aluminium of Greece, was used as a raw material for different mix compositions. After drying for 24h at 80 °C in a laboratory oven, the chemical composition was determined using X-ray fluorescence analysis. The mineralogical composition was investigated by XRD. Based on the results of the XRF, thermodynamic calculations with the software FactSage™ (version 6.4) were carried out to predict the occurring phase assemblage and the quantity of liquid phase present at 1100 °C. The temperature was chosen as a compromise between promoting the amount of liquid phase and simulating a realistic scenario for industrial applications on the other hand. For the FactSage™ calculations, the pure substances- (FactPS), the oxide- (FToxid) and the steel (FSstel) databases were used.

For the experimental part, different mixes consisting of BR, graphite and quartz were fired at 1100 ± 10 °C under Ar flow in a closed Fe crucible (with gas inlet and outlet tubes) using an induction furnace. After an isothermal step of 1h at the maximum temperature, the fired material was quenched by compressed air in order to get a semi-vitrified, solidified material.

The above material was separated from the Fe crucible and was milled in a vibration disk mill for 12 min. Subsequently, it was characterised by XRD. The IP were synthesised by using potassium silicate solution with a molar ratio of SiO_2/K_2O = 1.6 and H_2O/K_2O = 16, and an activating solution to solid ratio of 0.25. Pastes were poured in rectangular moulds (20 x 20 x 80 mm^3 as well as in 25 x 25 x 20 mm^3), sealed and cured at 60 °C for 72h in a drying oven.

Both compressive strength and flexural strength measurements were performed on the resulting IPs. The microstructure of polished samples was analysed using scanning electron microscopy.

Results and discussion

Characterisation of BR and design of mixtures

X-ray fluorescence data show that the chemical composition of the BR is dominated by Fe_2O_3 and Al_2O_3, CaO and SiO_2 (Table 1).

Table 1: Normalised chemical composition BR, based on semi-quantitative XRF analysis.

Oxide component	wt%
Fe_2O_3	47.9
Al_2O_3	18.9
CaO	11.0
SiO_2	9.6
TiO_2	6.5
Na_2O	4.0

The mineralogical composition of BR is shown in Figure 1. Zincite was mixed as internal standard material for subsequent quantification.

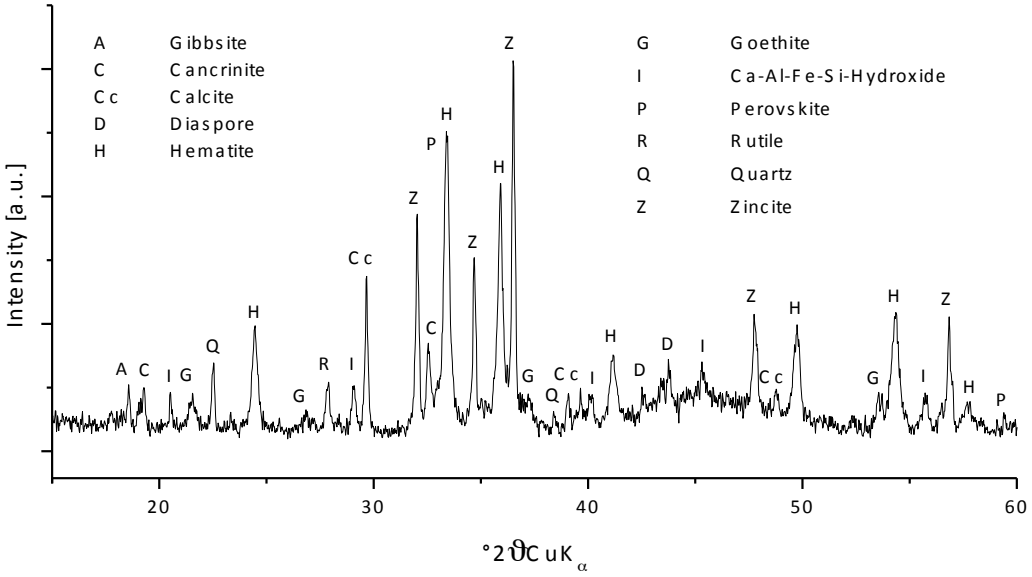


Figure 1: X-ray diffractogram of BR.

Based on the FactSage™ results, different mixtures were designed and are presented in Table 2.

Table 2: Investigated mixes.

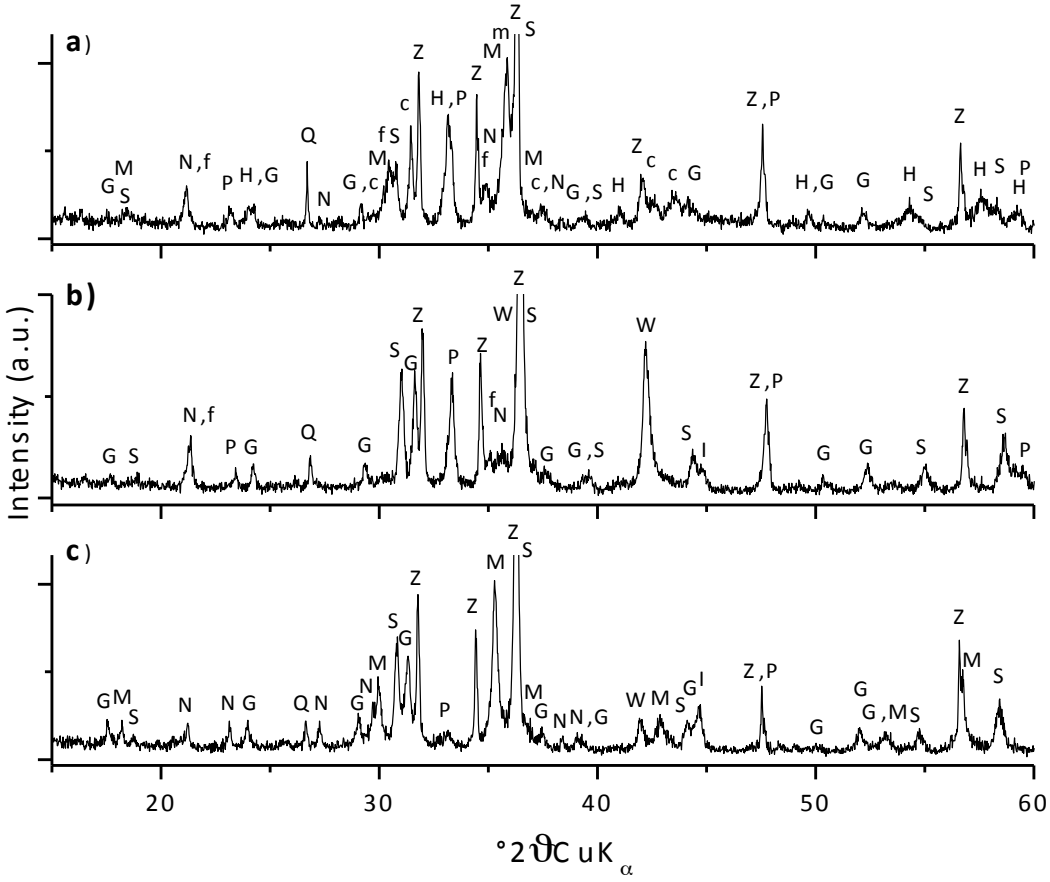
Mix	Bauxite residue (wt%)	Graphite (wt%)	Quartz (wt%)
100BR	100.0	0	0
98.4BR_1.6C	98.4	1.6	0
88.6BR_1.4C_10S	88.6	1.4	10.0

FactSage™ calculations predict mainly a formation of liquid phase, spinel, FeO and perovskite as main phases present at 1100 °C for carbon containing mixes. 100BR is characterised by corundum, calcium aluminium iron silicates, calcium aluminium iron oxides, nepheline and perovskite. Carbon additions of 1.6 wt% and 1.4 wt% were chosen to transform most of iron oxide into Fe^{2+} and thus promote the formation of liquid phase. The amount of slag phase and thus the expected amount of glassy phase after solidification, also increases with increasing SiO_2 content.

Characterisation of mixtures with BR after thermal treatment

The obtained precursor after thermal treatment is a sintered material with glassy content. All treated mixes are characterised by a colour change from red to brown (100BR) and dark grey (other mixes), which indicates most likely a change in oxidation state from iron (III) to iron (II).

The coexisting mineral phases after heat treatment of the different mixes are shown in Figure 2.



c Calcium Iron Oxide,f Iron Calcium Silicate, G Gehlenite, H Hematite, I Iron, M Magnetite, m Maghemite, N Nepheline, P Perovskite, Q Quartz, S Spinel, W Wüstite, Z Zincite, added for quantification.

Figure 2: Mineralogical composition of precursors:
a) 100 BR, b) 98.4BR_1.6C, c) 88.6BR_1.44C_10S

Due to the addition of carbon, a reduction of iron oxide to ferrous iron (wüstite) could be achieved. More phases were detected than obtained in the FactSage™ calculations which could be explained by the firing time which was probably not sufficient to reach equilibrium conditions. Minor components present in BR like MgO (not considered in the FactSage™ calculations) as well as the use of the iron crucible, also affect the present phase assemblage. A not sufficient homogenous reduction can be seen for 88.6BR_1.44C_10S where three oxidation states of iron can be reported. Further experiments are planned to optimise and adapt the heat treatment parameters.

Stereoscopic images of polished samples of synthesised IPs are displayed in Figure 3. The IP synthesised with 100 wt% BR (100BR) is characterised by a porous macrostructure with cracks and pores while 98.4BR_1.6C and 88.6BR_1.4C_10S show a denser structure.

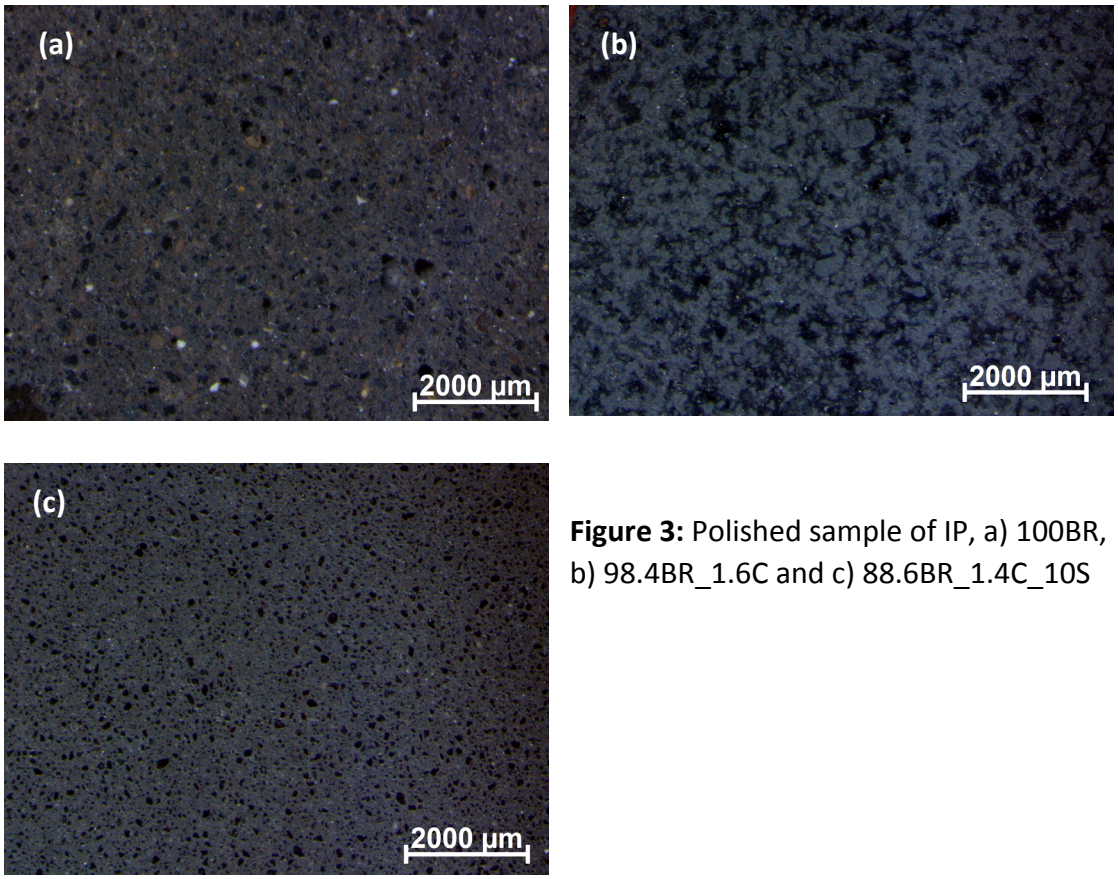


Figure 3: Polished sample of IP, a) 100BR, b) 98.4BR_1.6C and c) 88.6BR_1.4C_10S

SEM results (Figure 4) support these microstructure differences. The composition 88.6BR_1.4C_10S is a well-developed IP, with a clear binder surrounding non-dissolving grains that function as aggregates.

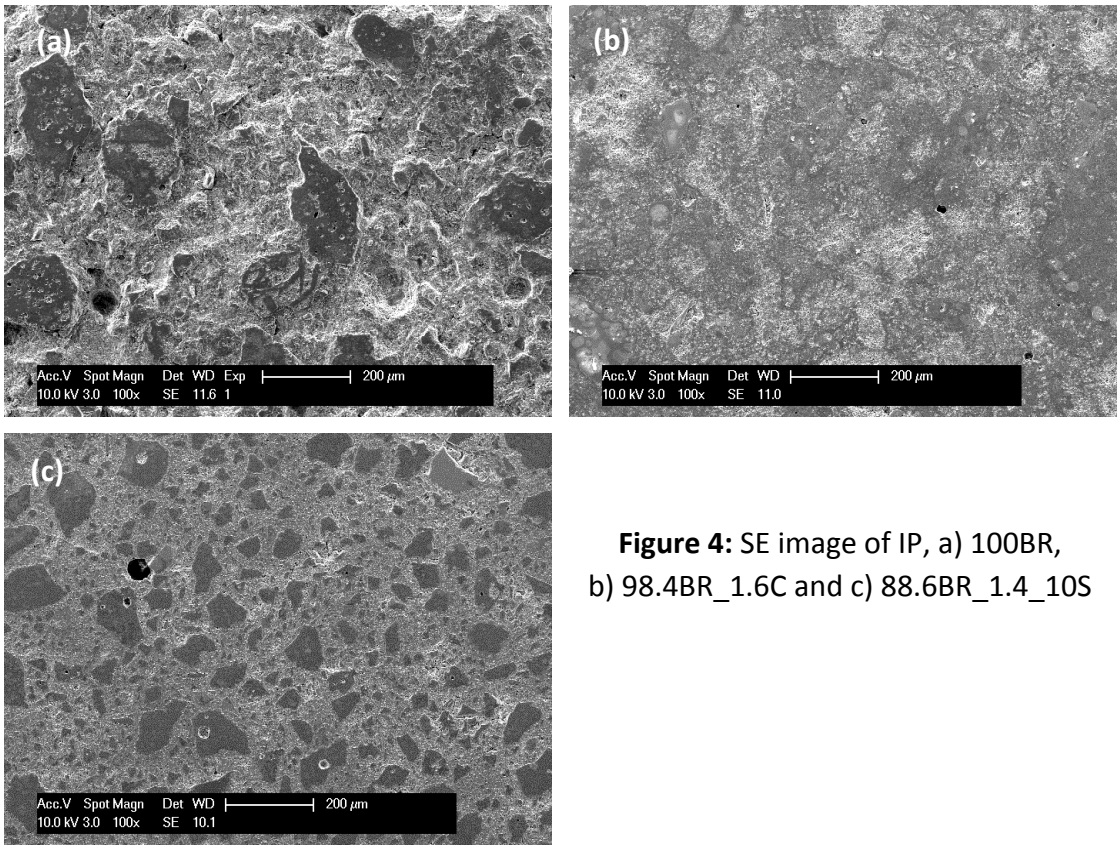


Figure 4: SE image of IP, a) 100BR, b) 98.4BR_1.6C and c) 88.6BR_1.4_10S

First indicative results for compressive and flexural strength are listed in Table 3.

Table 3: Indicative results for compressive and flexural strength.

Mix	Compressive strength	Flexural strength
100BR	13.4 ± 0.4 MPa	4.2 MPa
98.4BR_1.6C	19.7 ± 1.1 MPa	5.5 MPa
88.6BR_1.4C_10S	43.5 ± 0.5 MPa	9.8 MPa

As expected already from the microstructural characterisation, the additions of carbon and both, carbon and silica, lead to an increase in strength. More results will be communicated in the full publication.

The process within the alumina refinery and applications for the resulting materials

Synthesis of BR-based IP could be performed within the alumina plants using the existing infrastructure. A carbon source, like lignite, could be first mixed with the BR slurry followed by filter pressing to separate the cake from the alkaline liquor. This alkaline liquor will become the activating solution in the synthesis of the IP. To do so, it should be concentrated to increase the alkali content, e.g. by evaporating part of

the water and/or by adding additional alkalis, and could be also mixed with alkali silicates, such as waterglass. Firing of the cake can take place in an existing rotary kiln used for the dehydration of alumina (oxy)hydroxides, or in a dedicated microwave assisted furnace. The possible formation of metallic iron and magnetite during the heat treatment process leads to another possibility, where magnetic separation is introduced as an intermediate stage. In this event, a Fe-rich stream is generated that feeds a blast-furnace or any other established metallurgical process, whereas the Fe-poor stream, now enriched in glass containing most of the Si, Ca, Al, Ti, Na, is a more reactive precursor to synthesise IPs. With the above process, 100 % valorisation of BR can be achieved and the additions are trivial, thus not a cost or logistical challenge. The final IPs can be used for applications such as tiles, e.g. for floors, roofs or pavement. Considering the intended outdoor use, there is no real or perceived threat with respect to exposure to natural radioactivity.

Conclusions

A new process was suggested where bauxite residue is modified with the existing infrastructure in an alumina refinery, i.e. filter press and rotary kiln, and is subsequently transformed into a valuable construction material. Minor additions of silica and carbon are required. The envisaged process appears to be realistic for industrial scale up and aspires to transform the Bayer process into a truly zero-waste process.

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