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High Temperature Processing Options for the Valorisation of Bauxite Residue towards New Materials

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Abstract

The paper describes different processing schemes to transform bauxite residue (BR) into new binders for building applications, while recovering, depending on the chosen route, base metals. The flow chart consists of several unit operations. The first step is the chemical modification, by mixing BR with additives, such as C, SiO_2, and/or B_2O_3. Different blends are sintered or vitrified at temperatures ranging from 900 to 1200 °C. When silica and carbon are added, typically a semi-vitreous slag is generated, which can be either alkali-activated or used as a pozzolana in blended cements. Upon addition of B_2O_3, C and SiO_2, the formation of easy to recover metallic Fe is observed, while the Fe-depleted slag is a highly reactive precursor for an alkali-activated binder. The suggested options have been tested and demonstrated successfully at a laboratory scale. In order to evaluate the feasibility in a closer to real-life scenario, an upscaling pilot-plant project has been launched. This also contributes to a precise and realistic environmental and economic assessment, which is essential before commencing industrial implementation.

Keywords: Bauxite residue, alkali-activated binder, semi-vitreous slag, bauxite residue valorisation, pozzolana.

1. Introduction

Bauxite residue (BR) is the alkaline digestion residue of the alumina producing Bayer cycle. The annual generation rate worldwide exceeds 150 Mt [1] and the accumulated inventory is more than 4 Gt, stored at various disposal areas [2]. The chemical composition of BR, consisting mainly of iron oxides, aluminium hydroxides and titanates, turns the material into an interesting candidate for different applications, such as the recovery of base metals and rare earth elements [3,4], the use in ceramics [5,6] or in cementitious materials [7]. Next to the enormous amount of research papers published, there are already examples of processes incorporating BR at an industrial level, demonstrating the potential of using BR. Nevertheless, its current use sums up to merely 1 – 3 % of the yearly generated (mass of) BR. Concerns, such as uncertainty if the quality of the residue is constant, and thus of resulting products, public perception, the availability of well-established raw materials at low price and the strict legislation in some countries, rating BR hazardous due to its alkalinity, act as barriers against a successful market penetration of BR-based products [1,8].

A reuse of BR in building materials seems to be a promising route, since it is used as bulk at a large scale. Next to cements, the use as an inorganic polymer precursor or as a pozzolana in blended cements are possible routes. Inorganic polymers (IP) can be used as alternative building materials, which in contrast to the hydration of cement, gain their strength by polymerisation, after alkali dissolution, of a reactive, silica-rich material. Most often, Al-rich silicates are used (e.g. metakaolin or fly ash) but Fe-silicates are also reactive precursors [9]. The main advantages of IP are that various industrial residues can be used as raw materials and that the mechanical properties are often superior to those of conventional cements/concretes. In addition to the above, resistance to chemicals and to fire is often attained [10,11]. Pozzolanas (aka pozzolanic materials) are non-hydraulic, meaning that there is no reaction by blending them solely with water. However, the reactive silica and alumina (pozzolanas are typically aluminosilicates) react with portlandite ($Ca(OH)_2$), one of the cement hydration products (reaction 1), to produce strength-giving calcium silicate hydrate phases (reaction 2), calcium aluminate hydrates (reaction 3) or calcium aluminosilicate hydrates, such as strätlingite ($Ca_2Al_2SiO_7 \cdot 8\ H_2O$) [12,13].

$$Ca_3SiO_5 + H_2O \rightarrow x\mathrm{CaO}\text{-}y\mathrm{SiO_2}\text{-}z\mathrm{H_2O} + Ca(OH)_2 \tag{1}$$
$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow x\mathrm{CaO}\text{-}y\mathrm{SiO_2}\text{-}z\mathrm{H_2O} \tag{2}$$
$$Ca(OH)_2 + Al_2O_3 + H_2O \rightarrow x\mathrm{CaO}\text{-}y\mathrm{Al_2O_3}\text{-}z\mathrm{H_2O} \tag{3}$$

Despite these possibilities, using BR “as produced” in the above applications is not contributing to improved properties. In fact, BR shows low reactivity in hydraulic, pozzolanic and alkali-activated systems and behaves mostly as a filler. An exception to the above is BR generated via the sintering process, which contains hydraulic C_2S (Ca_2SiO_4), at levels even higher than 50 wt% [14]. To counterbalance this, in most of the cases dealing with the non-sintered (classical) Bayer process, BR is blended with another reactive raw material, such as metakaolin [11], fly ash [15,16] or FeNi slag [17]. The resulting mechanical properties are satisfactory, but they typically decline with an increasing content of BR in the solid raw mix. In rare cases, BR contributes to higher compressive strength (at least the first 28 days) [18], but this is most probably due to physical effects, in view of the fine granulometry, and maybe due to the alkali activation of cement; it is doubtful if it participates in the chemical reactions, as traditional pozzolanas (e.g. fly ash) would do. Moreover, in most works in the literature, aspects relating to the durability of these blended binders remain undiscussed.

In order to increase the reactivity of BR, thermal treatment has proven to be one of the suitable process options. Investigations [19] have proven that the calcination of BR in the range of 600 – 800 °C leads, for instance, to an increase in pozzolanicity in mixtures with Ordinary Portland Cement (OPC). A patent was filed by Votorantim Cimentos S/A and Companhia Brasileira De Alumínio studying the pozzolanic behaviour of a chemically and thermally modified BR by adding $CaCO_3$, such as limestone and a silica source, such as sand or clays, followed by firing in a temperature range of 1000 and 1500 °C [20]. Up to 30 wt% of the resulting material was blended with OPC. All requirements for pozzolanic materials were met. Thermal activation of BR also increases the solubility and its suitability as precursor for geopolymers/inorganic polymers [21]. The downside of a thermal modification of BR is the energy requirement associated with the operation of the furnace (possibly also dryer) and the corresponding emissions due to the burning of fuel and calcination. Additional costs caused by the use and transport of materials needed for transforming BR into a chemically reactive material, turn the often promising proposals into rather unattractive processes with respect to their economic and environmental impact.

In order to address the above mentioned downsides, integrated, near-zero-waste processes appear as a reasonable path forward. In these schemes, base and/or critical metals are recovered in an intermediate step before valorising the residual fraction typically towards building materials [22,23]. Potential additions are sourced from the vicinity of the alumina plant and/or BR disposal area and kept to a minimum. The drawback of such an approach is that it entails substantial risks: the integrated flow charts are rather complex, with substantial capex and opex, leading to a range of materials that are relevant for different markets (typically impossible to predict), each one having its own characteristics. An alternative approach is to develop processes that use the bulk of the material for a single application, i.e. building materials. Such a scheme is typically simple and robust, minimising operational uncertainties, yet, the value recovery from BR is also limited. Taking the above into consideration, different high temperature processing options are discussed in this study (Figure 1).

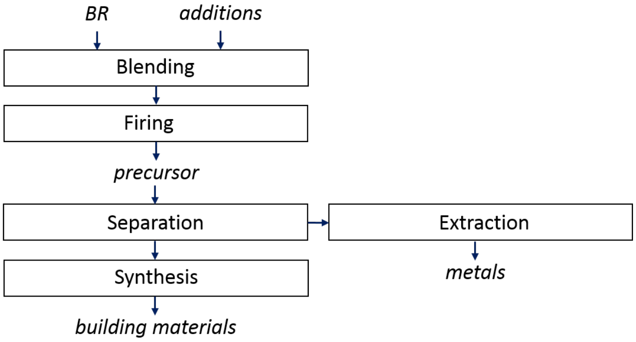

Figure 1. Unit operations (in boxes) to transform BR into new materials; input and output streams in italic.

The major aim of the heat treatment is on one hand the formation of phases which are suitable for the recovery of metals, such as iron, and on the other hand, the maximisation of the melt phase which can be transformed upon cooling into a reactive, amorphous fraction. This amorphous phase is assumed to dissolve in the alkaline environment of a cement pore solution and/or after addition of an alkaline activator used for the synthesis of inorganic polymers.

Previous work has shown that additions of C and SiO_2 lower the melting point of a fired BR blend, resulting in a higher formation of melt which solidifies as glass upon quenching [24]. Additionally, thermodynamic calculations have shown that also B_2O_3 is suitable for lowering the melting point due to the strong fluxing action, which is accompanied by formation of more glass phase upon quenching. Further addition of carbon leads to the formation of metallic iron which can be extracted in an intermediate step. The concept is presented herein as three case studies. Conceptual flowsheets with different unit operations are suggested for a potential industrial implementation, leading to materials suitable for different valorisation routes.

2. Characterisation of BR

The raw material used in all three case studies was BR cake, supplied by Aluminium of Greece (AoG). After drying at 105 °C, the chemical and mineralogical composition was determined using semi-quantitative X-ray fluorescence and X-ray diffraction analysis, respectively. The used BR is chemically dominated by (expressed as oxides) Fe_2O_3 and Al_2O_3, followed by SiO_2, CaO, TiO_2 and Na_2O below 10 wt% (Table 1).

Table 1. XRF data of AoG BR (estimated relative error 10%).

Oxide	**Fe_2O_3**	**Al_2O_3**	**CaO**	**SiO_2**	**TiO_2**	**Na_2O**	**Other**
wt%	47	23	9	9	6	3	<3

The main mineral phase of the present BR is hematite and various Al containing phases, such as diaspore, gibbsite and siliceous hydrogarnet are detected in the recorded XRD diffractogram. More characterisation data are presented in [24].

2. Case Studies

3.1 Case Study I: Chemical and Thermal Modification of BR and Subsequent Synthesis of Inorganic Polymers

Experimental procedure

A mix, consisting of 88.6 wt% BR, 1.4 wt% carbon (graphite) and 10 wt% silica (fine quartz) was prepared by mixing the components in ethanol using a laboratory shaker for at least 8 hours. The material was subjected to firing at a temperature of 1200 ± 20 °C in a closed alumina crucible (with gas in- and outlets), maintaining an inert atmosphere (N_2). The maximum temperature was held for 1 h before the sample was quenched by pouring the slag ("BR slag") into water in order to suppress crystallisation of the partially vitrified material. After drying the material was ground and characterized using X-ray diffraction in order to assess its amorphous content and reactivity.

Inorganic polymer samples were prepared by mixing BR slag with the activation solution (molar ratios $SiO_2/Na_2O = 1.6$, H_2O content of 70 wt%) according to an activator to solid weight ratio of 0.25. The samples were cured at 60 °C for 24 h and the compressive strength was tested 7 days after preparation.

In another approach, BR slag was dry-mixed with 70 wt% of dried, untreated BR before activation. An alkali activation solution (molar ratios $SiO_2/Na_2O = 1.6$ and $H_2O/Na_2O = 16$) according to a liquid to solid ratio of 0.2 was homogeneously sprayed on this solid blend, mixed, followed by press-shaping using a hydraulic press (~ 50 MPa). The compressive and flexural strength was tested 7 days after preparation.

Results

Quantification of the obtained XRD diffractogram (Figure 2) of the slag revealed 50 wt% of amorphous content after the heat treatment.

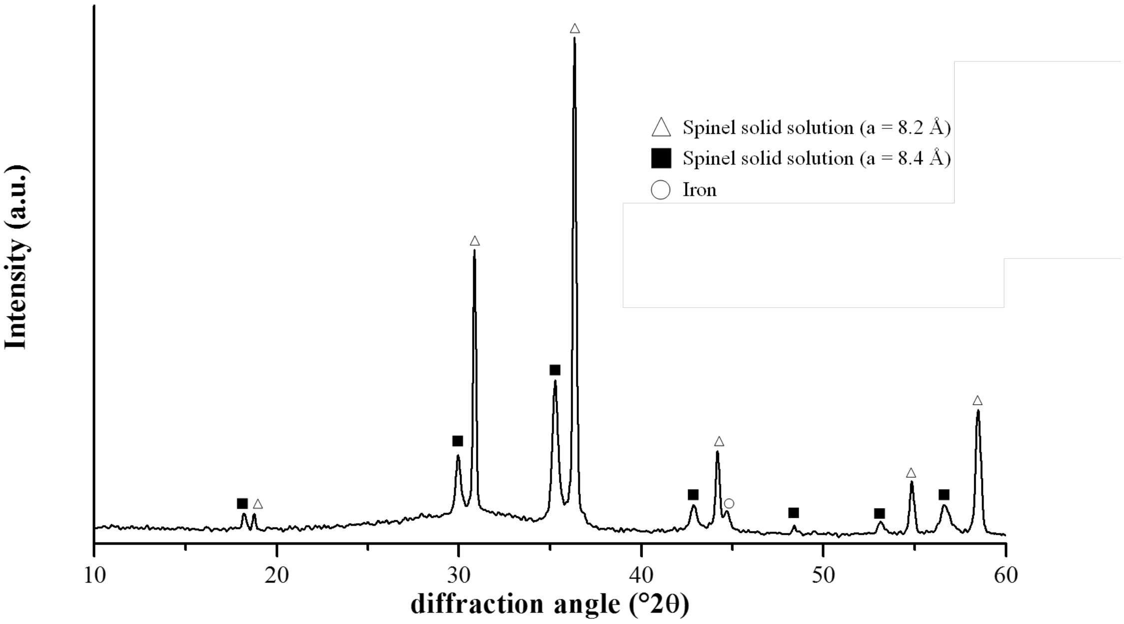

Figure 2. XRD analysis of BR slag 88.6 wt% BR, 1.4 wt% carbon and 10 wt% silica, including peak identification; the amorphous fraction is visible as featureless hump between 20 and 40 °2ϑ.

Both alkali activation approaches led to dense inorganic polymer bricks with satisfactory properties in comparison with conventional products (Table 2).

Table 2. Mechanical properties of synthesized inorganic polymers.

Solid Mix	Shaping	Compressive strength (MPa)	Flexural strength (MPa)
100 wt% BR slag	Casting	60	*not tested*
70 wt% BR, 30 wt% BR slag	Pressing	54 ± 15	16 ± 4

Flowsheet

An industrial implementation of the described process seems feasible. The additives can be mixed with BR slurry and the resulting mixture is dewatered using, for instance, a filter press or a steam pressure filtration unit (Figure 3). Vitrification (partial or full) can take place in a rotary kiln, a top blown rotary converter or even a microwave assisted furnace. The alkaline solution obtained after filter pressing can be concentrated (by evaporating water) and modified in order to provide a potential feedstock for activating the fired materials. Two different approaches are suggested where the alkaline activator is either blended with the BR slag or with a mix consisting of dried, untreated and BR slag in order to form inorganic polymer products. The use of untreated BR as a filler material reduces the amount of fired BR and thus the energy footprint of the final product.

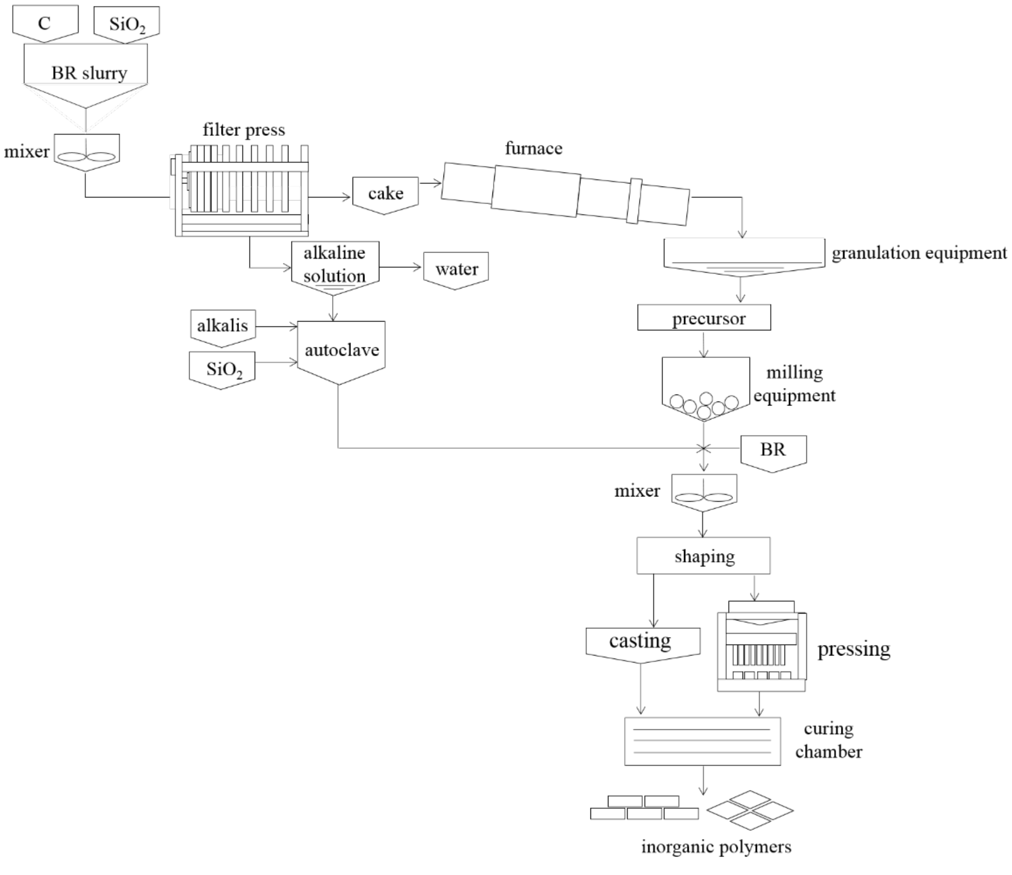

Figure 3. Flowsheet for Case Study I: Chemical and Thermal Modification of BR and Subsequent Synthesis of Inorganic Polymers.

3.2 Case Study II: Chemical and Thermal Modification of BR and Subsequent Synthesis of Pozzolanic Materials

Experimental procedure

A mixture consisting of 64 wt% BR, 1 wt% carbon and 35 wt% silica was treated and analysed in the same manner as described in section 3.1 For the potential use as pozzolana, this BR slag was mixed with 60 wt% of ordinary Portland Cement (OPC - CEM I) in order to produce mortars. The pozzolanicity was assessed based on standard tests for testing the activity (EN 196-5) and also by comparing the compressive strength of mortars with an OPC reference system.

Results

After higher addition of silica (compared to the mix design described in 3.1) and thermal processing at 1200 °C, the amorphous content is significantly higher, approx. 80 wt% (Figure 4).

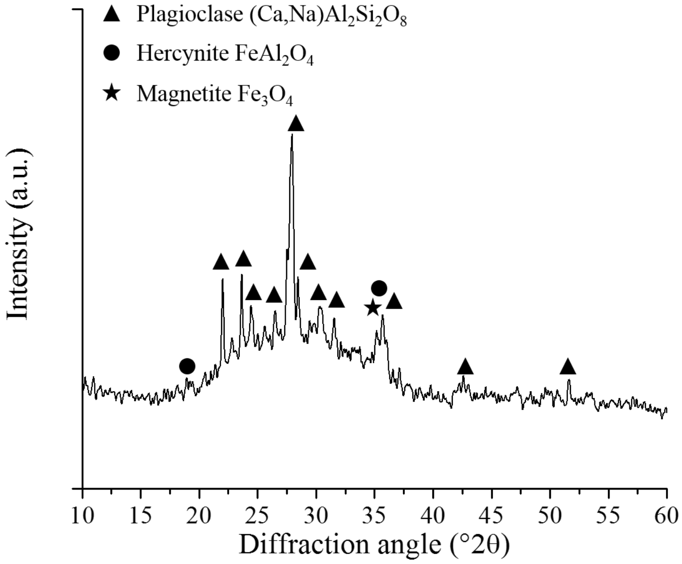

Figure 4. QXRD analysis of BR slag 64 wt% BR, 1 wt% carbon and 35 wt% silica, including peak identification.

The results of the pozzolanic tests (not presented herein) clearly demonstrate the pozzolanic activity of the material. This is also evident in the compressive strength results of the mortars, where after 28 d, 50 ± 1 MPa were reached for the OPC/BR slag mortars (OPC reference was 60 ± 1 MPa).

Flowsheet

In this flowsheet, the BR slag is mixed with cement and water to create a building material. The alkaline solution can be used for alternative processes, for instance, the activation of inorganic polymer precursors, or is brought back to the Bayer cycle (Figure 5).

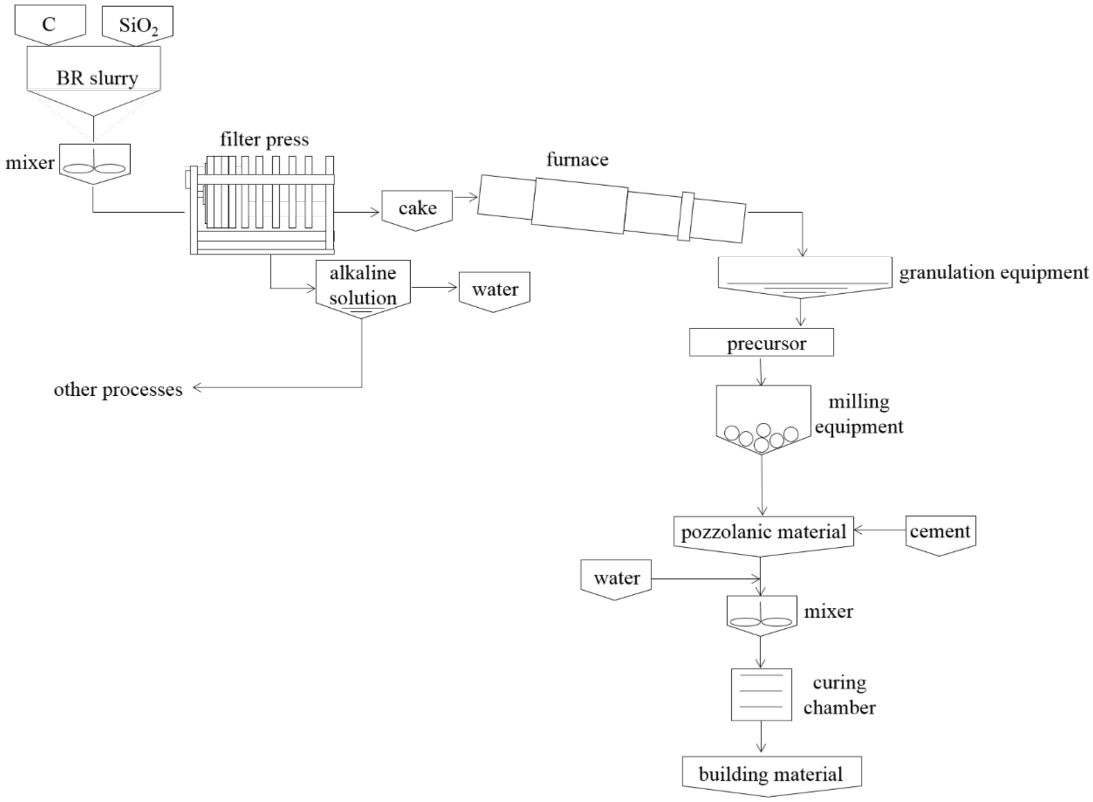

Figure 5. Flowsheet for Case Study II: Chemical and Thermal Modification of BR Subsequent Synthesis of Pozzolanic Materials.

3.3 Case Study III: Chemical and Thermal Modification of BR for Fe Recovery and Subsequent Synthesis of Inorganic Polymers

Experimental

A mixture consisting of 76 wt% BR, 5 wt% carbon, 9 wt% B_2O_3 and 10 wt% silica was treated and analysed in the same manner as described in section 3.1. The obtained slag was ground with a mortar and pestle in order to liberate the metallic particles that were then removed by hand. A magnet was used to separate the finer magnetic fraction from the residual slag. The non-magnetic fraction was activated using a sodium silicate solution with molar ratio of SiO_2/Na_2O of 1.6 and a water content of 70 wt% according to a liquid to slag ratio of 0.4.

Results

After removing the sample from the furnace, metallic parts were clearly observed which could be initially taken out by hand (Figure 6).

Figure 6. Sample 76 wt% BR, 5 wt% carbon, 9 wt% B_2O_3 and 10 wt% silica, treated at 1200 °C (dimensions of the tray are 20 x 15 cm).

The XRD results of the remaining slag show a high content of amorphous phase (estimated 90 wt%) – clearly indicated by the broad hump centred at about 27°2ϑ – next to metallic iron, corundum and spinel phases (Figure 7).

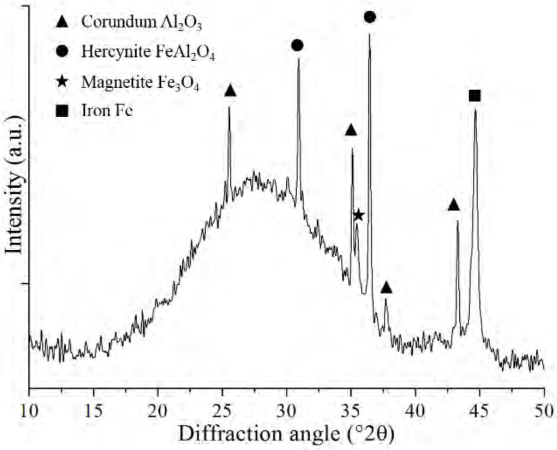

Figure 7. XRD diffractogram of sample 76 wt% BR, 5 wt% carbon, 9 wt% B_2O_3 and 10 wt% silica after recovery of Fe, treated at 1200 °C, including peak identification.

Preliminary tests have shown that the inorganic polymer samples set within 20 mins at room temperature. Two days after preparation, the specimen showed no deterioration after submerging it in boiling water for 2 h.

Flowsheet

Compared to section 3.1, this flowsheet includes an intermediate separation step where the magnetic parts of the fired material are separated from the non-magnetic fraction (Figure 8). The latter is activated towards inorganic polymers, but blended cements can also be a possibility. More results are expected within 2017.

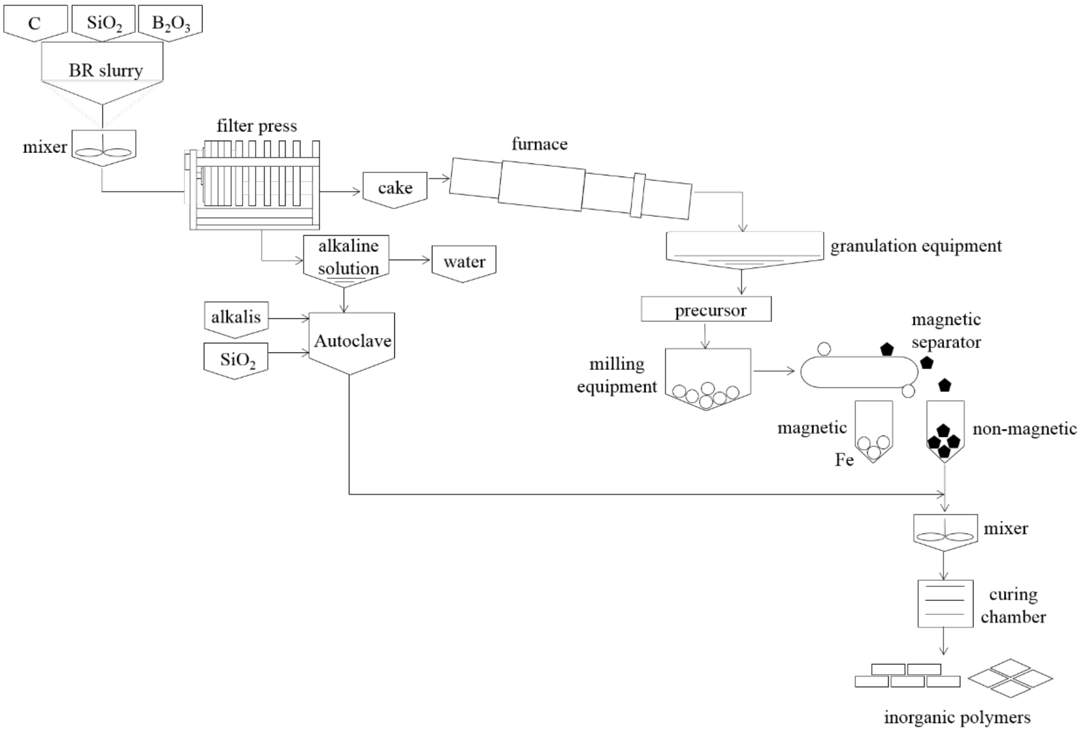

Figure 8. Flowsheet for Case Study III: Chemical and Thermal Modification of BR for Fe Recovery and the Synthesis of Inorganic Polymers.

4. Upscaling and Industrial Implementation

An upscaling project (*RECOVER*, *https://recover.technology/*) has been launched with the goal of testing the described flowsheets at a pilot-plant scale. The intention is to demonstrate the processes described above, on-site, at the facilities of the industrial partner, by using mobile upscaling units which are equipped with the needed infrastructure (Figure 9).

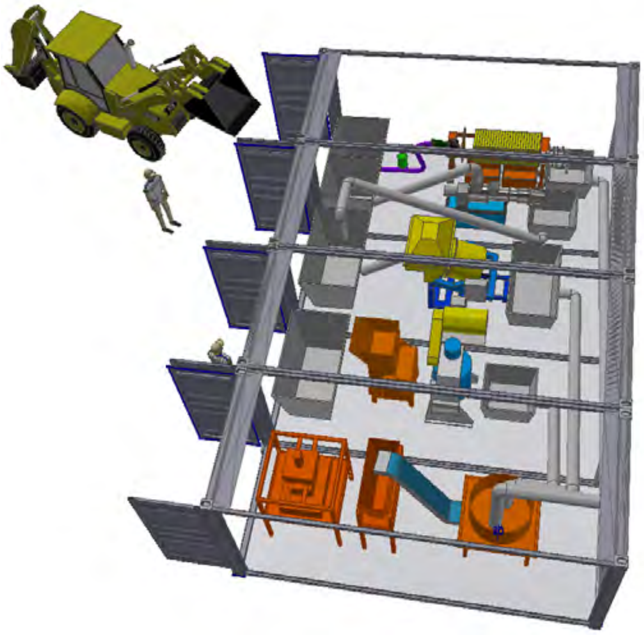

Figure 9. Mobile upscaling units.

This upscaling project also contributes to a precise and realistic environmental and economic assessment, which is essential in view of the envisaged industrial implementation. The selection of the most suitable flowsheet for an industrial implementation is, among other factors, dependent on the local availability and costs of additives, the quality of BR, for instance, its silica content, and the available infrastructure. Local industrial synergies might be conceivable, for instance, between the alumina and boron industry, when boron containing wastes potentially turn into a feedstock for the modification. The vicinity of alumina and cement plants would favour, for instance, the production of pozzolanic materials.

5. Conclusion

Several suggestions for a high temperature modification of BR towards valuable products are presented in this study. BR was successfully transformed into a precursor for inorganic polymers and a pozzolana and, depending on the additions, Fe was recovered in an intermediate step. After the successful demonstration in lab-scale, an upscaling project has been initiated in order to investigate the potential of the valorisation routes in a closer to real-life scenario. More data will be presented at the end of 2017, beginning of 2018.

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