INFLUENCE OF RECYCLED ANDALUSITE ON THE PROCESSING AND PERFORMANCE OF ANDALUSITE-BASED REFRACTORIES – PART 3: THERMAL SHOCK BEHAVIOR AND CORROSION RESISTANCE

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ABSTRACT

Andalusite is a widely used refractory raw material due to its excellent volume stability, resistance to SiO_2-rich slags, and outstanding thermal shock resistance. To reduce dependence on limited primary sources, secondary andalusite offers a promising alternative, as much of it remains untransformed after use. However, impurities and previous phase changes may influence its high-temperature performance.

This study examines the impact of secondary andalusite on the thermal shock resistance (TSR) and corrosion resistance of shaped refractories (bricks). Thermal shock resistance was assessed in situ by non-contact measurement of damage after five thermal shock cycles between 800 °C and 1600 °C. Results show that the seven tested bricks sustain minor irreversible damage, even after five thermal shock cycles. Most secondary andalusite-based products demonstrated a thermal shock performance that is almost comparable to that of a reference material (only made of primary andalusite). The materials containing secondary andalusite show a lower increase in stiffness through mullitisation at high temperatures. This discrepancy was reduced by using primary andalusite in the fine grain fraction (0-1 mm).

Besides TSR, the corrosion resistance was tested by performing crucible tests with an alkali-rich slag at 1350 °C and 1450 °C for 5 hours. The residual slags from previous use in service was observed to locally promote slag infiltration. The corrosion resistance of bricks that contained exclusively secondary andalusite was slightly lower than the reference material for 1350 °C but much worse (more material dissolution and infiltration) at 1450 °C, if no primary andalusite was used at all in the formulation. It can be concluded that secondary andalusite is a suitable replacement for a large proportion of primary andalusite, as it does not significantly compromise the key refractory properties. This is particularly the case if the fine fraction still consists of primary andalusite.

INTRODUCTION

Andalusite is a natural raw material, commonly used in refractories for high-temperature processes in steel-, glass-, and cement industry. The combination of good thermal shock behaviour, corrosion resistance, and volume stability that it brings to refractories up to process temperatures of 1600 °C makes it a popular raw material. However, it is only available in limited quantities and European refractories primarily dependent on imports from outside the EU for coarse grained andalusite aggregates up to 6 mm.

The favourable properties of refractory materials containing andalusite are primarily because andalusite transforms *in situ* at high temperatures into mullite and silica, while reaction kinetics depend on grain size and temperature [1]. This so-called 'mullitization' increases the stiffness and strength of the material, while the volumetric expansion of approximately 5 % associated with the transformation compensates for sintering shrinkage [2].

Our own investigations on secondary raw materials and andalusite-containing spent refractories show that these can still contain residual andalusite contents of up to 25 wt.-% with respect to crystalline phases. Therefore, secondary raw material represents a sustainable alternative to primary andalusite. This work is a part of a three-part series. The technological properties, phase composition, and thermomechanical properties (Refractoriness under Load, E-Modulus, and Modulus of Rupture at high temperatures) were discussed already in part 2 for the shaped products (bricks) [3]. Here, in part 3, we will focus on the thermal shock resistance and corrosion resistance of the same bricks at high temperatures to evaluate the effect of secondary andalusite on the overall wear resistance.

MATERIALS AND METHODS

Raw materials and sample preparation

Seven andalusite based refractory bricks were tested that are based on four types of andalusite raw materials. The reference raw material was a primary andalusite, Durandal D59 (Imerys S.A., Paris, France) and used for production of brick 1 (D59) in three particle size fractions: 0–1 mm, 1–3 mm, and 3–5 mm. The three secondary andalusite raw materials (R, R59, and R61) were supplied by Horn & Co. RHIM Minerals Recovery GmbH (Siegen-Weidenau, Germany). Each secondary quality was supplied in the fraction 0–1 mm, 1–3 mm, and 3–6 mm. The R grade is sourced from the glass industry, specifically from tank walls and recuperator parts. Grades R59 and R61 originate from the steel industry (pig iron ladle and torpedo ladle), specifically from the working lining and safety lining, respectively. Three bricks (Brick 2, 3, and 4) were produced that, apart from the bonding matrix (clay and phosphate-based binder), consisted entirely of one of the respective secondary raw materials. In three additional bricks (Brick 5, 6, and 7), primary andalusite was used in the 0–1 mm fraction (see also Tab. 1).

Tab. 1: Particle size distribution of andalusite bricks (Br.) in wt.-%.

Particle size (mm)	Br.1	Br.2	Br.3	Br.4	Br.5	Br.6	Br.7
0 – 1 D59	35				35	35	35
1 – 3 D59	30						
3 – 5 D59	25						
0 – 1 R		35					
1 – 3 R		30			30		
3 – 6 R		23			23		
0 – 1 R59			35				
1 – 3 R59			30			30	
3 – 6 R59			23			23	
0 – 1 R61				35			
1 – 3 R61				30			30
3 – 6 R61				23			25
Clay & phosphate binder	10						

All bricks were cured at 120 °C for 48 hours and fired at 1410 °C for 5 hours. After firing, test pieces for testing thermal shock and corrosion resistance were prepared from the bricks:

– Cylinders (diameter: 50 mm, height: 50 mm)
– Cuboids with dimensions of 100 mm × 100 mm × 65 mm with a central cylindrical borehole (diameter: 55 mm, depth: 45 mm).

Characterization Methods

Thermal Shock Resistance (TSR)

The thermal shock behaviour was tested using laser vibrometer method for *in situ* measurement of ultrasonic velocity at high temperature. Therefore, a cylindrical test piece is moved between two furnaces which are directly connected and can be heated individually. A fast heating up and cooling down by cyclic switching the test piece between both heating chambers induces thermomechanical damage that can be measured *in situ* using the contactless measurement setup. In this study five thermal shocks were performed for two test pieces of each material. The lower temperature was set to 800 °C (30 minutes holding time) and the upper temperature to 1600 °C (15 minutes holding time). A detailed description of the test apparatus was given by Brochen *et al.* [4].

The measured ultrasonic velocity was calculated based on signal runtime and the height of the test piece. The height was measured at room temperature before the test and corrected for high temperature by using thermal expansion data derived from Refractoriness under Load (RuL)-tests [3]. The ultrasonic velocity data were used to calculate a dimensionless damage parameter using Equation (1) according to Kachanov [5].

$$Damage\ parameter = 1 - \left(\frac{v_t}{v_0}\right)^2 \qquad (1)$$

With v_t as ultrasonic velocity after a certain test cycle at 800 °C and v_0 as the ultrasonic velocity at 800 °C before the first high temperature thermal shock.

Crucible test

The corrosion resistance against an alkali-rich synthetic ash (cf. Tab. 2) was examined by performing crucible tests [6] at 1350 °C and 1450 °C for 5 hours in oxidizing atmosphere. Therefore, the cylindrical borehole in the test pieces were filled with 60 grams of the slag forming ash. The test pieces were cut in half after the corrosion test. Photographs of the samples were taken of both halves for image analysis. The sizes of the reference, dissolved, and infiltrated area were determined for each halved crucible (see Fig. 1 for an explanation of the areas mentioned).

Tab. 2: Composition of alkali-rich ash

Component	Wt.-%
SiO_2	24,9
Al_2O_3	3,6
Na_2O	11,3
CaO	21,8
MgO	6,2
Fe_2O_3	7,4
K_2O	12,7
P_2O_5	4,6
SO_3	6,3
Mn_2O_3	1,2

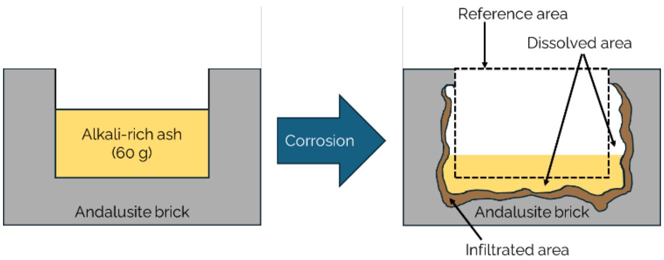

Fig. 1: Scheme of crucible test and the resulting areas (reference, dissolved, infiltrated) that were used for further evaluation of the test results (redrawn according to Reynaert et al. [6]).

The normalized corroded area (NCA) for dissolution and infiltration was calculated afterwards according to Equation (2):

$$NCA\ [\%] = \frac{corroded\ area\ [cm^2]}{reference\ area\ [cm^2]} \cdot 100 - 100 \qquad (2)$$

RESULTS AND DISCUSSION

Thermal Schock Resistance

The generally increasing ultrasonic velocity after the first thermal shock, i.e., a decrease of the damage parameter to negative values, reflects stiffening of the materials due to mullitization and further ceramic bond formation (cf. Fig. 2 and Fig. 3). This is plausible as the material is heated up to 1600 °C for 15 minutes for the first time after previous firing at 1410 °C as maximum temperature. Brick 6 behaves different, and the damage parameter increased to 0.34 after the first thermal shock. However, considering the results for Brick 3, which contained a higher amount of the same secondary andalusite of quality (R59), the first measurement for Brick 6 seems to be erroneous. The highest increasing stiffness (lowest damage parameter after second thermal shock) observed in the reference material (Brick 1) is likely due to its high andalusite fraction, which promotes intense mullite formation.

The damage parameters for materials composed entirely of secondary andalusite (Bricks 2, 3, and 4) decreased in general less than for the reference material. This can be explained by the lower proportion of reactive andalusite which is available for mullitization. After first thermal shock, the damage parameter remains relatively constant across all test cycles and close to zero, suggesting no significant microstructural damage/change. It seems that there is not much andalusite present that can transform into mullite under these conditions and over these periods of time.

Mixing secondary andalusite with primary andalusite, with the 0–1 mm fraction remaining primary, results in lower damage parameter values for Bricks 5 and 7. This means that the measured values for these materials are closer to those of the reference (Brick 1). Although damage increases slightly with each thermal shock cycle, it generally follows the same trend as the reference material, especially for Brick 7.

The values measured at the end of the experiment show impressively how microstructural damage increases (higher ultrasonic velocity, lower damage parameter), when hot refractory material cools down to room temperature. According to the damage parameter at room temperature, no qualitative difference between secondary and primary andalusite based bricks was noticeable. However, the *in situ* data at high temperatures show that the bricks behave differently in respect to their TSR. Even if the materials show excellent high temperature TSR (e.g., between 800 °C and 1600 °C), the resistance against 'cold thermal shock' (e.g., between 800 °C and room temperature) can be much different, also shown by Brochen *et al.* [4]. This underlines the drawbacks of usually performed standardized TSR-tests and at the same time highlights the advantages of the method used in this study. This way, the actual loads in service can be applied and the suitability of a material for a certain use case can be tested.

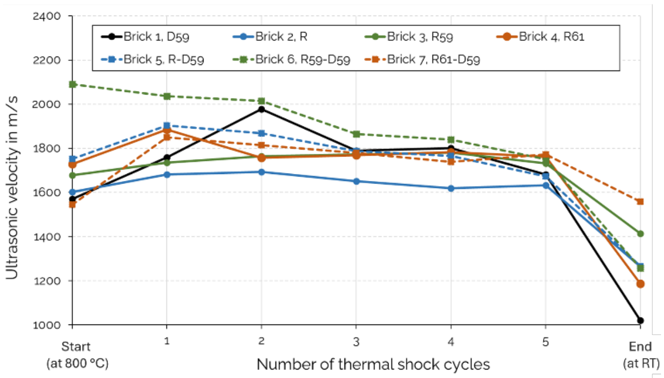

Fig. 2: Evolution of the ultrasonic velocity measured before, in between and after thermal shock cycles (between 800 °C and 1600 °C). Measurements were carried out at 800 °C, except for the last data at the end of the experiment which was acquired at room temperature (RT).

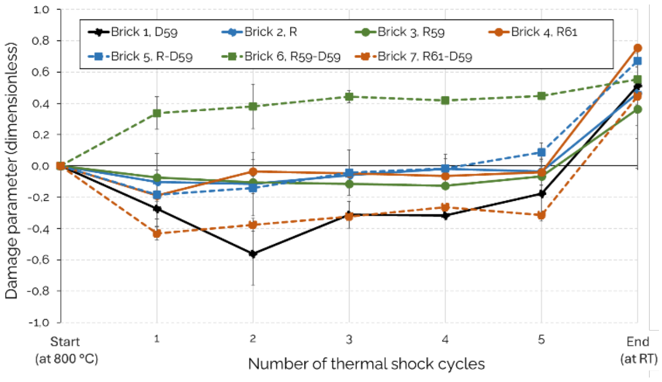

Fig. 3: Evolution of the damage parameter derived from ultrasonic velocity (cf. Fig. 2) after Kachanov [5] according to Equation (1). Measurements were carried out at 800 °C before, in between and after thermal shock cycles (between 800 °C and 1600 °C), except for the last data at the end of the experiment which was acquired at room temperature (RT).

Corrosion resistance

Corrosion resistance at 1350 °C was generally good for all materials but slightly worse for materials consisting exclusively of secondary andalusite. Bricks 2 and 3 exhibited a markedly more uneven corrosion front and more intense dissolution (see Fig. 4, upper part). Corrosion was more pronounced in areas with accumulated slag contamination from previous applications. Replacing the 0–1 mm fraction with primary andalusite (Bricks 5, 6, and 7) appears to reduce this 'channel-forming' effect and significantly enhance overall corrosion resistance despite a recycled content of 55 wt.-%. The corrosion front is much more evenly established, and dissolution and infiltration are less intense. This is particularly true of raw material R, which comes from the glass industry.

At 1450 °C, the relative corrosion resistance of the andalusite bricks was in general similar to 1350 °C. However, the more severe wear at this higher temperature made differences between the materials more apparent. To quantitatively assess the extent of corrosion for both testing temperatures and to allow a correlation with their composition, the dissolved and infiltrated areas were measured and normalized to the reference area (initial area of the borehole of the same image) according to Equation (2). The results, shown in Fig. 5 for the different materials in combination with the andalusite and amorphous phase fraction, based on the analysis presented in Part 2 of this study [3].

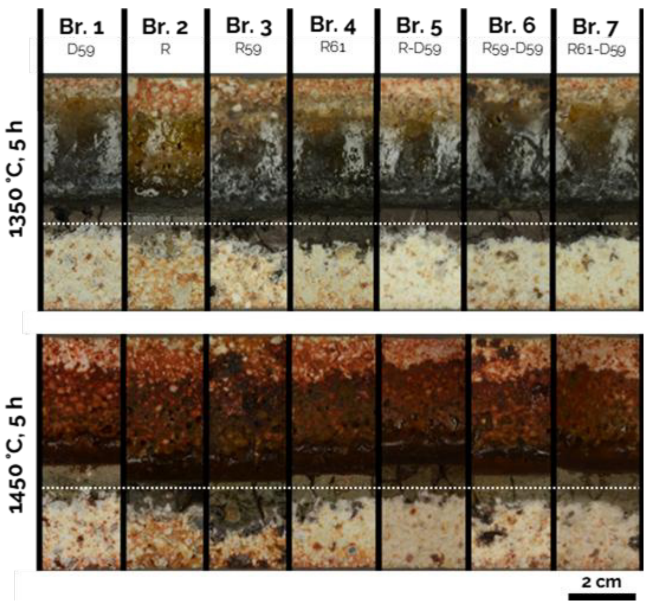

Fig. 4: Photographic image section of a crucible cross-sections from corrosion tests performed at 1350 °C and 1450 °C for 5 hours. The white dotted line indicates the original depth of the borehole in the brick.

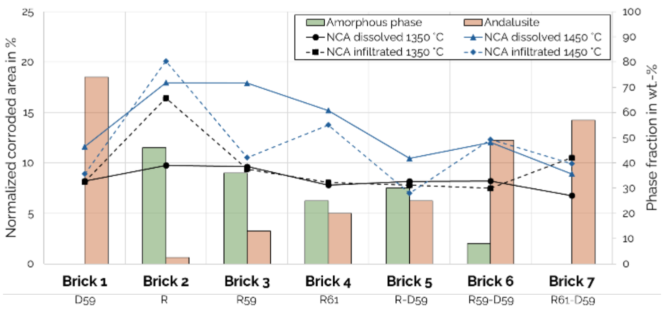

Fig. 5: Calculated normalized corroded area (NCA) with respect to the original reference area (initial size of the borehole before testing) and phase fraction (andalusite and amorphous phase).

It can be concluded that, for most of the tested materials, higher corrosion resistance is associated either with a higher proportion of andalusite or, conversely, with a reduced fraction of the amorphous phase. However, it is also crucial whether these phases and impurities are present predominantly in the fine or in the coarse grain fraction. This is evident from Brick 5, which deviates from this general trend. Brick 5 contains primary andalusite (D59, 0–1 mm) as well as secondary andalusite (R, 1–3 mm and 3–6 mm) and exhibited the highest corrosion resistance, comparable to that of the reference material. This is particularly noteworthy, since the poorest corrosion resistance under identical conditions was observed for Brick 2, which was made from the same secondary raw material, but for all grain sizes. Analogous to the thermomechanical properties [3], these findings suggest that the fine fraction is crucial for achieving favourable high-temperature performance in refractories, even when coarse-grained aggregates contain high amounts of secondary raw materials.

CONCLUSIONS AND OUTLOOK

The results of this study demonstrate that secondary andalusite can replace a substantial proportion of primary raw material in shaped refractories while maintaining good high temperature properties.

Even if the stiffening through mullitization at high temperatures was found to be less intense when secondary andalusite was used in andalusite bricks, the thermal shock resistance remained largely unaffected. Most formulations exhibited behaviour comparable to that of the reference brick, which was produced entirely from primary andalusite. Corrosion resistance was found to be more sensitive to the choice of raw material fractions. Bricks containing only secondary andalusite exhibited significantly reduced resistance at 1450 °C, where slag dissolution and infiltration became more pronounced. The use of secondary andalusite across all grain size fractions did not lead to corrosion progressing uniformly as a dissolution and infiltration front; instead, impurities – such as slag from prior service – promoted localized attack. In contrast, when the 0–1 mm fraction was retained as primary andalusite, corrosion resistance improved and in the case of Brick 5 even reached the level of the reference material. This underlines the decisive role of the fine fraction in controlling corrosion behavior.

Overall, the results indicate that a selective use of primary andalusite in the fine fraction enables the sustainable integration of large amounts of secondary andalusite (up to 55 wt.-% for this study) in coarser grain sizes, thereby reducing the need for primary raw material. Future work will include chemical and microstructural characterization (EDX, SEM) of the corroded test pieces to refine the understanding of corrosion mechanisms, as well as extending the investigation to castable systems with recycled andalusite.

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