BR12 - The use of Dealkalised Bauxite Residue in Cement Applications

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Abstract

The cement industry today is considering the use of alternative supplementary cementitious materials (SCM) in cement formulations to mitigate the environmental burden of cement clinker production. Special focus for development of new SCMs, apart from natural pozzolans and clays, is given to industrial by-products. Bauxite residue (BR) is the main by-product of the alumina industry, for which the use in a cementitious environment is still limited to less than 2% addition in the clinker raw meal. Extensive use of BR in cement either in clinker raw meal or as a SCM is currently impeded due to its high alkaline nature. Thus, dealkalisation of BR increases the potential for valorisation. In the present work, BR dealkalisation is achieved by a hydrothermal process, with calcium hydroxide, in which the insoluble alkalis are converted into soluble ones and removed by water washing. By conducting statistical analysis, the effect of processing time and liquid over solid ratio to sodium removal is underpinned. The dealkalised BR (DBR) produced, free of alkalis, is calcined with pure kaolin at 750 °C to be transformed into a SCM. Acceptable reactivity could be obtained from co-calcined DBR and kaolinite blends when mixed with water, but desirable strength development could not be obtained due to a false flash set that was observed microstructurally, as a result of the formation of some local high strength agglomerates. Along with these local points there were also other zones which were depleted in the necessary elements for producing the cement hydration products, required for defining the strength. Apart from the use of DBR as SCM, based on DBR's chemical and mineralogical characterisation its suitability for direct use in cement clinker production is demonstrated, which is currently limited by the alkali presence.

Keywords: Bauxite residue, Dealkalisation, Supplementary cementitious material, Blended cements, Calcination, Kaolin.

1. Introduction

Bauxite residue (BR) is the alkaline residue resulting from the production of aluminium hydroxide in the Bayer process [1], [2]. The cement industry has the potential to reuse the large amounts of BR that are available. Thus, researchers have explored several valorisation paths, including BR use as a supplementary cementitious material (SCM) [3] . However, the industrial implementation is inhibited mainly due to the high sodium (Na) content and the low reactivity of BR in cementitious environments [4]. A dealkalisation process has been proposed so that BR is transformed into a Na-free solid, the dealkalised BR (DBR), while recovering caustic soda, which could be reintroduced in the Bayer process. BR dealkalisation with lime addition was initially implemented on a laboratory scale back in the 1980s [5] and when it is compared to other methods as sintering [6], pyrolysis [7], calcification-carbonation [8], acid leaching [9], this method has considerable potential to be incorporated on an industrial scale as part of the desilication step in the Bayer process.

The effect of the slurry density, lime addition and processing time is examined on the Na removal. A leaching test on the heavy metals that could be released from the DBR is also performed in order to investigate the potential of DBR incorporation as raw material in clinker production without adverse impact.

However, even if the absence of Na from the DBR inhibits the undesired alkali-silica reaction when it is part of cementitious systems, the reactivity of the DBR still needs to be increased. Further beneficiation techniques to enhance the reactivity of BR have been proposed by researchers that entail the realisation of either pyrometallurgical or hydrometallurgical processes. To the best of our knowledge, DBR has not been processed further to be transformed into a potential reactive precursor for use in blended cements.

Co-calcination of DBR with pure kaolin is performed herein, which is based on the concept described in a study by Peys et al.[10] and can transform DBR into a reactive SCM that increases cement hydration. This paper presents the factors affecting the dealkalisation process, the optimal conditions for the maximum Na removal and the transformation of DBR with kaolin into a potential promising SCM.

2. Materials and Methods

BR samples were obtained from MYTILINEOS S.A., Greece. The chemical composition of the BR was determined with a SPECTRO XEPOS ED-XRF Analyzer, and the major oxides are presented in Table 1. Phase identification of BR was performed with Bruker™ DIFFRAC.EVA software and use of ICDD™ Diffraction databases PDF-4+ και PDF-4 Minerals. Quantitative analysis of the identified phases was performed with the Bruker™ DIFFRAC.TOPAS software and is presented in Table 2.

Table 1. Chemical composition of MYTILINEOS BR, as measured by XRF.

Element (as oxide)	**wt%**
Fe_2O_3	39.1
Al_2O_3	23.8
SiO_2	7.7
Na_2O	3.4
CaO	8.1
TiO_2	5.0
L.O.I.	10.4

Table 2. Mineralogical composition of the MYTILINEOS BR, as defined by Quantitative XRD.

Mineral phase	**wt%**
Diaspore	11.6
Anatase	0.3
Quartz	0.9
Gibbsite	7.5
Chamosite	3.2
Calcite	4.4
Perovskite	0.3
Hematite	30.6
Boehmite	2.5

Mineral phase	**wt%**
Cancrinite	13.6
Goethite	6.2
Katoite	19.1

Dealkalisation experiments were performed in a custom-made reactor set-up. The body of the reactor was built from Parr™ 4563 model parts, while the Teflon lid was suitable for leaching experiments at atmospheric pressure. Heating and stirring were controlled by a PLC unit. Various amounts of calcium oxide (10, 15, 20 wt%) supplied by Sigma-Aldrich (CAS number: 1305-78-8), were added in the reactor along with deionised water so that calcium hydroxide is produced. When the target temperature of 85 °C was reached, BR was added under predefined slurry densities (10, 20, 30, 40 w/v%). Lime additions, slurry densities and processing times were determined based on a factorial design of experiments using the JMP Software, supplied by SAS. Na removal was the crucial factor under investigation to assess the dealkalisation efficiency. At the end of each experiment, the dealkalised liquor was filtered and Na chemical analysis of the resulting aqueous solution was performed in a Flame Photometer (BXB XP Plus Enhanced Purpose Flame Photometer). The identified mineral phases of the DBR after treatment were quantitatively analysed. DBR compliance with the ELOT EN 12457-04 was tested for direct use in cement clinker. Batch leaching test, for 24 h, at a liquid-to-solid ratio of 10 L/kg for the DBR sample with a particle size below 4 mm and deionised water, was carried out. ICP-OES (PerkinElmer™ Optima 800 Optical Emission Spectrometer) analyses were performed to determine the metals concentration of the leachate.

A kaolinitic clay (supplied by VWR, Belgium) was used as additions (0, 10, 20, 30 wt%) in the DBR for calcination in order to enhance the reactivity of DBR and increase its potential use as a SCM. The four blends were calcined in a muffle furnace (Nabertherm) at 750 °C using a 1-hour dwell time and heating and a cooling rate of 3 °C/min.
The reactivity of the calcined materials was investigated using the cumulative heat release in the R3 test (ASTM C1897).

3. Results and Discussion

3.1 Dealkalisation Efficiency

Based on the factorial design's parameters effect, it is indicated that the dealkalisation process is negatively affected by the increased slurry density and positively by the increased lime addition (Figure 1) and processing time (Figure 2). Independently on the slurry density (either 10 or 40 %w/v), high removal efficiency rates are observed when lime addition increases and more precisely when it is equal to 20 wt%. Further increase in lime does not accelerate the removal rate, on the contrary it leads to a plateau above which, the rate decreases.

At the same time, increasing the slurry density when processing time also increases, accompanied by an excess of CaO, further enhances the Na removal or decreases the Na level remaining in the DBR (Figure 2). These effects are more visible when low slurry densities, e.g. 10 w/v% are combined with 20 wt% CaO, yielding high levels of Na removal even after a short processing time of 1 h. On the contrary, high slurry densities, 40 w/v% with the same CaO content (20 wt%) require longer processing times, up to 6 h, so that cancrinite dealkalisation occurs and Na_2O content in the DBR drops below 0.5 wt%.

Based on the above, the optimum dealkalisation window can be determined, in which either 10 w/v% slurry density-20 wt% CaO-1 h or 40 w/v% slurry density-20 wt% CaO-6 h should be selected for a potential industrial implementation. It should also be considered that different alumina refineries use different bauxite feeds, different dissolution temperatures and soda and lime additions leading to different desilication products (DSPs) in their BR, such as sodalite instead of cancrinite[11]. Therefore, the optimum dealkalisation conditions should be redefined in each case. This is evident in a previous work by Suss et al. [12] in which BR coming from different alumina refineries necessitate adjustment of the dealkalisation process.

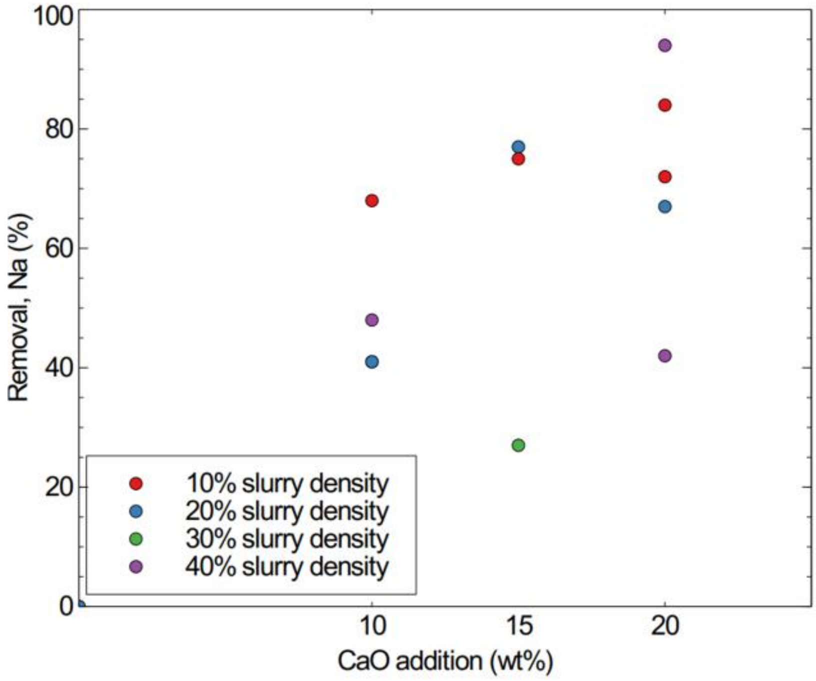

Figure 1. The effect of lime addition and slurry density on Na removal.

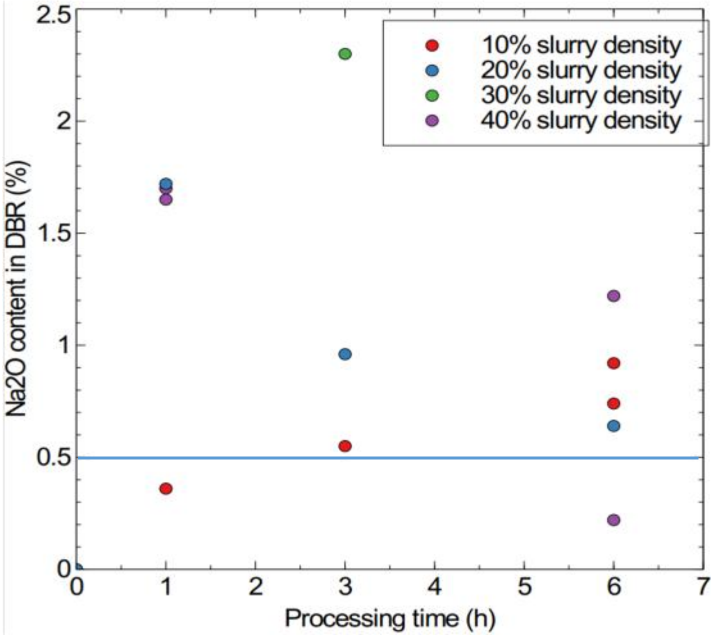

Figure 2. The effect of processing time and slurry density on Na_2O content in the DBR (wt%).

The dealkalisation process is a solid-liquid reaction between DSPs and Ca ions and more precisely it is based on the conversion of DSPs to hydrogarnet [13]. It has been concluded recently that the process initiates with the dissolution of calcium hydroxide in the liquid phase and the liberation

of the Ca ions, the agglomeration of the latter and the replacement of the structural base of the DSP, the disintegration of the DSP structure and finally the formation of hydrogarnet [14].
The different dealkalisation rates are linked to phase changes as depicted in Figure 3. The hydrogarnet content increases as the Na removal increases, due to the substitution of the Al and Si ions in cancrinite from the Ca ions to produce a calcium aluminosilicate hydrate phase, namely hydrogarnet. At the same time, the decrease in cancrinite content and the complete disappearance of the phase occurs above 83 wt% Na removal. When limited dealkalisation reaction of cancrinite is realised with no formation of hydrogarnet (at 0-80 wt% Na removal), there is probably only substitution of Ca and Na ions. The excess of Ca for the sake of dealkalisation reaction also results in the formation of a portlandite phase.

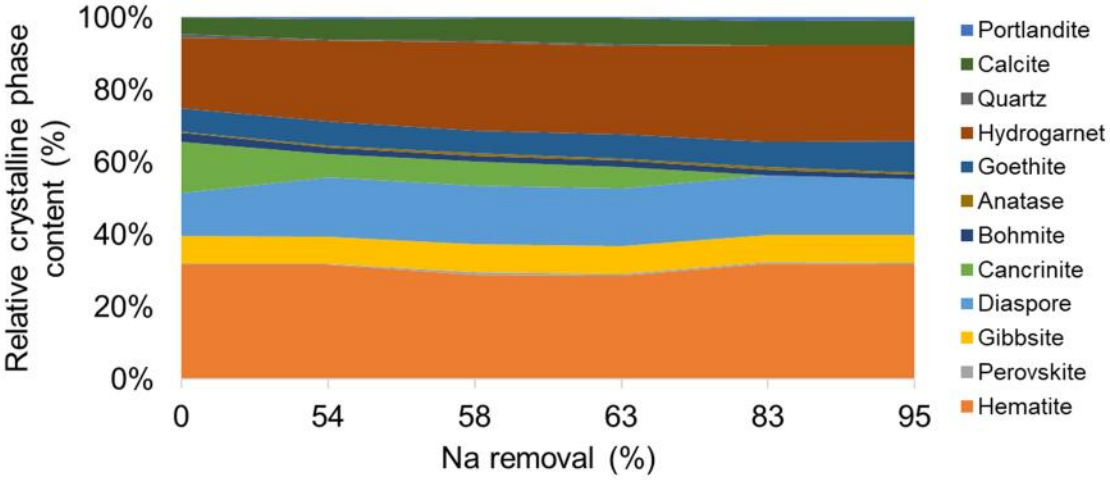

Figure 3. Quantification mineralogical assessment of the DBR at different Na removal amounts.

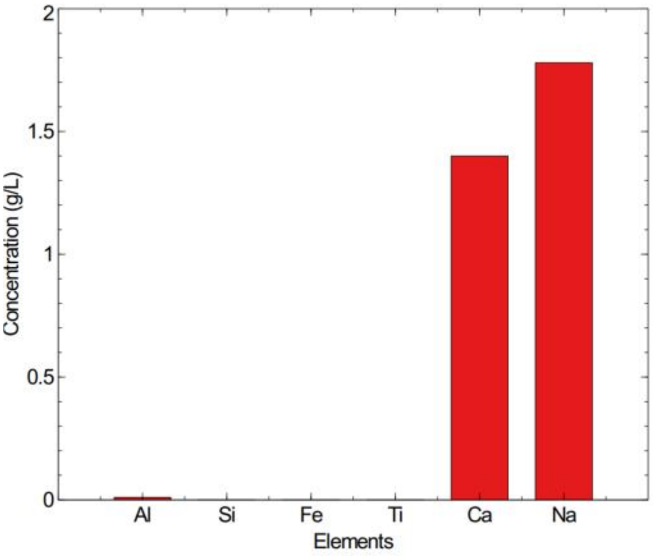

Figure 2. Dealkalisation solution concentration, resulted from dealkalisation experiment performed on the optimum operating window.

The caustic solution resulting from a dealkalisation experiment operated under the optimum conditions for maximum Na removal (10 w/v% slurry density-20 wt% CaO-1 h), is free of Al, Si, Fe and Ti and rich in Na (1.78 g/L) and Ca (1.28 g/L) based on Figure 4. With a view to implementing the process on an industrial scale, the caustic solution from the dealkalisation could be recirculated back into the Bayer process.

3.2 DBR use as a Raw Material in Clinker Production

Table 3 shows the chemical composition of the produced DBR Compared to the initial BR, the absence of Na and the increased CaO in the DBR, make it an attractive raw material that can be used as an iron or alumina source in the raw meal even in the production of low alkali cement clinkers.

Table 3: Chemical composition of DBR, as measured by XRF.

Element (as oxide)	DBR (wt%)
Fe_2O_3	30.8
Al_2O_3	18.9
SiO_2	6.3
Na_2O	0.2
CaO	22.5
TiO_2	4.1

3.3 DBR Co-Calcination with Kaolin for Use as a SCM

The co-calcination of DBR with kaolin has been shown to be effective for the formation of a C-A-S rich DBR with the main phases present to be calcio-olivine, quartz and muscovite with increased amorphicity when kaolin content is increased in DBR from 0 to 30 wt% (Figure 5).
The effect of kaolin addition on DBR reactivity following co-calcination is more evident on the respective graph (Figure 6), where the reactivities for different kaolin additions (solid lines) are compared to the reactivities of untreated BR co-calcined with the respective amounts of kaolin (dashed lines). The reactivity for the calcined DBR with kaolin blends is lower than of the respective BR in all cases. However, the reactivity for the DBR with 30 wt% kaolin addition reaches the target reactivity of 200-250 J/kg and can thus be considered as a SCM with moderate reactivity. The higher reactivity of untreated BR can be attributed to the desilication product e.g. cancrinite, which has been proven to be the reactive component in the BR increasing cement hydration [10]. It should be also noted that desirable strength development could not be obtained for the co-calcined DBR and kaolin blends. When mixing the co-calcined material with water a false flash setting was observed microstructurally, as a result of formation of some local high strength agglomerates. Along with these local points there were also other zones which were depleted in the necessary elements for producing the cement hydration products, as they are required for defining the strength.

4. Conclusions

Both alumina and cement sectors' sustainability drive favours the use of BR as a raw material either in clinker production or as a cement replacement. The challenge is the highly alkaline nature of BR, which limits its potential as a cement replacement in conventional binders. Thus, in this work dealkalisation of BR was achieved in order to transform it into a Na-free solid. The optimum conditions for dealkalisation were identified. Although co-calcination was achieved as a post-treatment step for reactivity enhancement, it was concluded that moderate reactivity was presented only for the DBR with 30 wt% kaolin addition. To transform the DBR into a promising SCM, other processes, such as vitrification, should be performed after the dealkalisation stage.

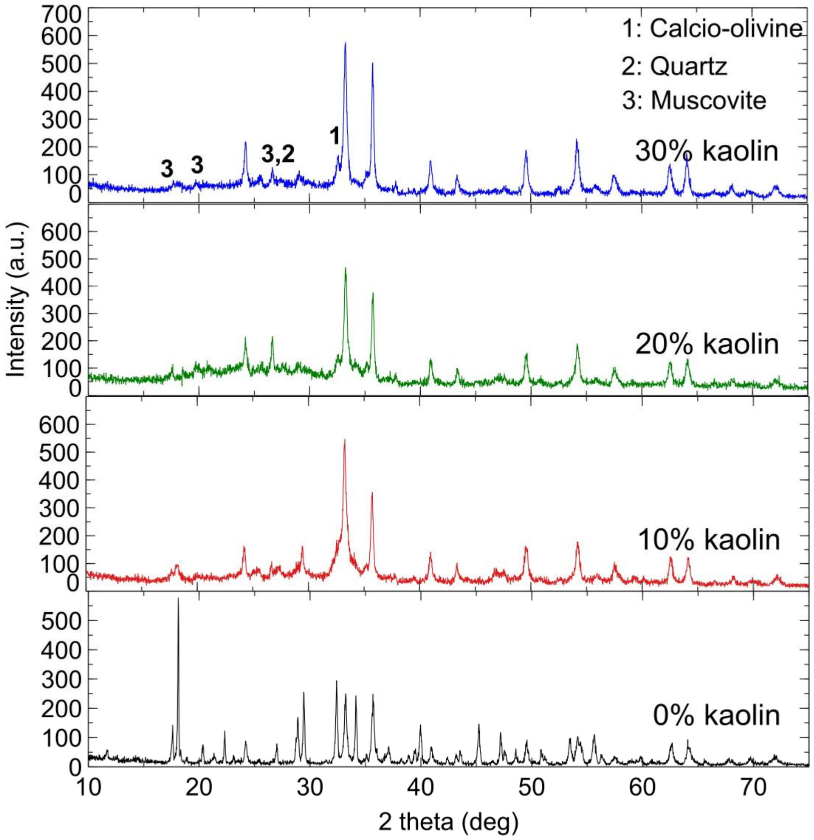

Figure 5. XRD patterns of co-calcined DBR with kaolin (with additions 0 wt%, 10 wt%, 20 wt% and 30 wt%).

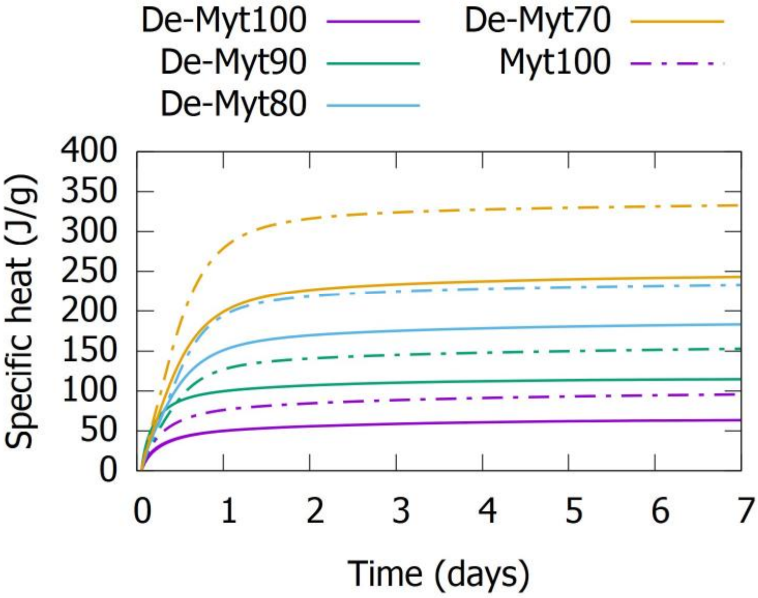

Figure 6. Heat release in the R3 test of the calcined materials with variable kaolin addition -solid lines- (De-Myt100, De-Myt90, De-Myt80, De-Myt70) and respective raw BR-dashed lines.

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6. References

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