Bauxite Residue

Towards waste based, iron-rich SCMs

By Michael Wenzel (RWTH Aachen University)

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SUMMARY

The ReActiv research project is centred around the Bayer-processes waste stream. It is focused to optimize and evaluate some of the already researched utilization pathways for bauxite residues (BRs). The generated bauxite residue will be converted into reactive secondary cementitious materials by the application of various activation processes.

The project is carried out by leading companies of the aluminium and cement sectors, as well as selected academic research institutions. The project focuses on a application related approach ranging from scientific research to the development of commercial products.

INTRODUCTION

The development of sustainable, recyclable buildings and infrastructure is the challenge of the 21st century the construction and cement industries have to meet. The European cement industry committed to the production of Climate-neutral concrete in 2050 [1,2]. This ambitious goal can only be achieved by complex, interdisciplinary, approaches. In this context, secondary cementitious materials (SCMs) remain essential components of sustainable cements.

BAUXITE RESIDUES AS CEMENT ADDITIVES

Currently blast furnace slags and fly ashes are the most common SCMs used in standard concretes. A continuous decrease in availability of these raw materials and the increasing demand for cement substitutes make the valorisation of other SCM sources necessary. Numerous viable alternatives are limited to niche applications due to available amounts or unpredictable variability in material composition [3]. This is especially true for materials originating from bio mass or domestic waste incineration. Industrial waste streams, are much more reproducible in composition, and hence much more likely to yield SCMs with sufficient reactivity and homogeneity.

Aluminium oxide and aluminium are important high-performance materials for many industrial sectors, which leads to a continuously growing demand for these materials. Primary aluminium is most commonly produced by the Bayer process, in which Aluminium is separated from the Bauxite residue via liquid extraction. A Sodium hydroxide rich solution is applied to leach aluminium from the parent ore. The main steps of the Bayer-Process are illustrated in **Error! Reference source not found.** . For a better understanding of this very diverse and complex process the reader can be referred to reviews [4–8] or numerous very specific publications[9–11].

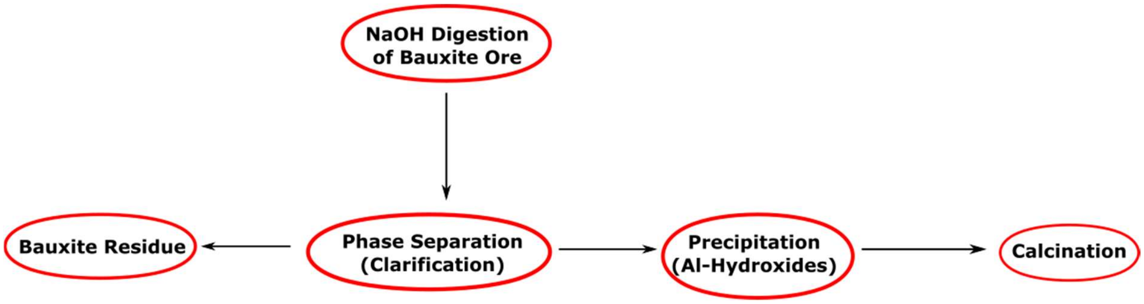

Figure 1 Scheme of the Bayer-Process leading to the production of alumina

The mineral residues resulting from the digestion of siliceous bauxites are also known as red mud. The Bayer process generates 150 to 180 million t of bauxite residue (BR) per year [12]. This is much less than the annual cement production of 4.4 billion tons, estimated for 2021 (US Geological Survey). This enables a complete reuse of this waste stream, which is reasonably sized to go through with the standardization process for a new cement type.

Due to precisely controlled process conditions, bauxite residues have a high homogeneity and constant stoichiometry, which are important criteria for a raw material or additive used in cement manufacturing. However, their mineralogy and chemical composition differ significantly from pozzolanic or latent hydraulic SCMs. This is illustrated in **Error! Reference source not found.**. The most important differences are the high contents of comparably inert iron rich phases like goethite and hematite as well as the initially high amount of sodium. This leads to changes in the microstructural development of cements and concretes and has an impact on durability properties[13,14].

The first publications on the use of BR as a secondary cementitious material date back to the early 2000s. Several independent research groups could demonstrate that an addition of 5 to 20 wt.% bauxite residue to Ordinary Portland Cement (OPC) is possible, while achieving concretes that reach compressive strengths of 30 to 40 MPa. This makes them suitable for many structural applications [15–17]. Nevertheless, higher substitution rates have to be feasible to make BR a common SCM for sustainable cements. Currently developed cements should aim for a clinker content of 50 wt.% or less, which is necessary for reaching the cement industry's sustainability goals[2]. Residues from Bayer processes do not show enough initial reactivity to realize these substitution factors. The development of thermal and chemical activation processes already showed promising results and seems a viable route for the utilization of this waste stream[18–21].

Similar to limestone and quartz powders, red mud shows a pronounced filler effect related to its fine particulate nature and high content of inert phases. If the chemical composition is considered, one tends to overestimate the reactivity of the bauxite residue due to approx. 5-20 wt.% Al_2O_3, 2-10 wt.% SiO_2 and 2-10 wt.% CaO.

The reason is the mostly crystalline, rather inert phase assemblage of the bauxite residue. The mineralogy is dominated by Al substituted iron(hydr)oxides (mostly hematites and goethites), crystalline aluminum(hydr)oxides and, in some cases, perovskites. Numerous minor phases like quartz, rutile or periclase may remain from the parent ore [12,22]. If the Al containing crystalline phases are thermally or chemically decomposed, a significant increase in reactivity can be observed due to the presence of amorphous aluminium hydroxides [19,21,23].

The composition, and not just the amount, of the desilication product may affect the long-term properties of blended cements. While all desilication product (DSP) species are readily soluble in an OPCs pore solution they should contribute differently to the cements strength development [21].

The reactivity of a Bauxite Residue, regardless of thermal treatment, is influenced by the content of hydroxy-sodalite ($Na_4[Al_3Si_3O_{12}]$ (OH)) and low carbonate cancrinites (i.e. Na_7Ca $[Al_6Si_6O_{24}]$ $(CO_3)_{1,5}$). The formed amounts and structures of cancrinite and sodalite are influenced by temperature, leaching times and other parameters of the Bayer process. Leaching times, temperatures and lime-wash addition are dependent on the bauxite ore used in the process.

The structures of sodalite and cancrinite found in Bauxite residue usually contain a certain amount of carbonate as anions and differ from the ideal mineral stoichiometry[24]. In most conditions sodalites form the majority of the DSP, since cancrinite is only generated by a phase transition of sodalite at elevated temperature. Furthermore, a partial replacement of sodium by calcium ions can be observed, if a calcium source is added during the desilication step [24–26].

In any case the alkali contents in BR are still much higher than those in common SCMs, which leads to dealkalization treatments being researched

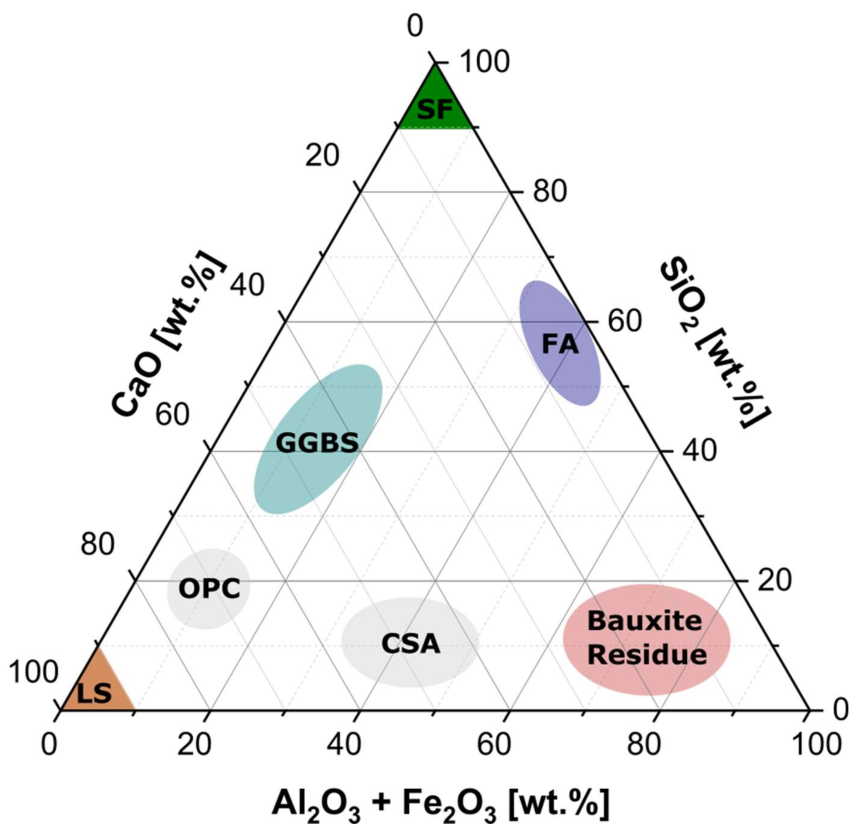

Figure 2 Ternary diagram of the most important oxides present in OPC systems. The difference of BR composition from traditional SCMs like BFS is illustrated schematically

The results of different research groups confirm that a reduction of the alkali content to about 0.5 wt.% is possible with different leaching processes [27,28].If an application in OPC systems is desired only basic or aqueous leaching are possible options for reducing the total sodium content. This is the case because the introduction of i.e. organic acids or chlorine has to be avoided, to prevent Cl-induced rebar-corrosion and retardation of the hydraulic reaction.

Such leaching treatments remove the alkali rich desilication product from the Bauxite residue and generate less soluble, alkali free phases, which makes the application of a further activation process crucial for a successful application as SCM.

Even though alkali hydroxides are only a minor component in cements they have a high impact on the hydration reactions, mainly due to the strong involvement in early-age reactions and their almost immediate effect on the pore solutions pH value. This leads to changes in the solubility products of all present ions and hence differing precipitation processes of the hydrate phases.

The composition of phases like CSH or monosulfate is changed, due to enhanced sodium substitution. At very high alkalinity the aluminate reaction is strongly affected and the preferential formation of monosulfates and hydro-garnets can be observed, while ettringite formation is retarded. On a macroscopic scale accelerated setting and a quicker development of early age strength are observed, while the long term strength development is hindered by too high alkali contents [29,30].

In an application related context, the workability of the concrete decreases with increasing alkali content, while the SCMs reactivity increases. Finally, the risk of Alkali-Silica-Reaction induced failure increases drastically and may lead to a restriction of the cement's application range.

Durability studies and the consideration <of fresh concrete properties are necessary to define the amount of BR that can be added to a cement for a specific application scenario. The results of this research will define the substitution limits for BR based SCMs and hence decide about their ecological and economic impact.

RESEARCH APPROACH OF THE REACTIV CONSORTIUM

The research project started with the development of dealkalization and activation processes that transform bauxite residues into reactive secondary cementitious materials. The 22 project partners are pursuing an interdisciplinary, clearly application-oriented approach, which can be summarized in **Error! Reference source not found.** .

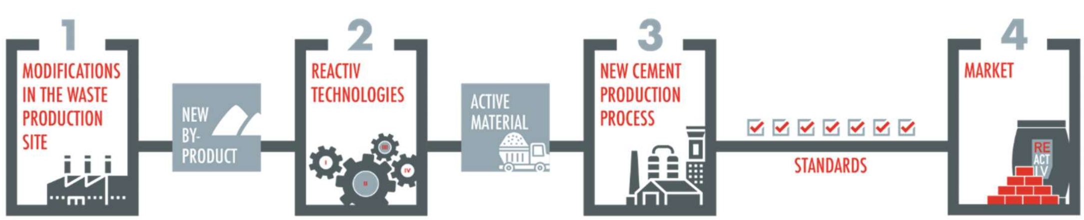

Figure 3 Scheme of the ReActiv consortiums research, courtesy of C. Georgopoulos (ENALOS).

Global players of the cement and alumina producing industry contribute representative raw materials and process engineering knowledge, while binder development and evaluation is predominantly provided by the academic partners. In addition to the development of innovative binders, the project focuses on the realization of the necessary activation technology on an industrial scale. Ecological and economic evaluations of the process are carried out, too. The scope of the project is the commercialization of the developed binders. The main objectives of ReActiv can be summarized as follows:

- Technology development for the upcycling of bauxite residue by thermal treatment and dealkalization.
- Development of binders containing at least 30 wt.% bauxite residues

- Laboratory and pilot plant scale production of developed binders.
- Evaluation of early/durability properties of the developed systems
- Evaluation of conformity with regulations/requirements in the construction industry
- Characterization of hydration behaviour, phase composition and micro-structure formation
- Evaluation of economic feasibility and ecological impact via life-cycle assessment and similar tools

The approaches summarized in Table 1 can be used to enhance the reactivity of bauxite residues. They enhance the overall reactivity either by concentrating the reactive components, removing inert phases, or enhancing the amount of soluble material through thermal degradation of crystalline phases and chemical modification.

Table 1 Possible approaches for transforming bauxite residues into reactive SCMs

Amorphization of crystalline phases	**Thermal Degradation** Calcination, Vitrification, Smelting
Adjustment of Element composition	**Reactive Additives** Calc. Clays, Fly Ash etc. **Processing Aids** Fluxes (SiO_2, CaO)
Removal of inert phases	**Magnetic Separation** Reduced Fe, magnetite

Hydration Studies and Durability Assessment

The Research team at the institute of building materials research (RWTH Aachen University) is primarily concerned with characterizing the durability behavior of promising binders. Buildings and infrastructure are exposed to a range of deteriorating conditions. This explains the need to assign exposition classes that describe the most critical environmental influence. While most interior walls are mainly deteriorating due to carbonation, streets and exterior walls may also experience Cl-ingress and freeze-thaw cycles. High Sulfate concentration in phreatic waters or other media leads to sulfate attack, while opal sand and similar aggregates may cause destructive Alkali-Silica-Reactions.

Due to the differences in mineralogy and chemistry of bauxite residue based SCMs from pozzolanic SCMs like fly ash or blast furnace slag a fundamental approach is needed to understand their interaction with the OPC. Especially for the attempted substitution rates of more than 30 wt.% no reliable data regarding changes in phase composition and microstructural development exist, which may be related to the high iron contents posing a challenge for important analytical methods like QXRD and NMR techniques.

Without a proper characterization of the microstructural development of these iron-rich systems a performance-oriented optimization, like the maximization of 2d strength, is difficult. Furthermore, a prediction of phase composition and durability performance is not possible.

After determining the influence, the addition of the BR containing SCMs has on the long-term phase composition and these data may be used to develop a fitting thermodynamic model of the binder system. This finally leads to an understanding of the mechanisms that are responsible for the differing durability performance of the investigated composite cements.

In addition to understanding the influence of activated bauxite residue on an OPC system a first set of data for the evaluation of iron-rich SCMs will be generated. This enables a meaningful comparison of bauxite residues with known SCMs of strongly differing composition in regards to a specific deterioration mechanism, which should deepen the understanding of the impact of upcycled BR on an OPCs hydration process.

CONCLUSION

The use of bauxite residues as cement substitute has been investigated for more than 10 years. In recent years, it has been shown that thermal or chemical activation of this homogeneous raw material is necessary to achieve sufficient reactivities for addition levels beyond 20 wt.%. Such replacement levels are necessary to reach the environmental standards of modern composite cements. So far, there is a lack of fundamental understanding of the reactions of BR and other iron-rich additives in Portland cement systems, industrial scale feasibility studies and representative durability tests. The ReActiv research project addresses these issues as research priorities and tries to enable a proper standardization of iron rich SCM containing binders.

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