DESIGNED POROUS AGGREGATES – A SOLUTION FOR MORE SUSTAINABLE STEEL LADLE REFRACTORIES

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ABSTRACT

Despite grain porosities significantly below 10 Vol.-% for white fused alumina (WFA) and tabular alumina (TA), the overall porosity of ladle refractories formulated with WFA and TA is often in the range of 10 to 30 Vol.-% due to the relatively higher matrix porosity. Consequently, slag penetration and corrosion starts in the matrix and becomes the performance limiting factor together with the relatively low thermal shock resistance of these high purity products. This paper investigates to which extend the dense alumina aggregates can be replaced by a newly designed smart aggregate (MagArmour/MagA) that contains spinel and calcium aluminate phases. It provides an elevated grain porosity of close to 30 Vol.-% and actively participates in in-situ reactions with the matrix. First applications of dry-gunning mixes containing up to 25 % MagA in steel ladle walls have demonstrated the required operational safety and longevity. The obvious advantage in terms of sustainability is an approximately 5% lower material requirement for the given ladle configuration. Surprisingly, despite the higher initial porosity, a longer service life was observed. This can be attributed to the thermal shock resistance that significantly improves with the addition of MagA.

INTRODUCTION

Alumina-spinel and alumina-magnesia ladle refractories have been largely improved over the last four decades since their first appearance in the 1980s. Especially a lot of progress has been seen in the design of the matrix. Multi-modal alumina powders, spinel powders of different compositions and grain size distributions, magnesia powders with improved hydration resistance, and the development of powerful polymer deflocculants have contributed to the significant matrix improvements. A great summary of these and many other achievements can be found in the F.I.R.E. compendium series, Vol. 1: Refractory Castable Engineering [1].
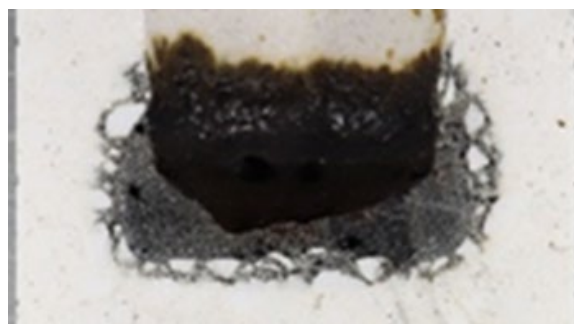

Fig. 1. Alumina spinel crucible after contact with steel ladle slag at 1600°C, 5h

A lot of progress in terms of slag penetration and corrosion resistance has been seen in the matrix, mainly through finding a good balance at ladle service temperature between alumina, spinel and CA6, combined with low porosity and small pore diameters.

Much less focus was given to the aggregates since white fused alumina (WFA) and tabular alumina (TA) provide already a very high refractoriness combined with very low grain porosity which is largely below the porosity of even the most sophisticated matrix designs. Consequently, the matrix still remains the most prone to slag penetration as can be seen in Fig. 1 that shows an example of an alumina spinel

refractory crucible that was in contact with an iron-rich steel ladle slag at 1600°C for 5h. Obviously, the matrix is strongly penetrated and reacted with slag while the coarse TA aggregates remain almost white and unreacted. They "swim" in the slag-penetrated matrix and start to lose their function as a strong backbone of the refractory material due to the surrounding, high liquid phase containing matrix.

In the literature studies can be found that demonstrate on one hand that increasing the open porosity of the alumina aggregates results in an increase of slag penetration and corrosion [2] while increasing micro-porosity and the amount of closed pores in the aggregates can have a beneficial effect on corrosion resistance [3]. Chen et al. [4] found that MA-spinel aggregates with increased porosity did not negatively impact the durability of a castable and resulted in a decrease of the material consumption and thermal conductivity of the ladle lining.
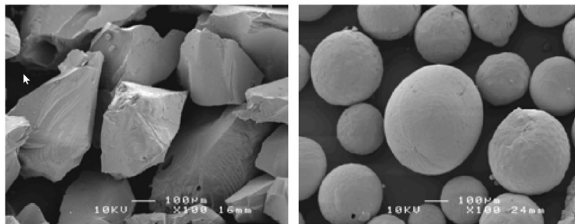

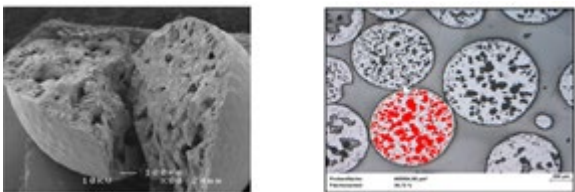Fig. 2. SEM images of standard dense WFA (left) and round and microporous WFA (right) [5]

Fig. 3. Microstructure of round microporous white fused alumina. SEM image of fracture surface (left) and polished section (right) [5]

Ressler et al. [5] reported about a spherical white fused alumina aggregate that contains about 30 Vol.-% closed porosity and almost no apparent porosity. Compared to standard WFA (Fig. 2) this round aggregate allowed to reduce water demand of castables through an optimized particle packing and thus resulted in a higher strength compared to the castable containing the standard angular WFA. Despite the 30 Vol.-% grain porosity in the round aggregate (Fig. 3), the resulting castable density only reduced by 2-3 % compared to the reference mix with standard WFA. It was assumed that the better particle packing compensated to a certain extent the lower grain density. On the other hand it is known that castables with combinations of alumina and 10 to 30 % MA-spinel mainly in the fine part of the recipe have proven to be more penetration and corrosion resistant than pure alumina castables [6,7]. A further improvement in the penetration resistance of castable matrixes was observed when using a Calcium Magnesium Aluminate (CMA) binder [8]. It is a powder resulting from grinding a sintered microporous CMA-clinker (Fig. 4) which consists of small magnesium aluminate (MA) spinel and calcium aluminate crystals.
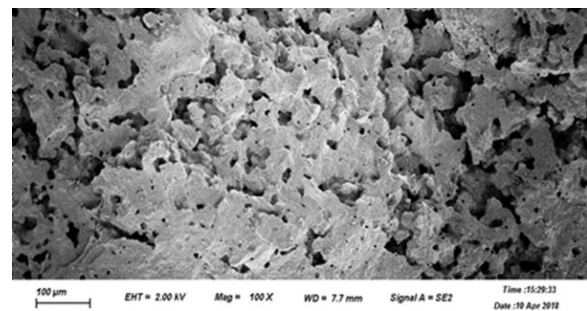

Fig. 4. Calcium Magnesium Aluminate (CMA) clinker

This lead to the idea to elaborate how a MA-spinel and Calcium aluminate phase containing aggregate (MagArmour, Imerys, Paris), that is already largely used as an additive to Magnesia-Carbon bricks [9, 10], would perform in an alumina-spinel refractory as a partly substitution for WFA

and TA. This paper investigates the physical, and thermomechanical properties of an alumina-spinel dry-gunning mix for steel ladle repairs that contains different amounts of MagArmour (MagA). Also the in-situ phase reactions in the gunning mix at service temperature are investigated. It will be highlighted that the MagA aggregates not only at their surface but also with their entire microstructure take part in the in-situ formation of a wear resistant refractory structure, thus becoming smart aggregates.

TEST MATERIALS AND METHODS

Details about the composition of the MagArmour aggregates (Imerys, Paris) can be found in previous papers [10, 11]. In summary, it is an aggregate consisting of 70 % MA-spinel and 30 % calcium aluminate (CA and CA2). Its total porosity is approximately 30 Vol.-% with partly closed and partly open pores. An image of the microstructure of MagA with its microcrystalline spinel phases (dark grey), interstitial calcium aluminate phases, and some clusters with calcium aluminate enrichment (light grey and white), and the micro porosity (black) is shown in Fig. 5.
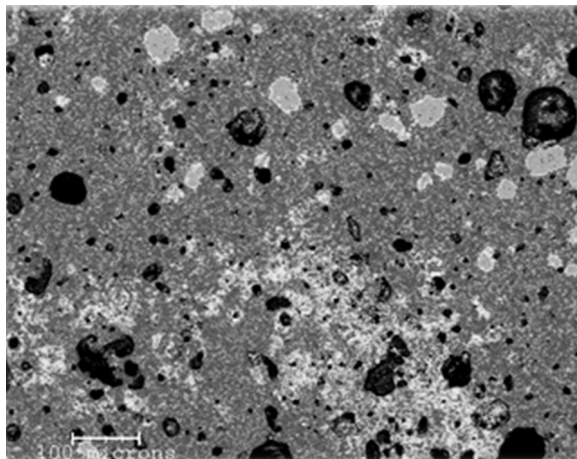

Fig. 5: Porous microstructure of MagA

Starting from a reference gunning mix that contains 69 % tabular alumina (TA), 8% sintered spinel (MA) powder and 10%

calcium aluminate binder (Secar® XR), between 15 and 25% of the tabular alumina aggregates have been substituted by MagA (Tab. I). As a second reference, an alumina-spinel gunning mix ("14% MA") with a 14 % higher spinel content (fraction 0-1 mm) and 2% higher calcium aluminate content versus the reference "0% MagA" has been investigated. This is to be able to differentiate between the impact of spinel alone (similar low porosity as the tabular alumina) and the effect of the porous MagA with its spinel and calcium aluminate phases.

The gunning mix samples have been prepared with a water addition of 11 % that allowed in all cases an easy densification in the moulds under slight tamponing. Only in case of sample "14% MA" an addition of 10 % water was sufficient to create the same consistency as with the other mixes. At 11 % water, this gunning mix started to create some unwanted flow properties.

Tab. I: Model dry-gunning mixes

wt. %		0% MagA	14% MA	15% MagA	20% MagA	25% MagA
Tabular Alumina	0-3 mm	69	53	54	49	44
MagArmour	**0-3 mm**	0	0	**15**	**20**	**25**
Sintered spinel	0-1 mm	8	22	8	8	8
Alumina powder		13	13	13	13	13
Calcium aluminate	Secar XR	10	12	10	10	10
Water addition		11	10	11	11	11
Total MA-spinel		8	22	18.5	22	25.5
Total Al2O3		94.6	90.5	90.1	88.6	87.1
Total CaO		3.5	4.2	5.0	5.5	6.0
Total MgO		1.9	5.3	4.9	5.9	6.9

The physical tests were conducted according to methods as described in EN 1402. Thermal shock resistance was

measured on prism of 160 x 40 x 40 mm that were pre-fired for 3 h at 1600 °C. The samples were then placed in a furnace at 1000 °C for 30 minutes followed by a rapid cooling to room temperature by blowing with compressed air. Ten thermal cycles have been conducted and the Modulus of Rupture (MOR) measured and compared with the value prior to thermal cycling. X-ray diffraction (XRD) was conducted on samples pre-fired at 1600 °C, 3h, using a Bruker D8 Advance analysing Cu K radiation at 30 mA and 40 kV for the angles 2θ from 5°to 80° with intervals of 0.0197°. With Rietveld refining the phase quantities have been determined.

RESULTS and DISCUSSION

It was somewhat surprising that the water demand to achieve similar wet mix consistencies, did not increase with the increasing amount of MagA in the formulation despite the high grain porosity compared to tabular alumina. This is different from a deflocculated low cement castable for which an increase of water demand was reported [11]. After drying at 110 °C the bulk densities of the reference mixes are at 2.72 g/cm3 (0% MagA) and 2.70 g/cm3 (14% MA). Compared to the reference "0% MagA" the introduction of MagA leads to a reduction of the bulk densities between close to 4 % for the mix with 15 % MagA and more than 5 % for the 25 % addition of MagA (Fig. 6).
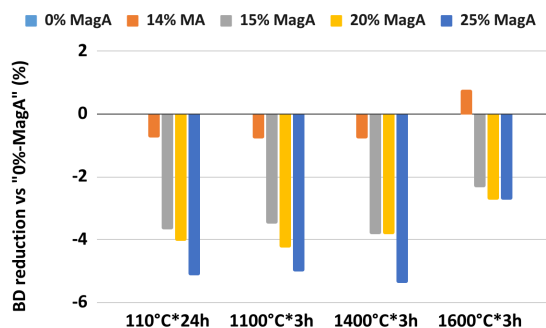
Fig. 6. Bulk density (BD) differences vs the reference "0% MagA"

This would directly translate into a 4-5 % lower material requirement for a given ladle lining configuration thanks to the porosity employed in the MagA grains.
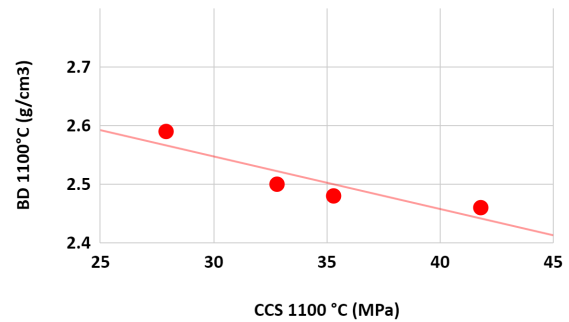
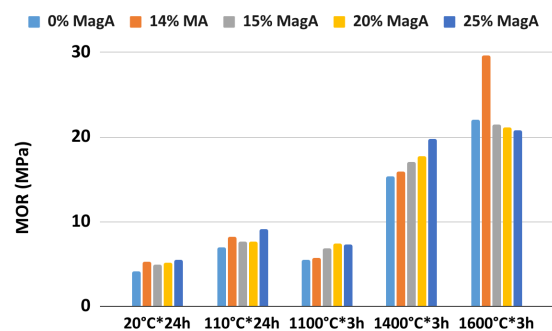Fig. 7. Bulk density (BD) and cold crushing strength (CCS) after firing at 1100 °C

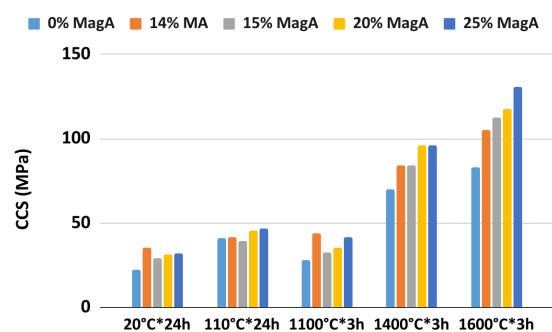Fig. 8. Modulus of rupture (MOR) as function of prefiring temperature

Fig. 9. Cold crushing strength (CCS) as function of prefiring temperature

Interestingly, and contrary to what one would normally expect, the strength does

not decrease with the decreasing density, but rather increases (Fig. 7). This was observed both, after curing and drying, and also after firing at 1100 and 1400 °C. Only after firing at 1600 °C the trend is somewhat different for the cold modulus of rupture (MOR) while the cold crushing strength (CCS) still shows the increasing trend (Fig. 8, 9). The "14% MA" mix achieves similar MOR as the reference "0% MagA" and is only after firing at 1600°C significantly above all other mixes. Despite the lower water requirement of "14% MA" the CCS is quite similar to all other mixes and even lower than the MagA containing materials after firing at 1400 and 1600 °C. This is especially surprising since this mix achieves a lower apparent porosity than all the other mixes, most likely due to the lower water requirement (Fig. 10).
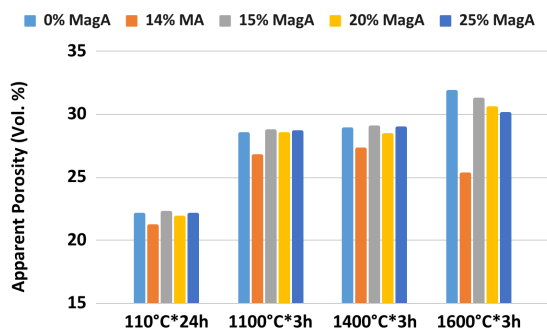

Fig. 10. Apparent porosity as function of prefiring temperature
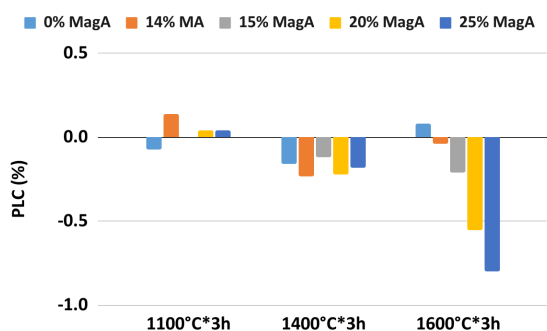

Fig. 11. Permanent linear change (PLC) vs samples dried at 110 °C

When comparing the permanent linear change (PLC), no significant differences are observed after firing up to 1400 °C (Fig. 11). However, after firing at 1600 °C differences become obvious. With increasing amount of MagA in the formulation the PLC significantly increases and reaches a shrinkage of 0.8 % with 25 % MagA.
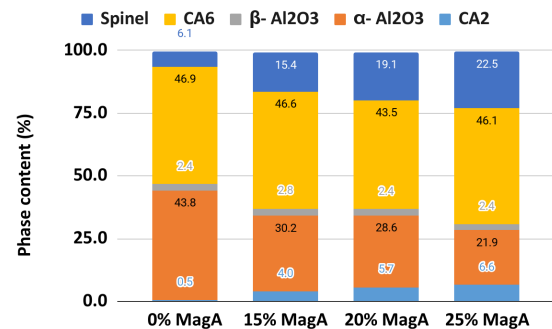

Fig. 12. Phase content of the mixes after firing 3 h at 1600 °C

Without surprise the phase content of the mixes changes with the addition of MagA as shown in Fig. 12 for samples after firing for 3 h at 1600 °C. The increased substitution of alumina by MagA leads to an increased amount of spinel and a decrease in alpha-alumina. However, despite the increase of total CaO content with the introduction of MagA, the amount of CA6 that is formed in-situ remains for all mixes close to the level of the reference (0% MagA) that has the lowest CaO content. Instead, the amount of CA2 increases from close to zero for the reference mix to almost 7 % for the highest MagA-containing mix. This indicates that the amount of reactive alumina in the system might not be sufficient to transform all CA2 (in matrix and aggregates) during the given sintering time of 3 h into the most temperature resistant calcium aluminate phase, CA6. In previous investigations about the addition of MagA to alumina spinel dry-gunning mixes [12] it was observed that around the tabular

alumina grains quite big rims consisting of CA2 were formed that probably slowed down the reaction kinetics to CA6 when most of the alumina in the matrix was already consumed by the in-situ formed CA6 and CA2 and only the alumina from the tabular alumina remained.

Since CA2 upon its in-situ formation in the microstructure has a less expansive character than CA6 it seems it cannot compensate for the shrinkage caused by the sintering reactions. To verify this hypothesis, the impact of a small formulation change has been investigated with the objective to offer more alumina in the matrix to support the continuation of the reaction from CA2 to CA6. For this purpose the formulation "20% MagA/V2" has been used in which 3 % more alumina powder was employed, compensated by 2 % less MA-spinel powder and 1 % less tabular alumina compared to the original "20% MagA" mix. The same change has also been applied for the reference formulation without MagA to allow a more direct comparison ("0% MagA/V2). As can be seen in Fig. 13, this small change in the recipe has achieved the desired improvement of the volume stability. While the original "20% MagA" mix showed a shrinkage of more than 0.5 % the modified version remains almost volume stable.

This observation is coherent with the mineralogy of "20% MagA/V2" that shows after firing for 3 h at 1600°C less alpha-alumina, despite a higher alumina powder addition compared to its original formulation (Fig. 14). The CA2 content is slightly lower than in the original "20% MagA" mix and consequently CA6 has increased which has obviously improved the volume stability and counteracted sintering-related shrinkage. Contrary to that the same formulation change applied to the matrix of the reference mix that doesn't contain MagA, did not change significantly the PLC

and did also not increase the CA6 content. Here it seems that all lime in the original mix was already combined in CA6, thus an increase of alumina powder in the matrix can in this case not lead to more CA6 formation but has rather a diluting effect so that in total even less CA6 is observed. Nevertheless here the amount of CA6 formation is anyway sufficient to create a small positive PLC.
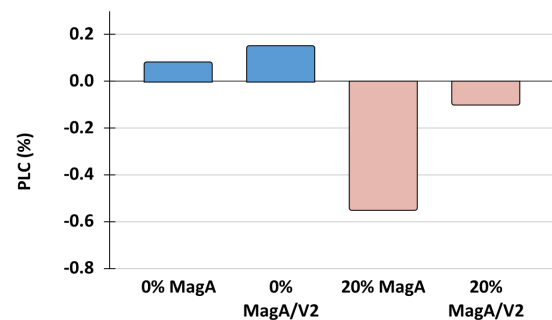

Fig. 13. Permanent linear change (PLC) of mixes with increased matrix alumina content ("0" MagA/V2", "20% MagA/V2") vs the original mixes ("0% MagA", "20% MagA")
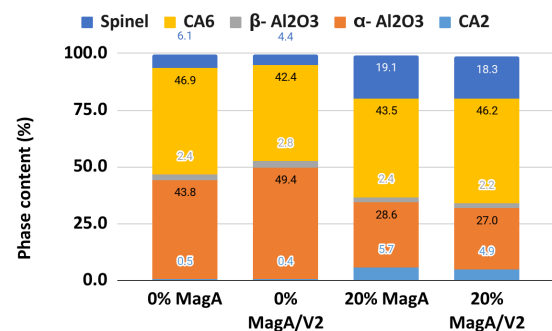

Fig. 14. Phase content after firing at 1600 °C, 3h

The introduction of porous MagA into the mixes has obviously changed their chemistry and accordingly the phase assemblage in the microstructure after firing. The next step was to investigate what impact that change has on thermal shock resistance (TSR) which is especially

interesting since we have now materials with somewhat higher porosity, lower density but contrary to what one would normally expect, still very similar or even higher strength versus the MagA-free reference "0% MagA". And indeed the introduction of MagA has created a very significant difference in thermal shock resistance, tested on samples after pre-firing at 1600 °C that were then treated in thermal cycles between 1000 °C and 20 °C (cold blowing with compressed air). The strength values before and after the cycling and also relative to the initial strength are shown in Fig. 15 and Fig. 16.
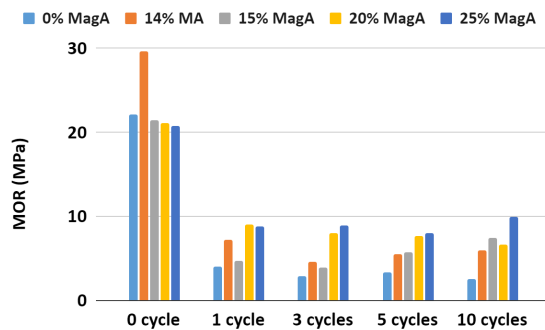

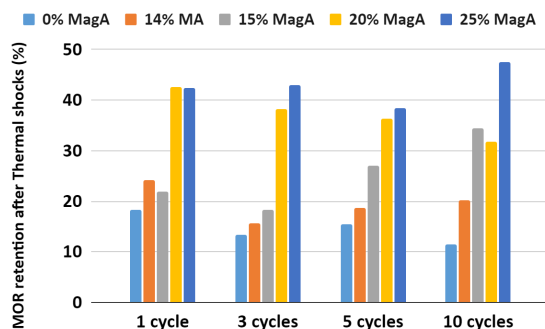Fig. 15. Modulus of rupture (MOR) before and after thermal cycling

Fig. 16. Relative MOR retention vs MOR before the themal cycling

The strength retention after thermal cycling was in the range of 40 % of the initial MOR for the higher dosage of MagA. This is a strength retention twice as high as without MagA. Mix "14% MA" gave

relative to the effect of MagA only a very small improvement of TSR. Interestingly, the mix with 15 % MagA showed improved MOR retention values as longer the thermal cycling test lasted. It seems as if a certain crack-healing effect occurs probably due to a continuation of calcium aluminate phase formation respectively transformation. Further investigations are necessary to validate this hypothesis. These encouraging laboratory results concerning the thermal shock resistance support the macroscopic observation that were previously made in a steel ladle with a MagA containing gunning mix vs a MagA-free formulation [12]. In that study it was observed that the MagA-containing mix not only connected better with the used castable lining substrate, but also performed significantly longer. Fig. 17 shows the respective linings at the end of their service life which was in case of the original gunning mix (alumina-spinel) 18 heats, while the new gunning mix in which some tabular alumina was replaced by MagA achieved 31 heats.
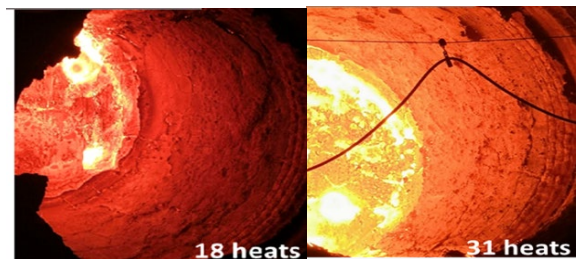

Fig. 17. Steel ladle linings with an alumina spinel dry-gunning mix (left) and with a new alumina MagA spinel gunning mix at the end of their respective service lifes [12]

CONCLUSIONS
The new refractory aggregate MagArmour (MagA) with its distinct multi-phase assemblage and elevated porosity compared to Tabular Alumina (TA) allows the formulation of more sustainable steel ladle refractories. They are lighter compared to the traditional alumina spinel refractories

and require less material per lining. The entire spinel-rich MagA grain takes actively part in in-situ CA6 formation. This has enabled a significant improvement of thermal shock resistance, which is in line with reports in the literature about increased service life when partly substituting tabular alumina with MagA. Concerning the formulation approach it is important to employ a sufficient amount of alumina powder in the matrix to enable a high degree of CA6 formation in the matrix and with/inside the MagA aggregates. This will then lead to the required volume stability and penetration and corrosion resistance.

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