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# 1 Mullite–zirconia composite for the bonding phase of refractory bricks in hazardous waste 2 incineration rotary kiln

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13 63 81 03.

## 14 Abstract

15 Although mullite–zirconia composites made from zircon, alumina, and andalusite meet the requirements for  
16 many refractory applications, little effort has been made to transfer these composites to the bonding phase (the  
17 ‘matrix’) of refractory bricks. In this paper, we investigate how this could be achieved through better control of  
18 secondary oxides. The high temperature phases were simulated with thermodynamic software and linked to the  
19 microstructures, mineralogy, and properties of the composites. The results revealed that the system is very  
20 sensitive to Na<sub>2</sub>O, which harmed the microstructure considerably. By contrast, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> additions proved  
21 beneficial, allowing complete zircon decomposition at 1550 °C while providing the required green strength.  
22 Decohesion between the matrix and aggregates due to high matrix shrinkage can be prevented by partially  
23 substituting andalusite with the volume-increasing mineral kyanite. Based on these findings, a novel refractory  
24 brick was developed and tested with success at an industrial scale.

25

26 Keywords: mullite/zirconia; reaction sintering; phosphate; cyanite; microstructure

27

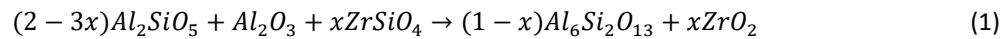
## 28 1 Introduction

29 Reaction-sintered mullite–zirconia ceramics that use zircon (ZrSiO<sub>4</sub>) as the zirconia source have many  
30 beneficial qualities as refractory materials, including refractoriness, chemical stability in contact with slag [1],  
31 high strength [2,3], and outstanding thermal shock resistance [4,5]. These properties make mullite-zirconia a  
32 promising candidate as bonding system of novel refractories for hazardous waste incinerators, because mullite-  
33 zirconia exhibits excellent thermal shock resistance in comparison with bauxite, andalusite or alumina-chromia  
34 refractory bricks or castables used nowadays. The *in-situ* formation of 20 vol% well-dispersed zirconia grains  
35 raises the material’s strength and fracture toughness by up to 50% [2] compared to that of plain mullite.  
36 Nevertheless, these results are obtained when using high-purity ceramic powders; it is difficult to transfer them  
37 to refractory bricks, where the bonding phase (the ‘matrix’) is made from raw materials containing impurities.

1 Therefore, despite the potential advantages of using a mullite–zirconia bonding phase, most refractory bricks are  
2 still mullite-bonded.

3 Refractory manufacturers use graded particle size distributions, with particle sizes ranging from a few  
4 microns to a few millimetres. The finer part of this distribution ( $\leq 200 \mu\text{m}$ ; typically 30–40% of the total raw  
5 material) forms the matrix; larger particles are considered aggregates. The matrix materials ought to be  
6 economically priced and accessible in large quantities.

7 Many studies in recent years have attempted to employ different aluminosilicates for the synthesis of  
8 mullite–zirconia composites. Minerals from the sillimanite group have attracted most attention [1,6–8]. These  
9 comprise sillimanite, andalusite, and kyanite, which are all polymorphs of  $\text{Al}_2\text{SiO}_5$ . In addition to the economic  
10 advantage, mullite-transformed andalusite can enhance the thermal shock resistance of the composite [1]. The  
11 starting materials  $\text{ZrSiO}_4$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Al}_2\text{SiO}_5$  react in several steps to form mullite and zirconia, which,  
12 simplified, can be summarised to reaction (1), where  $0 \leq x \leq 0.667$ .



13 The sintering reaction is very sensitive to the presence of secondary oxides [9], which are omnipresent in  
14 refractory-grade raw materials, either in the form of impurities or intentionally added as sintering aids, pressing  
15 aids, temporary binders, etc. In this respect,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ , and  $\text{P}_2\text{O}_5$  are critical.  $\text{Na}_2\text{O}$  is a major impurity in  
16 Bayer alumina.  $\text{TiO}_2$  is a common impurity in many raw materials, but it is also a common sintering aid for  
17 mullite–zirconia composites [3,10].  $\text{P}_2\text{O}_5$  is a prominent additive in the refractory industry as it provides the  
18 required green strength and plasticity [11], and reacts with alumina at high temperatures to form  $\text{AlPO}_4$ , which  
19 reinforces the refractory bonding [12]. However, while the effects of  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  on the sintering reaction  
20 have been studied in detail, the effect of phosphate is not well understood. Therefore, there is a need to  
21 investigate the effects of  $\text{P}_2\text{O}_5$  additives and to compare them to the effects of  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$ , for the  
22 refractories studied in this paper.

23 In this study, we apply a mullite–zirconia matrix made from zircon–alumina–andalusite/kyanite mixes to the  
24 bonding phase of refractory bricks and we investigate the effects of  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ , and  $\text{TiO}_2$  on the system. The  
25 findings offer an understanding of how to successfully control the reaction-sintering process in refractory bricks.  
26 First, we focus on the matrix itself, regarding the phases that form at high temperature. Second, we shed light on  
27 the matrix–aggregate interdependence within a refractory brick. We also address the problem of matrix  
28 shrinkage and explain how kyanite can help to solve this problem.

## 29 **2 Materials and methods**

### 30 *2.1 Fabrication of matrix samples*

31 Matrix samples were synthesised through a laboratory processing route that aims to reproduce the industrial  
32 process, albeit at a smaller scale. The task was to transfer the matrix, elaborated in the laboratory, to an  
33 industrial refractory brick made of matrix (bonding phase) and aggregates. The main requirements with regard  
34 to the industrial process are short and dry mixing, uniaxial pressing, and sintering below  $1600 \text{ }^\circ\text{C}$ .

35 Matrix samples were prepared by mixing the raw materials in a tumbler mixer (Turbula<sup>®</sup> T2C) for 2 h. The  
36 absence of aggregates was compensated by adding alumina balls ( $\text{Ø}10 \text{ mm}$ ) to aid the mixing process, which  
37 were subsequently removed. The blended mixture was then pressed into pills ( $\text{Ø}20 \times 10 \text{ mm}$ ) using a uniaxial

1 pressure of 150 MPa (5584, Instron, US). The matrix pills were sintered at various temperatures between 1450  
2 and 1600 °C. The heating and cooling rates were 2.5 °C/min and the holding time was 3 h.

3 Preliminary tests showed that using only very fine powders led to agglomeration during mixing and  
4 lamination during pressing. Both problems were resolved by designing a graded particle size distribution with  
5 fine zircon powder, intermediate alumina, and coarser andalusite or kyanite (Table 1). A portion of the  
6 andalusite was replaced with kyanite (percentage  $k$  in table 1) to mitigate matrix shrinkage (see Section 3.2).

7 Table 1. Raw material composition for matrix (without additives) and aggregate materials.

Matrix component	Grain size	Composition [wt%]										wt% of matrix
	[ $\mu\text{m}$ ]	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	ZrO <sub>2</sub>	
Micronized zircon	≈2	0.7	34.0	0.10	0.25	0.12	0.00	0.00	0.00	0.20	64.0 <sup>3</sup>	31.3
Calcined alumina	≈4	99.5	0.0	0.01	0.00	0.00	0.27	0.00	0.01	0.00	0.0	22.9
Fused alumina	≈50	99.7	0.0	0.02	0.00	0.00	0.16	0.00	0.01	0.01	0.0	15.2
Andalusite	<160	60.8	38.1	0.50	0.15	0.00	0.10	0.15	0.05	0.10	0.0	30.6- $k$
Kyanite	<125	57.5	40.3	0.6	1.2	0.15	0.04	0.07	0.04	0.03	–	$k$
<b>Matrix</b>	2–160	56.8	22.3	0.19	0.12	0.04	0.12	0.05	0.02	0.09	20.0 <sup>3</sup>	100.0
<b>Aggregate</b>												
Andalusite	100–1600	58.7	38.5	1.1	0.2	–	0.1	0.4	0.2	0.2	–	
Mulcoa 60 <sup>1</sup>	1000–6000	60.0	35.8	1.2	2.4	–	0.1	0.1	0.1	0.1	–	
FZM <sup>2</sup>	100–6000	45.8	17.1	0.1	0.1	–	–	–	0.1	–	36.5 <sup>3</sup>	

8 <sup>1</sup>High alumina chamotte; <sup>2</sup>Fused zirconia–mullite; <sup>3</sup>ZrO<sub>2</sub>+HfO<sub>2</sub>

9 To analyse the effects of Na<sub>2</sub>O, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub> oxide additions on the matrix properties and sintering  
10 reactions, fine powders of Na<sub>2</sub>CO<sub>3</sub>, rutile (TiO<sub>2</sub>), and monoaluminum phosphate (Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>) were respectively  
11 added to the raw materials, to give an equivalent oxide content of 1, 2, or 3 mol%.

## 12 2.2 Fabrication of brick samples

13 Brick samples (Wedges of 250 × 198 × 103/90 mm) were prepared by mixing the starting materials  
14 (aggregates, matrix components, water) in an Eirich-type mixer. The aggregate/matrix volume ratio was 7:3 for  
15 all samples. The amount of water was adjusted to yield 2 wt% moisture in every blend. The grain size  
16 distribution was designed following the modified Andreasen model developed by Dinger and Funk [13]. The  
17 maximum and minimum grain sizes of 6 mm and 2  $\mu\text{m}$ , respectively, were the same for all formulations. After a  
18 total mixing time of 30 min, the batch was pressed to bricks using a uniaxial pressure of 150 MPa. Finally, the  
19 bricks were dried overnight at 110 °C and fired at 1500, 1550, or 1600 °C. The heating rate and dwell time were  
20 the same as for the sintering step of the matrix samples (2.5 °C/min and 3 h, respectively).

21 The brick formulations contained the same matrix, composed of 31.3 wt% zircon, 37.8 wt% alumina,  
22 10.2 wt% andalusite, 15 wt% kyanite, 2.6 wt% (3 mol%) TiO<sub>2</sub>, and 3.1 wt% (2 mol%) P<sub>2</sub>O<sub>5</sub>. Various aggregate  
23 systems were evaluated, but only the two most suitable systems are presented in this paper. The first system  
24 used a combination of andalusite (0.1–1.6 mm) and high alumina chamotte (1–6 mm) aggregates, while the  
25 second system used fused zirconia–mullite (FZM; 0.1–6 mm) aggregates. The chemical compositions of the  
26 studied aggregates are summarised in Table 1.

### 2.3 Thermodynamic modelling

The equilibrium phases at 1000–1600 °C were calculated using FactSage® (version 6.4), a thermodynamic database computing software. The FactPS and FToxid databases (both updated in 2013) were used for pure substances and oxides, respectively. The ambient pressure was set to 1 atm. Due to missing/erroneous data of K<sub>2</sub>O compounds, the percentage of K<sub>2</sub>O was added to the Na<sub>2</sub>O content; since these alkali oxides are chemically alike, this should not considerably distort the resulting liquid portion.

### 2.4 Characterisation methods

The microstructures, mineral compositions, and properties (porosity, compressive strength) of the sintered samples were evaluated with regard to the thermodynamic calculation results. The microstructures were examined using scanning electron microscopy (SEM; JSM-6500F, JEOL, Japan) with polished and carbon-metallised samples. For better contrast between zircon, zirconia, and mullite, the backscattering mode was chosen. The crystalline phases in the matrix were determined for the matrix pills by X-ray diffraction (PANalytical X'Pert Pro, Netherlands) using Cu K $\alpha$  radiation. The open porosity was measured via Archimedes' method according to DIN EN 993-1. The cold crushing strength (CCS) of the refractories was measured according to DIN EN 993-5 on cubes of 50 × 50 × 50 mm.

## 3 Results

### 3.1 Effects of secondary oxides on mineralogy and microstructure

The diffraction patterns in Fig. 1 of zircon–alumina–andalusite mixtures (without additives) sintered at different temperatures demonstrate that zircon dissociation actually takes place between 1450 and 1570 °C.

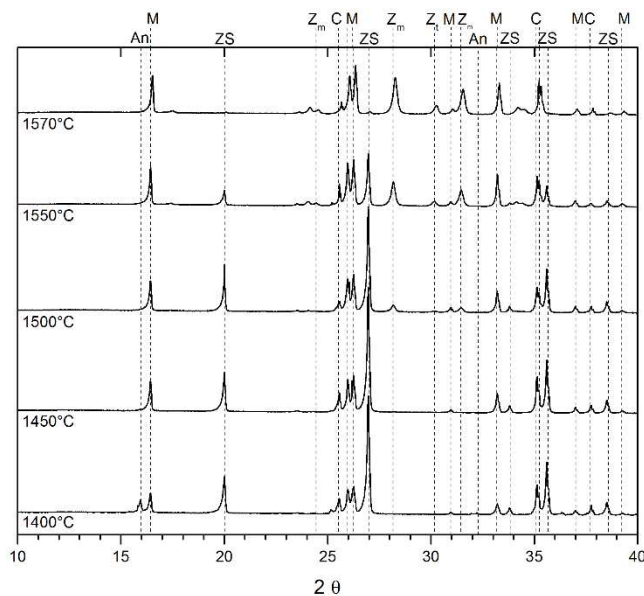
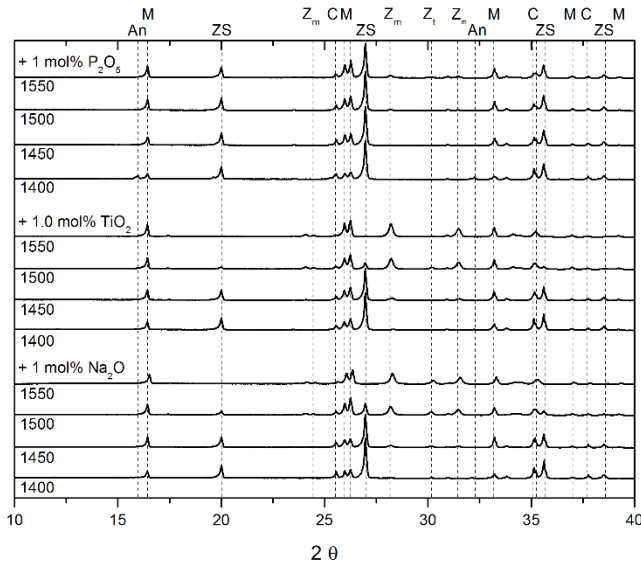


Fig. 1. X-ray diffraction patterns of a zircon–alumina–andalusite mixture (without additives) sintered at different temperatures. The mineralogical phases are C – corundum (Al<sub>2</sub>O<sub>3</sub>), M – mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>), An – andalusite (Al<sub>2</sub>SiO<sub>5</sub>), ZS – zircon (ZrSiO<sub>4</sub>), Z<sub>m</sub> – monoclinic zirconia (m-ZrO<sub>2</sub>), and Z<sub>4</sub> – tetragonal zirconia (t-ZrO<sub>2</sub>).

The effects of secondary oxides are illustrated in the diffractograms in Fig. 2. Adding 1 mol% (0.34 wt%) Na<sub>2</sub>O lowers the zircon transformation start and finish temperatures by approximately 50 °C. By 1500 °C,

1 almost all the zircon has already dissociated. The obtained zirconia particles comprise tetragonal and monoclinic  
 2 modifications.

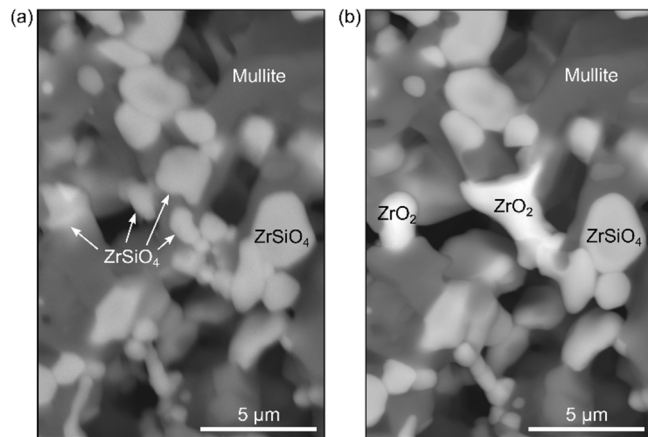


3  
 4 Fig. 2. X-ray diffraction patterns of zircon–alumina–andalusite–additive mixtures sintered at different  
 5 temperatures. The mineralogical phases are C – corundum ( $\text{Al}_2\text{O}_3$ ), M – mullite ( $\text{Al}_6\text{Si}_2\text{O}_{13}$ ), An – andalusite  
 6 ( $\text{Al}_2\text{SiO}_5$ ), ZS – zircon ( $\text{ZrSiO}_4$ ),  $Z_m$  – monoclinic zirconia ( $m\text{-ZrO}_2$ ), and  $Z_t$  – tetragonal zirconia ( $t\text{-ZrO}_2$ ).

7 Among the three investigated oxides,  $\text{TiO}_2$  is the most effective at promoting zircon dissociation. The zircon  
 8 peaks have mostly disappeared in the diffractogram of the sample fired at 1500 °C, whereas the zircon peaks are  
 9 still well pronounced in the  $\text{Na}_2\text{O}$ -doped sample sintered at the same temperature. Tetragonal zirconia was not  
 10 detected in any of the  $\text{TiO}_2$ -doped samples.

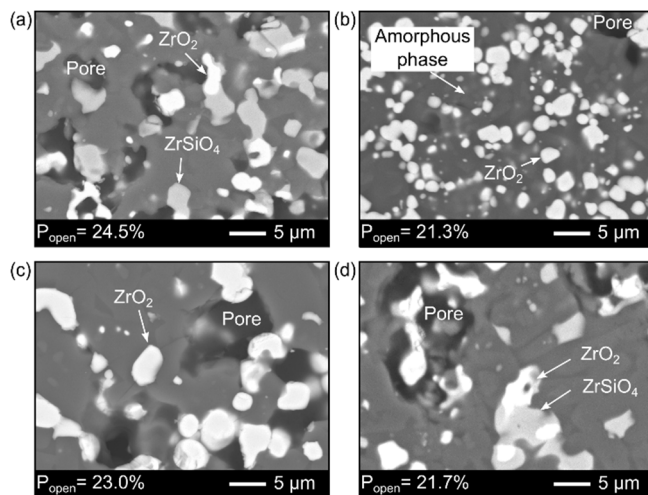
11 For the  $\text{P}_2\text{O}_5$ -doped samples, the X-ray survey testifies a slight shift of both andalusite and zircon  
 12 dissociation towards higher temperatures. After sintering at 1550°C, the zircon peaks are yet well visible on the  
 13 diffractogram. Contrary to our expectations, crystalline  $\text{AlPO}_4$  was not detected by X-ray diffraction.  $\text{AlPO}_4$   
 14 might have been incorporated into the silica-rich amorphous phase, considering that  $\text{AlPO}_4$  and  $\text{SiO}_2$  are  
 15 chemically similar [14]. To verify this, a silica-free matrix was fabricated from alumina, zirconia, and  
 16  $\text{Al}(\text{H}_2\text{PO}_4)_3$ . X-ray diffraction measurements confirmed that in this case, crystalline  $\text{AlPO}_4$  is indeed formed.  
 17 Therefore, when in contact with the silica-rich amorphous phase present in the mullite–zirconia composites,  
 18 phosphate is likely to form an amorphous phase instead of crystalline  $\text{AlPO}_4$ .

19 In order to observe how zircon starts to dissociate, the same area of an additive-free matrix sample was  
 20 imaged sequentially after heating to 1450 and 1475 °C. The SEM images in Fig. 3 show two newly formed  
 21 zirconia grains after the second heating step, which emerged from several adjacent zircon particles. Meanwhile,  
 22 non-transformed zircon particle clusters did not coalesce.



1  
2 Fig. 3. SEM images of a zircon–alumina–andalusite matrix sample (without additives) after heat treatments at  
3 (a) 1450 °C and (b) 1475 °C.

4 The effects of the three additives on the microstructures can be compared in Fig. 4. When Na<sub>2</sub>O is added  
5 (Fig. 4 (b)), the resulting ZrO<sub>2</sub> particles are 0.5–3 μm in size, which is noticeably smaller than those in the other  
6 samples. However, there are notable amounts of amorphous phase. The liquid phase causes densification of the  
7 matrix sample, leading to reduced porosity.



8  
9 Fig. 4. SEM images showing the impact of additives (1 mol%) on the final microstructure and open porosity  
10 (P<sub>open</sub>) of zircon–alumina–andalusite mixtures sintered at 1550 °C: (a) without additives, (b) 0.34 wt% Na<sub>2</sub>O, (c)  
11 0.88 wt% TiO<sub>2</sub>, and (d) 1.55 wt% P<sub>2</sub>O<sub>5</sub>.

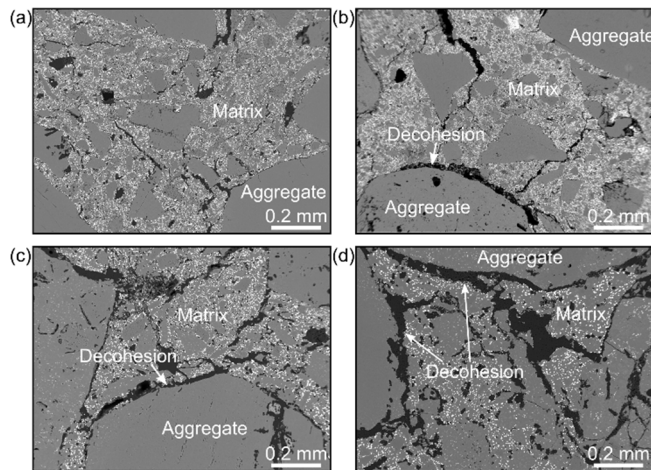
12 With the addition of TiO<sub>2</sub> (Fig. 4 (c)), zircon is completely transformed after sintering at 1550 °C.  
13 Nevertheless, the microstructure does not vitrify, contrary to the case for Na<sub>2</sub>O, although the porosity is still  
14 reduced somewhat compared to that in the additive-free matrix. The final zirconia grains are about 5 μm in size,  
15 similarly to the zirconia grains in the additive-free matrix with fully dissociated zircon (sintered at 1570 °C).

16 The impact of P<sub>2</sub>O<sub>5</sub> on the zircon decomposition is marginal (Fig. 4 (d)). The morphology is similar to that  
17 of the additive-free matrix, with some zircon particles still remaining after sintering at 1550 °C. However, the  
18 porosity is reduced on account of the improved compaction during pressing.

1 Further experiments revealed that a combination of 2 mol% P<sub>2</sub>O<sub>5</sub> and 3 mol% TiO<sub>2</sub> provided optimal green  
 2 properties and complete zircon dissociation at 1550 °C. Therefore, these combined additives were chosen for the  
 3 brick samples.

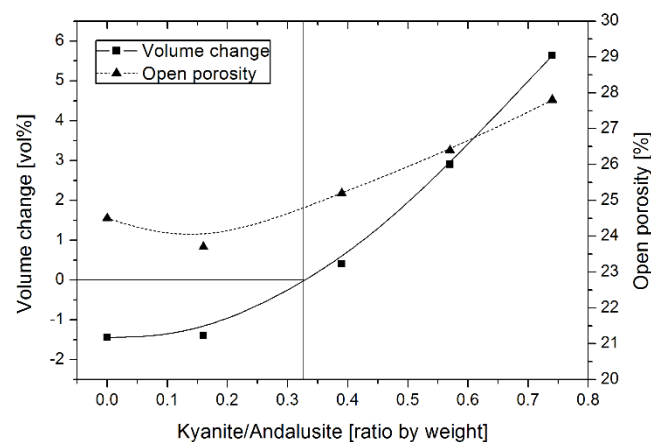
### 4 3.2 The preparation of bricks

5 During the development of the bricks, there was a noticeable drop in mechanical strength when a certain  
 6 sintering temperature was surpassed. SEM observations revealed that this was caused by high shrinkage of the  
 7 matrix, as it led to decohesion between the aggregates and matrix. An example is illustrated in Fig. 5.



8  
 9 Fig. 5. SEM images of a mullite-zirconia-bonded brick sintered at (a) 1450 °C, (b) 1500 °C, (c) 1550 °C, and  
 10 (d) 1600 °C, revealing decohesion between the matrix and aggregates (Mulcoa 60) caused by matrix shrinkage.

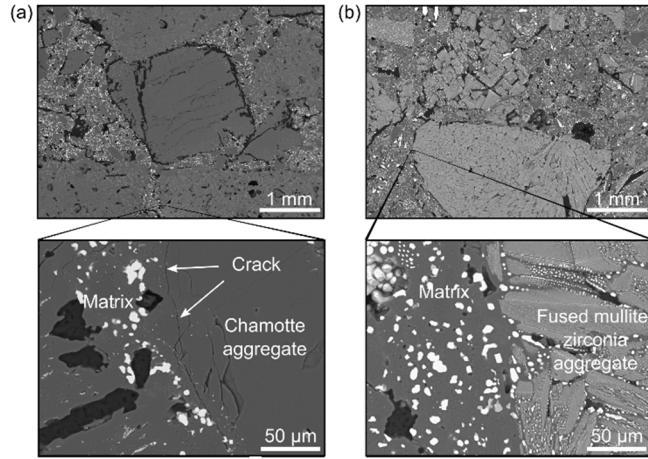
11 It is possible to counter high matrix shrinkage by employing materials that increase in volume during  
 12 sintering. Kyanite (Al<sub>2</sub>SiO<sub>5</sub>), a polymorph of andalusite, has such an effect. Thus, to counterbalance the  
 13 shrinkage, the andalusite in the matrix was gradually replaced by kyanite. Fig. 6 shows that, in the additive-free  
 14 matrix, approximately one third of the andalusite needs to be replaced by kyanite to obtain a matrix that neither  
 15 shrinks nor expands at 1550 °C. Accordingly, the kyanite and andalusite contents of the matrix were adjusted to  
 16 attain zero shrinkage when sintering at 1550 °C.



17  
 18 Fig. 6. Impact of kyanite on the volume expansion and porosity of a reaction-sintered (1550 °C) mullite-  
 19 zirconia (20 wt% ZrO<sub>2</sub>) matrix made from andalusite/kyanite, alumina, and zircon (without additives).



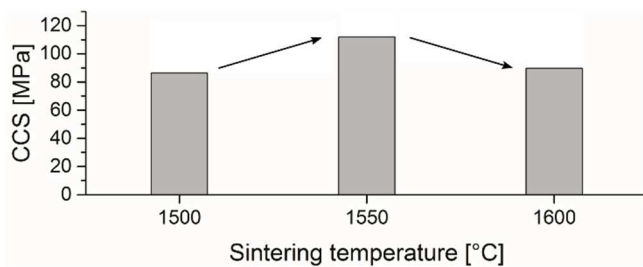
1 Representative microstructures of the bricks with andalusite/Mulcoa 60 and FZM aggregates are depicted in  
 2 Fig. 7 (a) and (b), respectively. In both cases, the zirconia particles are well distributed and there are no large  
 3 gaps between the aggregates and matrix. However, fine cracks appeared at the matrix/aggregate interface when  
 4 using andalusite/Mulcoa 60 aggregates, which were absent when using the FZM aggregates.



5  
 6 Fig. 7. SEM images of mullite–zirconia-bonded refractory bricks made with (a) andalusite/Mulcoa 60  
 7 aggregates and (b) fused zirconia–mullite aggregates (FZM). Both bricks used the same matrix (31.3 wt%  
 8 zircon, 37.8 wt% alumina, 10.2 wt% andalusite, 15 wt% kyanite, 2.6 wt% (3 mol%) TiO<sub>2</sub>, and 3.1 wt%  
 9 (2 mol%) P<sub>2</sub>O<sub>5</sub>) and sintering temperature (1550 °C).

### 10 3.3 Properties of novel bricks and applications

11 The sintering temperature had a clear impact on the mechanical properties of the bricks (Fig. 8). Because the  
 12 andalusite/kyanite ratio and additive content were respectively designed to give zero matrix shrinkage and  
 13 complete zircon dissociation at 1550 °C, a maximum in strength was obtained when sintering at 1550 °C. If the  
 14 sintering temperature is above or below this designed temperature, the desired matrix properties are no longer  
 15 guaranteed.



16  
 17 Fig. 8. Cold crushing strength (CCS) vs. sintering temperature of a mullite–zirconia-bonded brick (Aggregates:  
 18 andalusite/Mulcoa 60).

19 Fig. 9 compares the properties of bricks sintered at 1550 °C with and without P<sub>2</sub>O<sub>5</sub> in the matrix. The  
 20 phosphate addition lowered the porosity and greatly increased the strength. This effect was even more  
 21 pronounced for the brick with FZM aggregates, because the phosphate bonds between the aggregates and matrix  
 22 are intact (see Fig. 7). The typical compressive strengths obtained with FZM aggregates and P<sub>2</sub>O<sub>5</sub> doping were  
 23 >200 MPa, which is exceptional for refractory bricks.

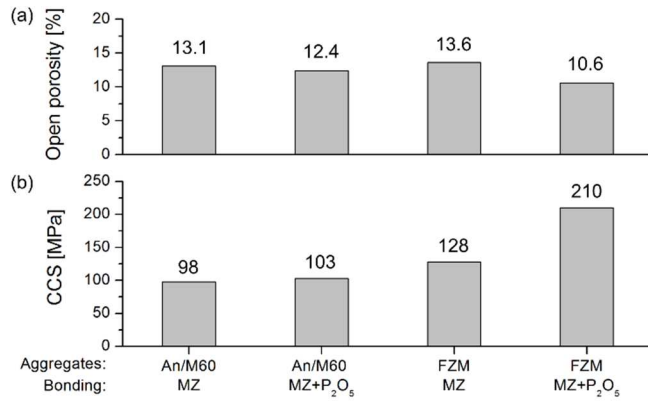


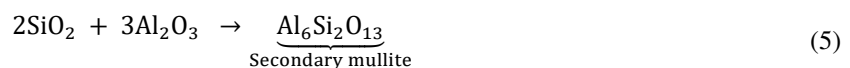
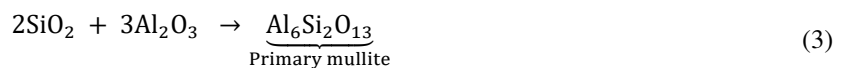
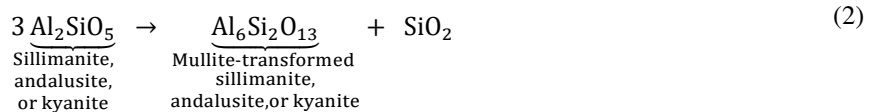
Fig. 9. Comparison of (a) open porosity and (b) cold crushing strength (CCS) of mullite–zirconia (MZ)-bonded bricks with and without 2 mol% P<sub>2</sub>O<sub>5</sub> in the matrix. Andalusite/Mulcoa 60 (An/M60) and fused zirconia–mullite (FZM) aggregates were used. All bricks were sintered at 1550 °C.

The mullite–zirconia-bonded brick with FZM aggregates was produced industrially and tested in two rotary kilns for hazardous waste incineration. The material had very good performance in the kiln inlet, where the refractory bricks were exposed to mechanical load caused by solid wastes and to thermal shock provoked by cold liquid wastes dropping on the hot refractory lining [15]. After 20 months of use, the lining thickness was reduced in the first kiln from 250 to 180 mm and in the second kiln from 250 to 200 mm. With these slow wear rates, a lifetime of five to seven years is expected to be attained, in comparison to only one to two years for the previously used bauxite, andalusite, and alumina–chromia refractory bricks or castables.

#### 4 Discussion

Prior studies have showcased the benefits of mullite–zirconia composites made from zircon, alumina, and andalusite. In this study, we investigated the possibility of applying this material as the bonding matrix phase of refractory bricks, with a focus on the impacts of secondary oxides on the high temperature sintering reactions, microstructure, and resulting properties.

The sintering process of ZrSiO<sub>4</sub>–Al<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>SiO<sub>5</sub> mixtures can be divided into four steps, represented by Reactions (2)–(5).



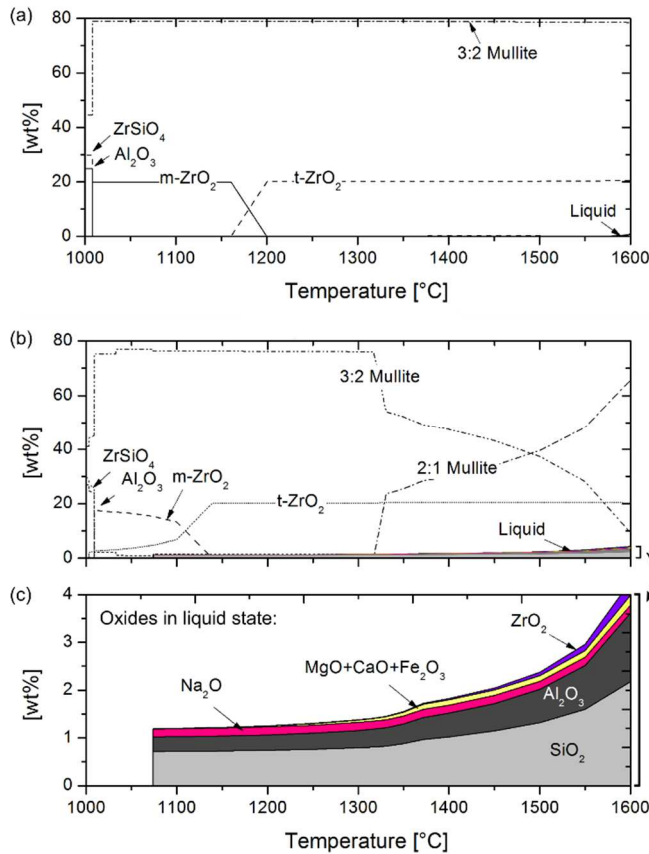
The first two mullitisation steps (Reactions (2) and (3)) begin at about 1300 °C upon heating and conclude at around 1400 °C [1,16]. From a technological point of view, the critical step is zircon decomposition (Reaction (4)), because it requires a high temperature. Pure zircon dissociates into zirconia and silica at 1673 °C [17]. In the presence of alumina, this temperature reduces to 1450–1600 °C, depending on the reactivity and purity of

1 the starting powders [9,18,19]. The last step (Reaction (5)) is the reaction between the zircon-released silica and  
2 the remaining alumina to form secondary mullite.

### 3 *4.1 Role of impurities and alkaline/TiO<sub>2</sub> sintering aids*

4 All four reactions (2) – (5) are diffusion dependent, making them sensitive to the presence of a liquid phase.  
5 This explains why impurities, in particular fluxing agents, are so critical to this system – in both a positive and  
6 negative sense [9]. On one hand, they accelerate the reaction sintering processes, but on the other, they can harm  
7 the microstructure and deteriorate the final properties.

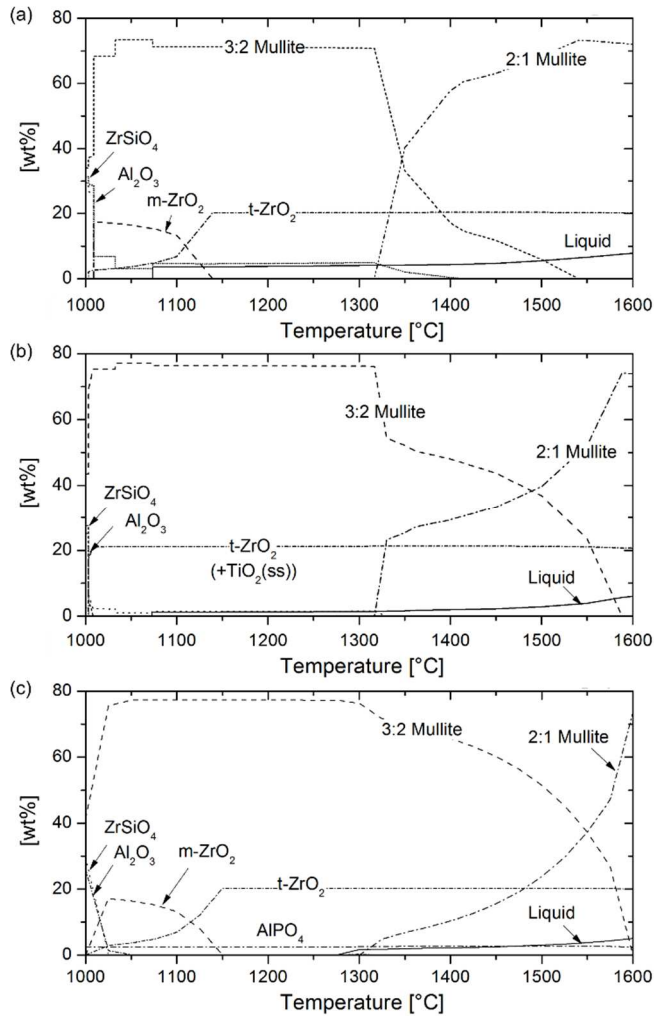
8 The thermodynamically stable phases of a theoretical 30% ZrSiO<sub>4</sub>–36% Al<sub>2</sub>O<sub>3</sub>–34% Al<sub>2</sub>SiO<sub>5</sub> (wt%) mixture  
9 without impurities and those of the same mixture including impurities (0.17 wt% Na<sub>2</sub>O, 0.12 wt% TiO<sub>2</sub>,  
10 0.19 wt% Fe<sub>2</sub>O<sub>3</sub>, 0.09 wt% MgO, and 0.02 wt% CaO) are shown in Fig. 10(a) and (b), respectively. In the  
11 theoretical composition without impurities, insignificant amounts (0.2 wt%) of liquid phase appear at 1556 °C.  
12 However, when the impurities are considered, a liquid phase emerges at only 1074 °C. This phase contains some  
13 SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and all the accessible Na<sub>2</sub>O. By 1200 °C, the liquid phase comprises 1.3 wt% of the matrix. At  
14 1300 °C and above, MgO, CaO, and Fe<sub>2</sub>O<sub>3</sub> enter the liquid state and increasing amounts of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and  
15 some ZrO<sub>2</sub> dissolve. At 1550 °C, 3.0 wt% liquid is formed. Moreover, between 1300 and 1600 °C, mullite  
16 transforms from 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> (3:2 mullite) to 2Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub> (2:1 mullite). This transformation is possibly related  
17 to the liquid phase, as it does not occur in the impurity-free calculation. It should be noted that zirconia is  
18 thermodynamically preferred over zircon (ZrSiO<sub>4</sub>) at 1008 °C. However, from a kinetic point of view, this  
19 temperature is too low for the diffusion processes, so zircon does not actually decompose at this low  
20 temperature. This also implies that ZrO<sub>2</sub> does not transform back into ZrSiO<sub>4</sub> during cooling.



1  
 2 Fig. 10. Equilibrium phases of a 30% ZrSiO<sub>4</sub>–36% Al<sub>2</sub>O<sub>3</sub>–34% Al<sub>2</sub>SiO<sub>5</sub> (wt%) mixture (a) excluding and (b)  
 3 including impurities (0.17 wt% Na<sub>2</sub>O, 0.12 wt% TiO<sub>2</sub>, 0.04 wt% P<sub>2</sub>O<sub>5</sub>, 0.19 wt% Fe<sub>2</sub>O<sub>3</sub>, 0.09 wt% MgO, and  
 4 0.02 wt% CaO). (c) Expanded view of oxides in liquid state for the impurity-containing matrix. m- and t-ZrO<sub>2</sub>  
 5 are monoclinic and tetragonal zirconia, respectively.

6 These thermodynamic calculations demonstrate that even a low impurity content in the raw materials  
 7 generates non-negligible amounts of liquid phase, which reduce the zircon decomposition temperature. In our  
 8 experiments, the zircon decomposition had begun by 1470 °C and was completed by 1570 °C, despite the  
 9 relatively coarse-grained raw materials.

10 The effects of secondary oxide additions (Na<sub>2</sub>O, TiO<sub>2</sub>, and P<sub>2</sub>O<sub>5</sub>) are exhibited in the equilibrium phase  
 11 diagrams in Fig. 11. The Na<sub>2</sub>O addition had a strong but negative impact. According to the thermodynamic  
 12 calculations depicted in Fig. 11(a), an addition of 0.3 wt% Na<sub>2</sub>O would triple the liquid portion at 1200 °C (from  
 13 1.3 to 3.8 wt%) and more than double it at 1550 °C (from 3.0 to 6.6 wt%). Consequently, Na<sub>2</sub>O shifted the first  
 14 two mullitisation steps to lower temperatures. This might explain the smaller zirconia grain sizes obtained when  
 15 Na<sub>2</sub>O was added: the low temperature liquid could have promoted primary mullite growth (Reaction (3)), and  
 16 the zirconia grains from zircon decomposition could have been trapped within the primary mullite network,  
 17 hindering the zirconia grains from growing together. Unfortunately, while the small grain size is desirable, the  
 18 final matrix exhibited very high amounts of a glassy phase. Thus, Na<sub>2</sub>O is highly undesirable for refractory  
 19 purposes.



1  
 2 Fig. 11. Impacts of 1 mol% oxide additions on the thermodynamic equilibrium of a 30% ZrSiO<sub>4</sub>–36% Al<sub>2</sub>O<sub>3</sub>–  
 3 34% Al<sub>2</sub>SiO<sub>5</sub> (wt%) mixture (including impurities): (a) +0.34 wt% Na<sub>2</sub>O, (b) +0.88 wt% TiO<sub>2</sub>, and (c) +1.55  
 4 wt% P<sub>2</sub>O<sub>5</sub>. m- and t-ZrO<sub>2</sub> are monoclinic and tetragonal zirconia, respectively. ss: solid solution.

5 The TiO<sub>2</sub> addition showed a completely different behaviour. It effectively promoted zircon dissociation  
 6 while generating minor amounts of amorphous phase (Fig. 11 (b)). The addition of 1 mol% (0.88 wt%) TiO<sub>2</sub>  
 7 generates 1.3 and 3.9 wt% liquid at 1200 and 1550 °C, respectively, which is slightly greater than that in the  
 8 additive-free matrix. Moreover, the results indicate that TiO<sub>2</sub> forms a solid solution with ZrO<sub>2</sub>, which stabilises  
 9 the tetragonal zirconia (t-ZrO<sub>2</sub>) modification below 1170 °C. These results are in accordance with those of Melo  
 10 et al. [20], who emphasised that TiO<sub>2</sub> forms a transitory liquid phase at about 1400 °C and then diffuses into the  
 11 ZrO<sub>2</sub> and mullite crystals, which can both accommodate 4 wt% TiO<sub>2</sub>. Nevertheless, the stabilising effect of TiO<sub>2</sub>  
 12 on the t-ZrO<sub>2</sub> phase suggested in the literature and our thermodynamic calculations was not observed  
 13 experimentally in our TiO<sub>2</sub>-doped samples. It could be that TiO<sub>2</sub> merely did not have enough time to diffuse  
 14 from the transitory liquid phase into the zirconia grains. Furthermore, the rather high zirconia grain size (5 μm)  
 15 and the high porosity both work against the tetragonal zirconia stabilisation. Nonetheless, zirconia stabilisation  
 16 is a rather unimportant detail for refractory materials, because their operating temperatures are usually above the  
 17 m↔t transformation temperature. Overall, TiO<sub>2</sub> is a suitable sintering aid for mullite–zirconia-bonded refractory  
 18 materials.

#### 1 *4.2 Role of phosphate*

2 In mullite-bonded bricks, plasticity and green strength are provided by clay. However, owing to the high  
3 silica content of clay, it can only be used in reaction-sintered mullite–zirconia at the expense of reducing the  
4 zircon content or by accepting a portion of free silica in the sintered matrix.  $P_2O_5$  precursors represent a more  
5 suitable alternative to clay. Just a few percent of a viscous monoaluminum phosphate solution assures sufficient  
6 green strength by delivering the required plasticity and forming chemical bonds at ambient temperature [11]. At  
7 high temperatures,  $AlPO_4$  is formed [12], which can reinforce the mullite–zirconia bonding.

8 In the investigated materials,  $P_2O_5$  considerably reduced the porosity and increased the mechanical strength  
9 owing to the improved pressing behaviour and additional (amorphous)  $AlPO_4$  bonding. The impact of phosphate  
10 on the high temperature equilibrium was marginal (Fig. 11 (c)). The liquid phase accounts for 3.9 wt% of the  
11 matrix at 1550 °C, which is the same as that for the  $TiO_2$ -containing matrix, and only 0.9 wt% more than that in  
12 the additive-free mixture. However, thermodynamic modelling suggested that  $P_2O_5$  has a slight retarding effect  
13 on the liquid phase formation. In the  $P_2O_5$ -doped mixture, the calculations predict the formation of a liquid  
14 phase at approximately 1300 °C, i.e. 200 °C higher than that for the additive-free matrix. Consequently, the  
15 primary mullitisation step and the zircon decomposition were delayed. To enable full zircon dissociation at  
16 1550 °C, the phosphate needed to be added in conjunction with  $TiO_2$ . The matrix with 2 mol%  $P_2O_5$  and 3 mol%  
17  $TiO_2$  yielded the most promising results. A patent covering this bonding phase has been applied for.

#### 18 *4.3 Problem of and solution for matrix shrinkage*

19 While shrinkage does not pose a substantial problem in classic ceramics, shrinkage is undesirable in  
20 refractory matrices. This is because the coarse and dense aggregates show practically no shrinkage during  
21 sintering. In fact, they form a rigid structure of closely packed aggregates which prevent the brick from  
22 shrinking. Hence, a shrinking matrix does not pull the aggregates closer together, but instead causes decohesion  
23 between the aggregates and matrix, as illustrated by the micrographs in Fig. 5. The high shrinkage associated  
24 with reaction-sintered ceramics therefore poses a serious problem for refractory bricks.

25 We have demonstrated that kyanite is a well-adapted solution to this problem. Kyanite has the same  
26 chemical composition as andalusite ( $Al_2SiO_5$ ) but a higher density. Upon heat treatment, both kyanite and  
27 andalusite are analogously dissociated into mullite and a silica-rich amorphous phase [21]. The volume change  
28 of this mullitisation process can be calculated from the molar volumes, specified in [22]. Assuming complete  
29 mullitisation according to Reactions (2) and (3), the resulting theoretical expansion is 18.3 vol% for kyanite, yet  
30 only 4.6 vol% for andalusite. By substituting a portion of the andalusite for kyanite, the net volume change of  
31 the matrix can be reduced to zero at a given sintering temperature. Evidently, kyanite's enormous volume  
32 change can cause cracking, cavities, and increased porosity if excessive kyanite is added; therefore, it should be  
33 dosed cautiously.

#### 34 *4.4 Implications for the sintering curve*

35 By tailoring the matrix shrinkage to a specific sintering temperature, it is paramount to strictly comply with  
36 this exact temperature during fabrication. Otherwise, decohesion between the matrix and aggregates is likely to  
37 occur, weakening the material.

38 Slow heating and cooling rates are also suggested for the following reasons. Our SEM observations revealed  
39 that adjacent zircon particles dissociate simultaneously, and that the newly formed zirconia particles  
40 subsequently grow together. It can be deduced that the silica released upon zircon dissociation activates the

1 dissociation of the surrounding zircon particles and enables the coalescence of particles. This supports the  
2 theory of Di Rupo and Anseau [18]; the released silica first forms a viscous pre-mullite phase that gradually  
3 dissolves the neighbouring alumina before eventually crystallising. This viscous pre-mullite phase may enable  
4 the embedded zircon and zirconia particles to merge together, increasing the  $ZrO_2$  grain size. On the contrary, if  
5 the primary mullite crystals are well developed before zircon starts to dissociate, they could help to inhibit  
6 coalescence. Therefore, slow heating rates or a dwell at 1400 °C should be conducted to obtain smaller  $ZrO_2$   
7 grains.

8 At high temperatures, 2:1 mullite is thermodynamically preferred over 3:2 mullite, especially when the  
9 liquid portion is high. It is likely that the 3:2 → 2:1 mullite transformation accelerates liquid formation even  
10 further because it releases free silica. In other words, the liquid itself promotes the formation of more liquid.  
11 Schmücker et al. [23] investigated the mullite transformation experimentally, and found that the liquid phase is  
12 essential to enable the diffusion of Si and O out of the mullite crystal and Al from the surrounding alumina  
13 particles into the 2:1-mullite crystal. Conversely, this suggests that a slow cooling rate or even a dwell at  
14 1300 °C is preferred to give the diffusion-controlled back reaction from 2:1 → 3:2 mullite time to occur, which  
15 would reduce the amount of glassy phase in the final composite.

#### 16 *4.5 Aggregate choice*

17 To successfully transfer the good matrix properties to the brick, the choice of aggregate is important.  
18 Mulcoa 60 (high alumina chamotte) had a loose interface with the matrix and therefore bestowed relatively poor  
19 strength. The loose bonding probably had two origins. First, there is a thermal expansion mismatch between the  
20 matrix and chamotte, which provoked cracking. Second, the  $TiO_2$  impurities in Mulcoa 60 caused higher matrix  
21 shrinkage. In contrast, FZM aggregates suited well; the chemical similarity of the matrix and aggregate  
22 materials led to strong cohesion at the matrix/aggregate interface.

## 23 **5 Conclusions**

### 24 (1) Effects of additives and secondary phases

25 Phosphate precursors provide the necessary green strength and plasticity to the raw material mix. Moreover,  
26 although  $P_2O_5$  slightly retards the zircon decomposition temperature, it effectively reduces the porosity and  
27 increases the final strength.  $TiO_2$  is well-adapted to stimulate zircon decomposition in refractory materials,  
28 as it does not create much liquid at high temperatures.  $Na_2O$  has a highly undesirable effect on the sintering  
29 reaction because it produces excessive amounts of liquid phase at relatively low temperatures – this is even  
30 true for contents as low as 0.3 wt%  $Na_2O$ . Therefore, the raw materials must be selected carefully with  
31 respect to alkali oxides.

### 33 (2) Preparation of bricks

34 Matrix shrinkage should be avoided because it leads to decohesion at the matrix/aggregate interface.  
35 Partially replacing andalusite with kyanite helps to reduce the net matrix shrinkage to zero. FZM aggregates  
36 are well-suited for use with a mullite–zirconia matrix, whereas high alumina chamotte and coarse andalusite  
37 aggregates lead to cracking at the matrix/aggregate interface.

38 The understanding of the high temperature phase transformations suggests to apply low heating and cooling  
39 rates, for the following reasons. Slow heating rates, or a dwell at 1400 °C, should help to develop primary  
40 mullite crystals before zircon decomposition. A well-developed primary mullite network may inhibit

1 zirconia coalescence and eventually reduce the zirconia grain size. Slow cooling rates or, if possible, a  
2 dwell at 1300 °C are recommended to encourage the 3:2 → 2:1 mullite transformation and reduce the  
3 amorphous phase fraction.

### 4 5 (3) Applications

6 A novel mullite–zirconia-bonded refractory material has been produced and field-tested in a rotary kiln  
7 incinerator, where the material was exposed to thermal shock and mechanical load. The material persisted  
8 much longer than mullite- and alumina–chromia-bonded refractories. We believe similar success could be  
9 achieved in other refractory areas, especially if alternative and more cost-effective aggregates could be  
10 found that are compatible with this matrix.

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13 was financed by BONY SA and the French National Association for Research and Technology (ANRT).  
14 Industrial tests were conducted in two hazardous waste incineration plants operated by SARPI-VEOLIA.

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