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Energy Efficient Refractories for the Foundation Industries

Jafar Daji*, Joshua Parkin*, James Eales**, Ebele Ahizi**, Jack Cornwall** and Paul A. Bingham** discuss the primary findings of an industry-based research project to develop novel additive technologies to enable lower temperature and faster firing of refractories.

The need to reduce greenhouse gas emissions is critical in the Foundation Industries (FI). PSR falls within two FIs – ceramics (manufacturer) and glass (supply chain), where its operations are energy intensive.

The UK refractory industry is a cornerstone of our ceramics industry and supplies other FIs, and exports, that are vital to the UK economy.

Glass is one of the most important basic materials in the world and PSR and other refractory suppliers are considered key enabling technology manufacturers. For example, PSR remained open and maintained manufacturing operations throughout the Covid-19 pandemic, being

an essential supplier to manufacturers of glass packaging. Now the industry is faced with the need to meet the challenges caused by climate change and the need for long-term sustainability.

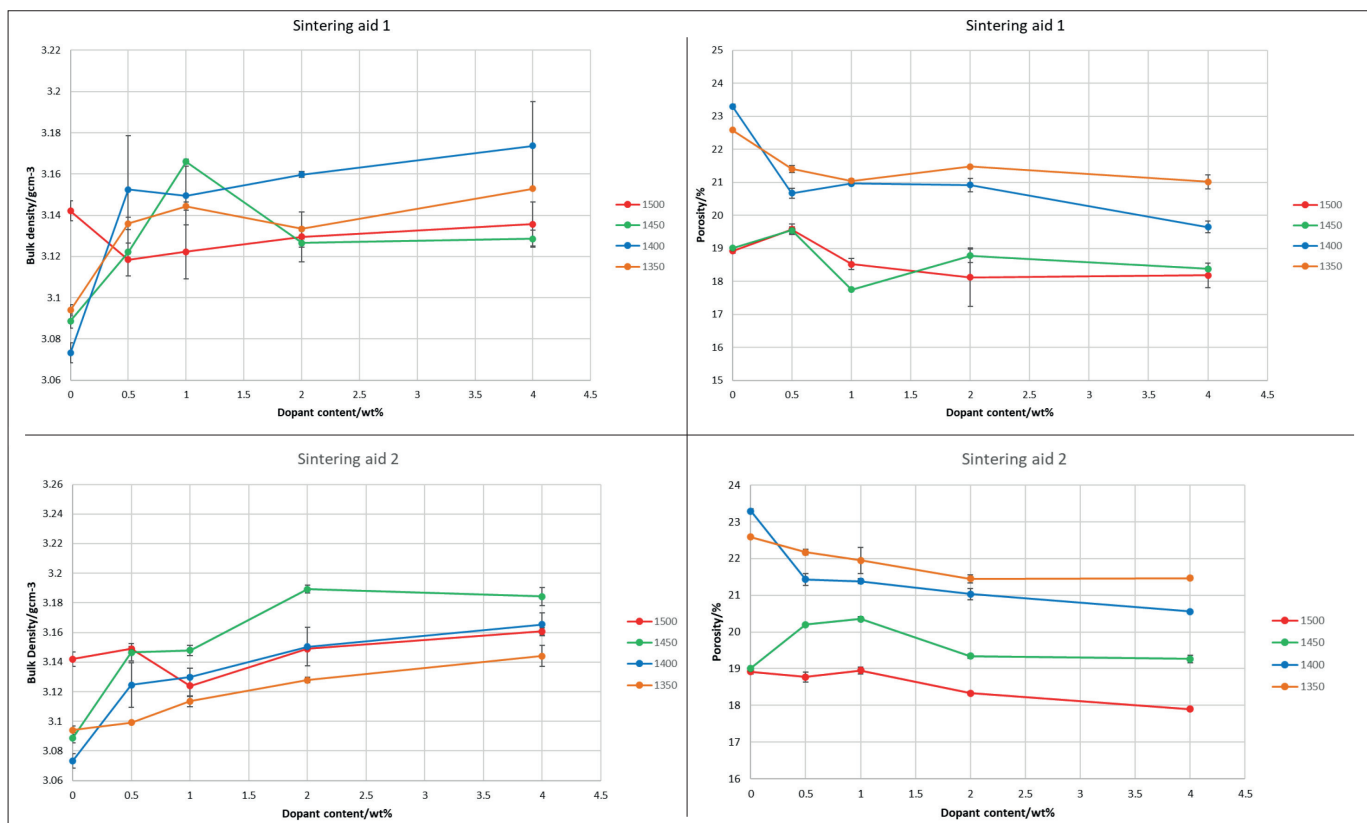
It is thus, vitally important to reduce fossil fuel energy consumption in the refractory manufacturing process to achieve the target of net zero carbon emissions by 2050, thereby supporting the global FI sector in a sustainable manner.

The UK ceramics industry (including refractories), accounts for approximately £2 billion in annual sales including £0.5 billion in exports, with 75% of companies being SMEs. The UK sector is energy-

intensive and consumes around 4.7TWh of delivered energy/year, and total emissions of 1.2 million tonnes CO₂.

The need to decarbonise has been highlighted in several ceramic industry decarbonisation roadmaps [UK Govt - Parsons Brinckerhoff (2015) / UK Ceramics industry - BCC (2017) / Ceram-Unie - EU (2014)], with the need for developing new ceramic mixtures or adding other components to the raw materials to improve firing efficiencies being identified. This project directly addresses these recommendations and working with our partners – Sheffield

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▲ Fig 1. Bulk density and apparent porosity dependence on sintering temperature for single phase dopants, as a function of dopant concentration.

Hallam University, Ceramics UK and Innovate UK – to produce a commercially viable solution to this need.

For refractories manufacturing, the sintering stage involves firing materials in high-temperature kilns run over several days at temperatures exceeding 1500°C in most cases, depending on the product. That means a lot of time and energy going into the making of refractories that are essential to the FI.

This stage in the process is consequently costly to the manufacturer but more importantly it is energy and emission-intensive with resultant large amounts of CO₂ being produced.

With PSR's business strategy now including decarbonisation, there is a drive to find opportunities to reduce energy use, where one idea was to look for a way to lower sintering temperatures and run times.

However, PSR needed to do this without compromising the appropriate level of sintering and densification of the refractory material to be suitable for its application.

The focus of the study was the use of dopant additives in alumina-zirconia-silica (AZS) refractory mixtures to enable firing at reduced sintering temperatures and times (without any detriment to the materials).

The project used two approaches for

using dopants – firstly, to use low melting phase dopants to enhance sintering and mass flow and secondly, to use grain boundary pinning dopants to control grain boundary growth.

These effects have been explored before in an academic context where, researchers showed that sintering temperatures could be lowered by using metal oxide dopants in solid solutions which can: enhance diffusion kinetics by increasing defect populations; produce a liquid phase which can facilitate particle rearrangement; reprecipitation and increase zirconia dissociation. These processes have been shown to promote sintering at lower temperatures and reduce energy input.

The project consisted of integration of several dopants into AZS refractories as a function of and sintering temperatures (1350-1500°C). Effects on mixing were evaluated first to attain the viability of dopant integration with our AZS-based formulations.

Dopants that passed this stage were then fired at the various sintering temperatures outlined above and tested for bulk density and apparent porosity. Materials successful in the sintering regard were then brought forward to more application-specific testing.

Due to the proprietary nature of the work, it is not possible to divulge in this

piece the nature of the dopants used in the study, also, due to the large amount associated data, only the salient features of the results will be presented below.

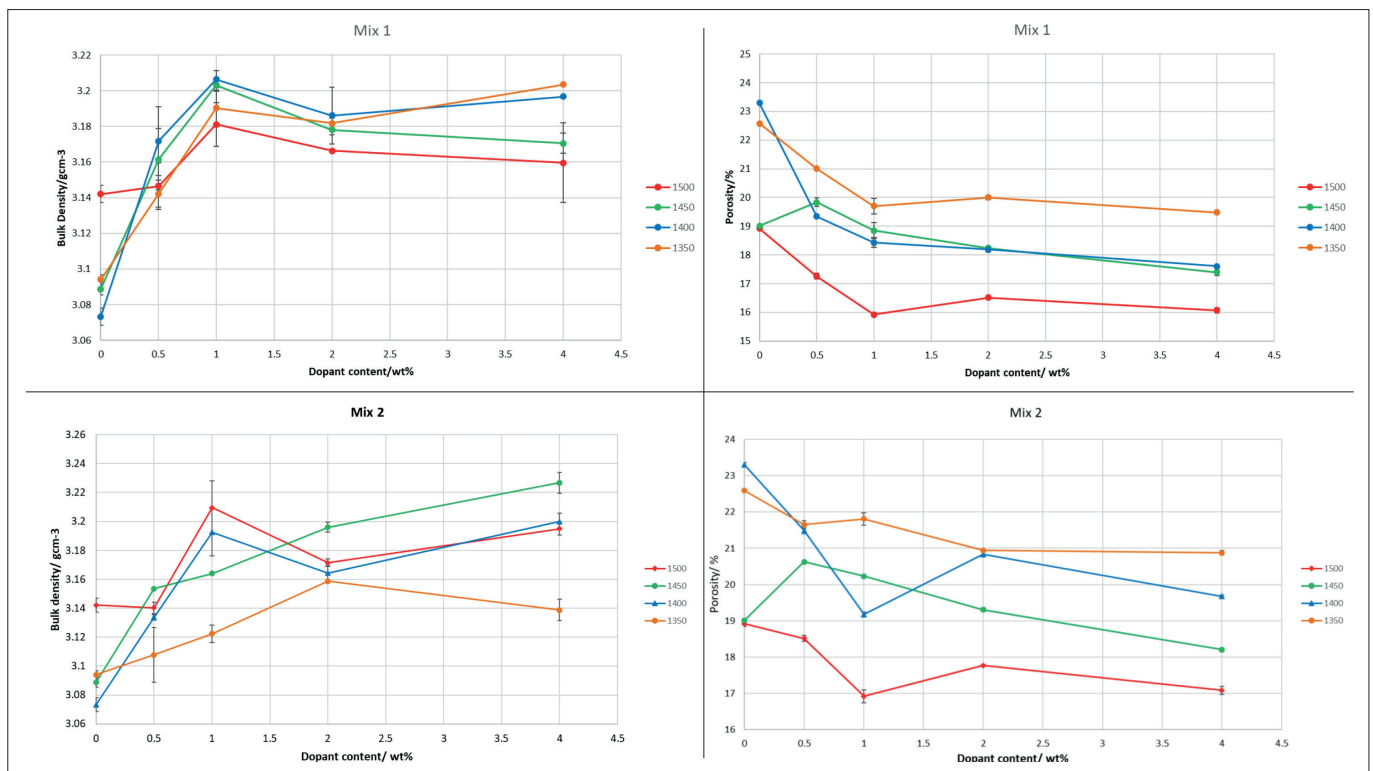
Industrial mix feasibility

The first major consideration for industrial mixes that is overlooked in academic journals is the effect of dopant integration on particle dispersion and flow characteristics of the resultant mixes.

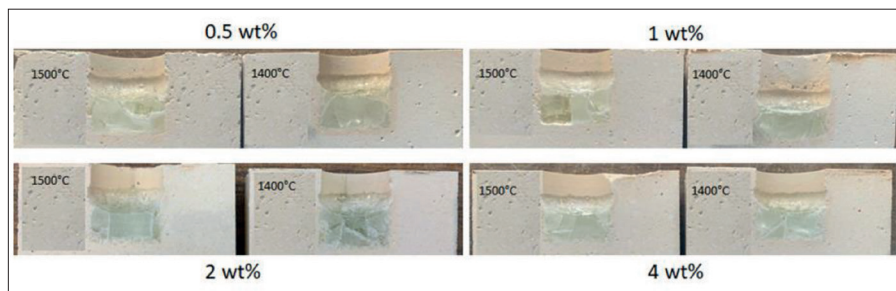
Industrial mixes typically consist of particles of varying size distributions and therefore optimal packing ability of these particles is paramount for both flow characteristics and properties after firing. Given the emphasis on a slip-casting production method at PSR, these factors were crucial to maintain.

Some dopants were found to be suitable for producing mixes with consistent rheological properties. These led to mixes with high stability that were easy to cast. There were other dopants however that resulted in mixes with poor dispersion and flow characteristics. The reasons for this unsuitability may be attributed to pH, dopant particle radii size, surface chemistry, which can affect particulate dispersion and rheology.

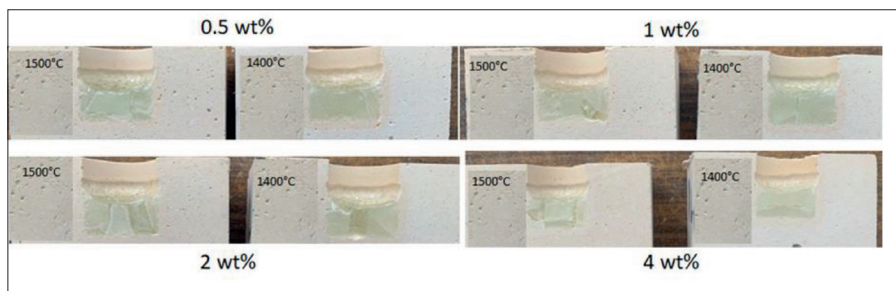
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▲ Fig 2. Bulk density and apparent porosity dependence on sintering temperature for co-dopants mixtures, as a function of dopant concentration.



▲ Fig 3. GC test results for co-doped samples (Mix 1) sintered at 1500°C and 1400°C.



▲ Fig 4. GC test results for co-doped samples (Mix 2) sintered at 1500°C and 1400°C.

Single Dopant Mixes

The next stage of dopant candidate selection consisted of porosity and density testing.

This would indicate the effect the dopants have on the sintering process and the structure of the fired product.

Generally, dopant content had a positive effect on density at lower sintering temperatures. Notably, a particular dopant, 'Dopant 1', at a 1400°C sintering run gave: (1) the greatest increase in density and (2) the most substantial density values overall.

This gave a 2.5% approximate improvement in bulk density, giving a comparable value to the standard AZS material that is currently fired to 1500°C.

Another dopant, 'Dopant 2', also exhibited improvements in bulk density values (**Fig 1**). Although, these typically occurred at higher sintering temperatures and dopant concentrations than that of Dopant 1.

However, apparent porosity values did not see as dramatic an improvement as bulk density. Both 1500°C and 1450°C sintering runs gave consistent porosity values across all the dopant contents comparable to the standard AZS material.

Dopant 2 had little effect on porosity values with decreasing sintering temperatures (**Fig 1**). Overall, reducing sintering temperatures leads to an increase in porosity. Increasing dopant content resulted in largely consistent porosity values associated with that decrease in sintering temperature. The

lack of effect on porosity for both dopants could be due to the increased mass flow kinetics, this leads to areas of high and low densification.

X-ray diffraction (XRD) data confirmed sintering effects occurring at lower temperatures. Firstly, zirconia dissociation was promoted at lower sintering temperatures by all dopant integrated materials mentioned. Greater dopant concentrations resulted in higher proportions of zirconia present in the final sintered product.

Mullite formation was seen to occur at 1400°C (>1wt%). Exceeding this concentration led to further increases in mullite formation at lower temperatures, which exceed even that of the standard material.

Co-Dopant Mixes

Following the initial results of the primary select dopants, the subsequent work focussed on combining them with grain boundary pinning dopants to see if further density and porosity gains could be made.

The first of these was a D1-based co-dopant mixture (Mix 1). The results showed a rather surprising result with a greater improvement in bulk density for most dopant concentrations at all sintering temperatures (**Fig 2**).

This is highlighted by the fact that all samples with dopant contents $\geq 1\text{wt}\%$ exhibit greater bulk density values than the standard AZS mix, this was the case for all sintering temperatures. Samples with

2 and 4 wt% dopants were consistently achieving bulk densities above 3.20gcm^{-3} , the greatest achieved so far with any of these dopant mixtures.

Also, a major improvement over the previous dopant mixtures tested is seen in the porosity values. Where values below that of the that of the standard AZS material are observed.

Mix 2 (a D2-based co-dopant system), yet again exhibited an improvement in bulk density over the single-doped counterpart (**Fig 2**). Similar to the D2 material, the 1450°C sintering run produced the most improved bulk densities and apparent porosity values compared to the standard material.

A peak of 3.22gcm^{-3} was recorded at 4wt% dopant concentration in this particular case. Porosity values were consistent with that of the standard AZS material, rather than a distinct improvement.

XRD data yet again showed promotion of zirconia dissociation and mullite formation for the doped materials.

However, these effects were not greatly improved from the single doped materials, implying the improved porosity and density values were due to grain boundary pinning effects rather than improved sintering.

Due to these results, Mix 1 and Mix 2 co-doped mixes were progressed to further mechanical and application-specific testing.

Glass Corrosion Resistance

Glass Corrosion (GC) is a dominant factor affecting the lifespan of a glass-contact refractory part. Resistance to this process is dependent on both the phases present in the material and its microstructure.

Zirconia offers a degree of chemical resistance to molten glass, so increased zirconia dissociation is a benefit dopant could provide. The occurrence of dopant-zirconia intermediate and glassy phases could also provide their own resistances to glass corrosion (Toperesu, et al. 2021).

Comparing the GC results of the two co-dopant systems, Mix 1 and Mix 2, overall, they displayed excellent GC performance when compared to the standard AZS material at 1500°C sintering temperatures (**Figs 3** and **4**).

A more defined glass-refractory boundary was observed for lower sintering at the standard temperature for both doped materials. Dopant 2 exhibits

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greater improvements in this regard due to the intermediate phases produced, potentially producing a higher quality refractory product overall.

Overall, the 1400°C sintered samples exhibit improved performance over the standard material fired at 1500°C. Another major benefit is the lack of glass colouration seen in these samples.

The formation of eutectics and intermediate phases leads to improved density and porosity values, these also have lower solubility in molten glass, and therefore, greater corrosion resistance and extended lifespans.

Thermal Shock Resistance

Thermal shock resistance concerns the integrity of the refractory part after rapid changes in temperature. This consists of allowing the sample to reach elevated operating temperatures (1200°C), cooling the sample rapidly and repeating for 5-10 cycles. Observations of structural integrity are then made.

Mix 1 and Mix 2 both exhibited hairline cracks on all samples after five cycles. Hairline surface cracking is typical after this degree of exposure to heat and cooling. The behaviour observed in these doped samples doesn't diverge from our typical AZS refractories.

Feasibility Study/Commercial considerations

To garner more information on the economic effects of these chemical dopants analysis of kiln firing energy

use data was conducted to estimate the potential annual savings if firing to a sintering temperature of 1400°C (down from the current 1500°C).

Some preliminary data analysis shows an approximately 15% predicted saving on PSR's shuttle batch kilns, and a predicted saving of approximately 10% on PSR's moving hood kilns. Consequently, this would lead to equivalent reductions in CO₂ emissions of 15% and 10%, respectively. Furthermore, it would improve asset utilisation by kiln firing times being reduced by 11 to 14 hours per firing, respectively.

Conclusion

The sector is highly energy intensive. Production of such materials is costly in this regard, so even modest reductions in temperature/firing times produce sustainability and potential economic advantages.

The benefit of this project offers the opportunity to produce products with a lower carbon footprint for an important foundation industry. Any benefits gained would also benefit the downstream user with a higher-value proposition – materials that have been supplied with a lower carbon footprint/improved properties/longer lifetime.

PSR plans to introduce the use of more energy efficient technologies in future, to support the development of energy/carbon-efficient manufacturing technologies, to create or safeguard jobs and increase competitiveness, to increase

or improve manufacturing and, to move towards a more circular economy. ■

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