INFLUENCE OF RECYCLED ANDALUSITE ON THE PROCESSING AND PERFORMANCE OF ANDALUSITE-BASED REFRACTORIES – PART 2: THERMOMECHANICAL PERFORMANCE OF SHAPED REFRACTORIES IN RELATION TO COMPOSITION

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ABSTRACT
Andalusite-based refractories are valued for their thermal shock resistance and volume stability. As resource scarcity and environmental concerns grow, recycled andalusite emerges as a promising alternative, though challenges remain due to impurities and variable grain decomposition of andalusite into mullite. This study examines its impact on the thermomechanical performance of shaped refractory products with varying ratios of unrecycled and recycled andalusite. Comparative X-ray diffraction analyses indicated a higher concentration of amorphous phase in the refractory composition when recycled andalusite is used, especially with more contaminated recycled grades. This increase in amorphous content correlates with a reduction in the refractoriness of the materials confirmed by refractoriness under load and impulse excitation technique measurements with lower softening temperatures for bricks containing only recycled andalusite. However, a selective approach, replacing only the coarse fraction with recycled andalusite while retaining fine unrecycled andalusite, effectively limits the concentration of amorphous phase and therefore preserves thermomechanical performance close to that of the reference material. This strategy appears promising for combining sustainability with high performance.

INTRODUCTION
The refractory industry is increasingly challenged by sustainability concerns, driven by the depletion of high-quality raw materials and the large volumes of spent refractories generated each year. Globally, tens of millions of tons of refractory waste are produced annually, primarily by the steel and cement industries [1].
These materials often retain valuable mineral phases, making them attractive candidates for closed-loop recycling, where spent refractories are reprocessed and reused as raw materials for new refractory products. This sustainable approach offers both environmental and economic benefits by reducing raw material consumption and carbon footprint of production, lowering waste volumes, and helping to stabilise supply chains, particularly in light of growing price volatility and geopolitical pressures on critical mineral resources [1], [2].
Among the various types of refractories, andalusite-based bricks are widely used in high-temperature industrial processes due to their excellent thermal shock resistance, high creep strength, and good refractoriness and corrosion resistance. Part of these properties can be attributed to the in-situ transformation of andalusite into mullite and silica during service, a reaction that ensures high volume stability upon firing [3], [4], [5], [6].
In this context, the recycling of spent andalusite bricks presents an opportunity for circular use of valuable raw materials in refractory production. However, uncertainties remain regarding the impact of recycled andalusite on the performance of newly produced brick, particularly when impurities and the degree of andalusite decomposition are involved. This lack of understanding hinders the broader adoption of secondary andalusite as raw material by both manufacturers and end users.
To address this, this study aims to evaluate the effect of incorporating recycled andalusite, with varying degrees of purity and particle size, into new refractory bricks.
This work is part of a three-part series. This Part 2 focuses on the thermomechanical properties of refractory bricks.

MATERIALS AND METHODS
Raw materials
Four types of andalusite were used in this study. The first was unrecycled andalusite, Durandal D59 (Imerys S.A., Paris, France), available in three particle size fractions: 0–1 mm, 1–3 mm, and 3–5 mm. The other three were recycled andalusite aggregates supplied by Horn & Co. RHIM Minerals Recovery GmbH (Siegen-Weidenau, Germany) : R, R59 and R61; for each quality the fraction 0–1 mm, 1–3 mm, and 3–6 mm were used. 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.

Sample preparation
The particle size distribution (PSD) of all mixes were designed according to the Andreassen model, using a fixed q-value of 0,4. Seven different compositions were prepared:
– One reference mix containing only unrecycled andalusite (D59)
– Three mixes containing only recycled andalusite
– Three mixes combining unrecycled andalusite (fine fraction 0-1 mm) with recycled andalusite (coarse fraction 1–6 mm).
The exact compositions are reported in Table 1.

Tab. 1: PSD for andalusite brick formulations (wt.%)

Particle size (mm)	D59	R	R59	R61	D59 R	D59 R59	D59 R61
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 matrix & phosphate based binder	10						

Andalusite, water, phosphate-based binder and clay matrix were mixed thoroughly before shaping. The mixtures were then pressed using a mold dimension of 230 × 114 × 64 mm. Both the mixing and pressing operations were carried out by an industrial partner; therefore, which is why the specific parameters for this production steps are not available. The resulting bricks were cured at 120 °C for 48 hours, followed by firing at 1410 °C for 5 hours. After firing, the bricks were cut into specific dimensions for the following tests:

- Cylinders with a diameter of 50 mm and a height of 50 mm, featuring a central hole of 12 mm diameter, for Refractoriness Under Load tests
- Bars measuring 15 mm × 25 mm × 130 mm for Impulse Excitation Technique
- Bars measuring 25 mm × 25 mm × 150 mm for Hot Modulus of Rupture tests.

Sample characterisation

X-Ray diffraction analysis (XRD)

XRD analyses were conducted on powdered brick samples using a Malvern Panalytical Empyrean diffractometer operated in Bragg-Brentano geometry. The instrument was equipped with a Cu anode X-ray tube operating at 45 kV and 40 mA, with a goniometer radius of 240 mm. Data were collected within a 2θ range from 3° to 70°, with a step size of 0,0167°, and a scanning speed of 6,5° per minute. Phase identification was performed using Diffract.EVA version 5.2.0.3 software, and quantitative phase analysis was carried out using Rietveld refinement in HighScore+ version 5.2 software, applying the K-factor method as described in [7].

Refractoriness under load measurements (RUL)

RUL tests were performed using a Pyrox apparatus (Rambouillet, France). T_0 corresponds to the temperature at which the material's expansion, corrected to compensate for displacement caused by the internal alumina tube, reaches its maximum. $T_{0,5}$ is defined as the temperature at which this corrected maximum expansion decreases by 0,5%.

E-modulus determination vs temperature using impulsed excitation technique (IET)

IET measures the flexural resonance frequency of a test piece by striking it with a small hammer and recording the resulting vibrations with a transducer. The frequency data, combined with the test piece's dimensions and mass, is used to calculate the elastic modulus (E) as a function of temperature using the Equation 1.

$$E = 0{,}9465 \times \left(\frac{m \times f_f^2}{\omega}\right) \times \left(\frac{L^3}{t^3}\right) \times T \qquad \text{(Equation 1)}$$

where f is the resonance frequency (s^{-1}), m the test piece mass (g), L the length (mm), w the width (mm), t the thickness (mm), T a correction factor (approximately 1,1).

The tests were conducted with a GrindoSonic MK7 device (GrindoSonic BV, Leuven, Belgium) coupled with a high-temperature furnace, allowing for E modulus measurement up to 1500 °C. In this study, the maximum temperature determined by the RUL test was defined as T_0 for each specific composition, or set to the device limit of 1500 °C when T_0 exceeded this value. Heating and cooling were conducted at a rate of 5 °C/min, with a 10-minute dwell time at T_0 before cooling.

Hot modulus of rupture (HMOR)

HMOR tests were conducted at temperatures ranging from 1000 °C to 1500 °C, in accordance with the EN 993-7 standard. Three temperatures were selected: one corresponding to the T_0 specific to each composition, as determined by RUL, provided that this T_0 did not exceed 1500 °C; otherwise, the test was carried out at the temperature as close as possible to 1500 °C. A second test was performed around 1000 °C, and the third at an intermediate temperature between 1000 °C and T_0. This ensured that strength measurements were within the range in which the material behaves brittle or ductile and does not already exhibit no residual strength. For each composition and at each temperature, three test pieces were evaluated.

RESULTS AND DISCUSSION

Bricks composition

Quantitative XRD results are presented in Tab. 2.

Tab. 2: XRD analysis of the different brick samples (wt.%).

Sample	Andalusite	Mullite	Amorphous phase
D59	74	22	Below detection limit
R	2,5	47	46
R59	13	44	36
R61	20	48	25
D59 R	25	42	30
D59 R59	49	38	8
D59 R61	57	37	Below detection limit

All samples contain minor amounts (< 5 wt.%) of aluminium phosphate, quartz, corundum, and cristobalite, which are not presented in the table.

After the first firing, sample D59 still contains the highest amount of andalusite, although a partial decomposition into mullite has already occurred. In samples R, R59, and R61, the andalusite content varies significantly depending on the recycled material used in production. An inverse relationship with the amount of amorphous phase was also observed. Based on this, the following qualitative classification can be established with respect to the andalusite content and the amount of amorphous phase: D59 > R61 > R59 > R.

Samples combining both recycled and unrecycled andalusite exhibit intermediate characteristics. In particular, the sample combining the fine fraction of unrecycled andalusite with the highest-purity coarse grain of recycled andalusite (D59R61) shows an amorphous phase content below the detection limit, in contrast to the pure R61 sample. This result indicates that the amorphous phase mainly originate from the fine fraction of the recycled andalusite. This interpretation is supported by the fact that finer andalusite grains transform into mullite more rapidly and are therefore more likely to generate silica rich amorphous phase as well [4].

Thermomechanical properties

RUL tests

T_0 obtain an initial assessment of the refractoriness of the samples, RUL test was conducted to determine the temperatures T_0 and $T_{0,5}$. The results are summarised in Tab. 3.

Tab. 3: T_0 and $T_{0,5}$ values obtained from RUL measurements for the different compositions.

Grade	Sample	T_0 (°C)	$T_{0,5}$ (°C)
Unrecycled	D59	1620	1704
Recycled	R	1252	1473
	R59	1294	1548
	R61	1456	1615
Mixture	D59 R	1431	1667
	D59 R59	1460	1691
	D59 R61	1535	1705

The complete replacement of non-recycled andalusite with recycled andalusite leads to a reduction in both T_0 and $T_{0,5}$, with the magnitude of this decrease being more pronounced when the amorphous phase content formed by recycled andalusite is higher.

Fig. 1 illustrates the relationship between T_0 and the amount of amorphous phase. The R^2 value of the correlation is not particularly high, likely due to the difficulty of precisely quantifying the amorphous phase and the complexity of the decomposition phenomenon of andalusite into mullite. Despite this, a general trend can be observed whereby T_0 decreases as the amorphous phase content increases.

Replacing only the coarse fraction of non-recycled andalusite with recycled andalusite reduces the amount of amorphous phase compared to a sample containing only recycled andalusite. This selective substitution helps to limit the decrease in T_0 and $T_{0,5}$ relative to the reference brick D59. In particular, the D59R61 composition, which incorporates recycled andalusite R61 with the lowest amorphous phase content, presents a $T_{0,5}$ similar to the reference material.

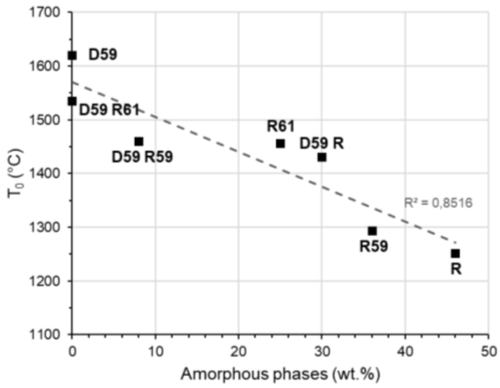

Fig. 1: Relation between the initial softening temperature (T_0 obtained by RUL) and the amorphous phase content (wt.%) for the different refractory compositions.

E-modulus evolution over temperature

Fig. 2 and Fig. 3 show the evolution of E-modulus with temperature determined from IET measurements. Samples containing recycled andalusite, either partially or fully, demonstrate higher initial values dynamic Young's modulus than the reference D59. This behaviour is attributed to a higher content of mullite and glassy phase, which contribute to increased stiffness of the samples.

All materials exhibit a similar overall behaviour which can be divided into three stages:

– Stage 1, up to around 900 °C: a progressive increase in the E-modulus is observed, attributed to the closure of microcracks induced by thermal expansion. The inflection point between 800°C and 900°C may be attributed to the glass transition of amorphous phase, which are increasingly formed through the reaction of aluminium phosphate with silica and alumina, leading to the gradual development of amorphous material within the samples, both the initially present phase and those generated by the transformation of andalusite.
– Stage 2, between 900 °C and 1000 °C - 1300 °C (depending of the material composition): this stage is characterized by a sharp increase of the elastic modulus followed by a more or less pronounced plateau. This behaviour reflects the competition between two phenomena. Initially, the softening of viscous phase promotes material densification through liquid-phase sintering, thereby increasing the elastic modulus. But as the temperature rises, the viscosity of the amorphous phase drops while their volume fraction increases, resulting in a balance between densification and softening of the material.
– Stage 3, above 1000 °C – 1300 °C: the softening effect of the viscous phase becomes predominant, leading to a rapid drop in the dynamic Young's modulus.

The temperature at which the E-modulus begins to drop is lowest for the R composition, followed by R59, D59R59, R61, D59R, and finally D59R61. Samples in which the fine fraction of recycled andalusite was replaced by unrecycled andalusite (Fig. 3) exhibit thermomechanical behaviour more closely matching that of the reference material D59, compared to samples made exclusively of recycled andalusite (Fig. 2). In particular, the D59R61 sample, containing the R61 recycled andalusite as the coarse grain fraction, displays a E-modulus profile almost identical to that of the reference sample D59. This indicates that the fine fraction of unrecycled andalusite plays a significant role in governing the thermomechanical behaviour of the material.

As for the RUL tests, the amount of amorphous phase seems to play a role in the softening behaviour observed by IET. However, this experiment must be repeated to more precisely determine the temperature at which softening occurs and to clarify the exceptions observed for samples D59R59 and D59R. Specifically, the former softens earlier than expected based on its amorphous phase content, whereas the latter softens later than anticipated. This discrepancy could be due to measurement uncertainty or, possibly, the presence of impurities within the sample. Such impurities may influence the formation of amorphous phase and, consequently, affect the softening temperature, as reported in the literature [4], [8].

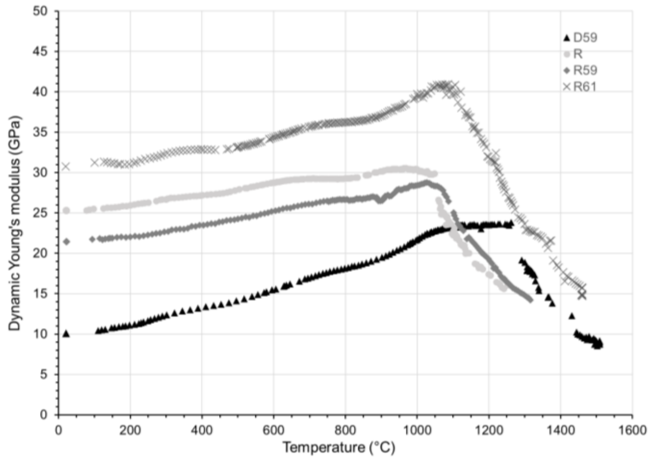

Fig. 2: Evolution vs temperature of elastic modulus E for D59 (▲), R (●), R59 (♦) and R61 (✕) refractory bricks.

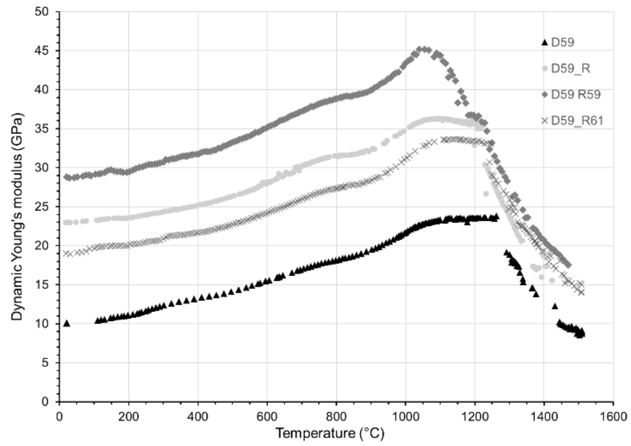

Fig. 3: Evolution vs temperature of elastic modulus E for D59 (▲), D59 R (●), D59 R59 (♦) and D59 R61 (✕) refractory bricks.

HMOR tests

The HMOR results, presented in Tab. 4, are consistent with the results obtained from IET measurements. Samples containing recycled andalusite exhibit higher strength at room temperature, which can be attributed to their higher mullite and glassy phase content (higher grade of vitrification). This may also be due to differences in the type of surface between recycled and non-recycled andalusite grains, which could lead to differences in adhesion with the matrix at room temperature.

For all samples, the moduli initially increased up to 1000 °C, followed by a gradual decrease with further rise in temperature. This behaviour could be associated with the growing proportion of amorphous phase and the reduction in their viscosity at elevated temperatures.

Tab. 4: MOR and HMOR results for andalusite based refractory bricks

Sample	Temperature (°C)	MOR (MPa)
D59	22	6,3 ± 1,0
	1000	8,6 ± 1,3
	1370	2,7 ± 0,2
	1470	1,6 ± 0,2
R	22	8,7 ± 0,7
	1000	12,4 ± 2,5
	1100	6,9 ± 0,6
	1250	2,7 ± 0,5

R59	22	8,6 ± 0,3
	1040	15,3 ± 1,0
	1140	9,5 ± 0,9
	1290	4,0 ± 0,2
R61	22	11,2 ± 0,2
	1000	17,0 ± 2,1
	1200	6,9 ± 0,2
	1450	2,4 ± 0,1
D59 R	22	8,2 ± 0,5
	1000	13,9 ± 4,3
	1280	6,0 ± 1,0
	1430	3,2 ± 0,7
D59 R59	22	9,1 ± 0,1
	1000	14,7 ± 0,4
	1210	6,2 ± 0,5
	1460	2,6 ± 0,5
D59 R61	22	10,0 ± 0,1
	1000	13,0 ± 1,0
	1280	5,7 ± 0,3
	1480	2,5 ± 0,4

CONCLUSIONS

This study highlights the critical influence of amorphous phase content on the thermomechanical properties of refractories. The use of recycled andalusite in refractory bricks increases the amount of amorphous phase, which affects the refractoriness of the bricks. Samples in which unrecycled andalusite was fully replaced by recycled andalusite exhibit noticeably lower T_0 and $T_{0,5}$ values. However, combining a fine fraction of unrecycled andalusite with a coarse fraction of recycled andalusite reduces the amorphous phase content and helps maintain high temperature of deformation, particularly when the coarse recycled fraction itself contains minimal amorphous phase. The thermomechanical behaviour of such mixed compositions closely matches that of the reference bricks made exclusively with unrecycled andalusite, which is a promising result. This higher amount of amorphous phase introduced by recycled andalusite may help relieve thermal stresses at lower temperatures and improved high-temperature thermal shock resistance and slag infiltration resistance, which are key properties for refractories. These aspects are examined in more detail in Part 3 [9].

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