# HIGH PERFORMANCE GUNNING MIX WITH ALUMINA PLASTICISER

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**ABSTRACT**

CT10SG is a special calcined alumina which has high water retaining property and is ideal to add stickiness to gunning mixes. CT10SG as a new plasticiser was studied in high performance gunning mixes as replacement for conventional plasticiser such as soft clay and silica fume. Matrix slurries and laboratory test bars from the gunning mixes were investigated at Wuhan University of Science and Technology. The matrix study showed that the slurry containing CT10SG had an equivalent rheological behaviour when compared to that with traditional plasticisers. Tabular alumina based gunning mix with CT10SG displayed good consistency and stickiness, high volume stability (low permanent linear change), high hot modulus of rupture and good slag resistance.

**Introduction**

Gunning mix or gunite normally refers to dry gunning process. For application the mix is transported by pressurised air to a nozzle, where the mixing water is added, and the wet mix is sprayed on a surface. This process is widely used in the refractory industry for the installation of new original lining or maintenance of worn lining. Compared to wet shotcreting, the gunning process is more applicable to smaller installations or to installation with frequent interruptions. And it has the advantage of quick installation and ease of set-up. The equipment cost and manpower required are less when compared the shotcreting process.[1)] The influence of cement content to the performance of the mix was investigated by Gregory et al.[2)] In the traditional gunning mix, silica containing materials such as silica fume and soft clay are used to achieve the desired rheological behaviour of the mix, thus increasing the stickiness and reducing the rebound during operation. These materials are often referred to as plasticisers. Silica containing plasticisers can significantly downgrade the performance of the refractory material because they form low melting phases when reacting with calcium aluminate cement used as the binder. This reduces the lining life of the gunning mix in the application.

In the present study the special calcined alumina CT10SG was investigated for application in gunning mixes. CT10SG as a plasticiser replaced silica fume and soft clay to provide the desired viscosity and stickiness. CT10SG has a high specific surface area of 13 m²/g and d50 of 3 µm. It has unique water retaining property, which is ideal to add stickiness to the gunning mix.

Unfortunately, an applicable uniform standard for the manufacture of samples and testing of gunning mixes on laboratory scale does not exist. Therefore sample bars were prepared by vibration casting as it is applied for normal castable testing. In addition a matrix slurry test was performed to give an indication on the rheological behaviour of the mix after installation. Gunning mixes shall not slump after wet spraying on vertical surfaces.

**EXPERIMENTAL**

For the gunning mix the rheology behaviour is very critical since it will influence the material behaviour after spraying onto typically vertical surfaces. For such mix a pseudo-plastic fluid is required to reduce the rebound or slumping of the mix from the application area. Therefore slurries with the gunning mix matrix materials were made to evaluate the rheological behaviour. The basis of the slurry was tabular alumina fines (-45 MY) plus calcined alumina CT800SG as fine filler plus calcium aluminate cement CA-270 as the binder. As plasticiser either CT10SG (slurry A), soft clay (slurry B), or silica fume (slurry C) were added. The solid content in the slurry was 65wt.%. All slurries were subjected to an ultrasonic dispersion before testing.

A rotary viscosimeter was used for the rheology test. First the slurry was stirred at a speed of 100r/s for two minutes and then stilled for another two minutes. Afterwards the test was conducted by increasing the shear speed from 0 to 200r/s and measuring shear force and viscosity. Once the shear speed reached to the limit of 200r/s (red curve / see arrow), it was gradually reduced back to zero (dark curve). The rheological curves are shown in Fig. 1.

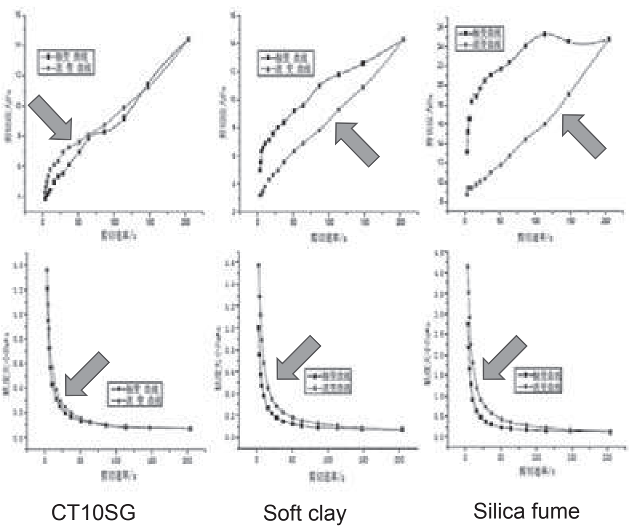



*Fig. 1: Shear force (top, [Pa]) and viscosity (bottom, [Pa.s]) as a function of shear speed (0-200 [r/s]) for tabular/cement matrix slurry with different plasticisers.*

For all slurries the viscosity goes down as the shear speed increases, and the viscosity goes up while slowing down the shear speed. This is beneficial for the gunning process in order to reduce slumping after gunning process. When the gunning mix is sprayed onto the surface, the viscosity increases and the material remains in place.

**GUNNING MIX SAMPLE PREPARATION**

The gunning mixes were made by the standard castable method. The materials were dry blended in a Hobart mixer for one minute and then wet mixed for four minutes after water addition. The mixes were then casted in steel moulds and cured for 24 hours. After de-moulding the sample bars were dried for twelve hours at 110°C. Firing was done at 1100°C for 3h and 1550°C for 3h respectively.

As plasticiser CT10SG (5wt.%) was compared to a combination of silica fume (2wt.%) and soft clay (3wt.%) in three different gunning mixes which used tabular alumina, brown fused alumina (BFA), or bauxite as the aggregate. The test recipes are given in table 1. The bauxite based mixes required a higher water addition (14.3% vs. 11.7%) to achieve the desired consistency when compared to the tabular and BFA mixes.

Tab. 1: Test mixes with different aggregates and plasticisers

| Gunning mix | | Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 | Mix 6 |
|---|---|---|---|---|---|---|---|
| Tabular | 1-3 mm | | | | | | |
| | 0.5-1 mm | 60 | 60 | | | | |
| | 0-0.5 mm | | | | | | |
| | –45 MY | 13 | 13 | | | | |
| BFA | 1-3 mm | | | | | | |
| | 0.5-1 mm | | | 60 | 60 | | |
| | 0-0.5 mm | | | | | | |
| | –45 MY | | | 13 | 13 | | |
| Bauxite | 1-3 mm | | | | | | |
| | 0.5-1 mm | | | | | 60 | 60 |
| | 0-0.5 mm | | | | | | |
| | –45 MY | | | | | 13 | 13 |
| Calcined | CT800SG | 12 | 12 | 12 | 12 | 12 | 12 |
| | CT10SG | 5 | | 5 | | 5 | |
| Silica fume | | | 2 | | 2 | | 2 |
| Clay | | | 3 | | 3 | | 3 |
| Cement | CA-270 | 10 | 10 | 10 | 10 | 10 | 10 |
| CMC* | Culminal | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 |
| Plastic fibres | | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 | 0.06 |
| $H_2O$ | | 11.7 | 11.7 | 11.7 | 14.3 | 11.7 | 14.3 |

*Carboxymethyl Cellulose

**RESULTS AND DISCUSSION**

Fig. 2 shows the permanent linear change of the sample bars after firing at 1550°C for 3 hours. All gunning mixes containing CT10SG (mix 1, 3, and 5) show lower firing shrinkage when compared to silica fume plus clay. The lowest shrinkage is achieved with tabular alumina based mix 1 and CT10SG plasticiser. High firing shrinkage would induce cracks in the gunned lining and would reduce the lining life. The higher firing shrinkage of the silica fume plus clay mixes is caused by the formation of low melting phases due to the silica content which leads to liquid phase sintering when firing at 1550°C. In mix 3 and 5 some silica is contributed to the gunning mix matrix by the -45 micron fines from the BFA and bauxite aggregate. Therefore these mixes show higher shrinkage than mix 1 based on tabular alumina, and would

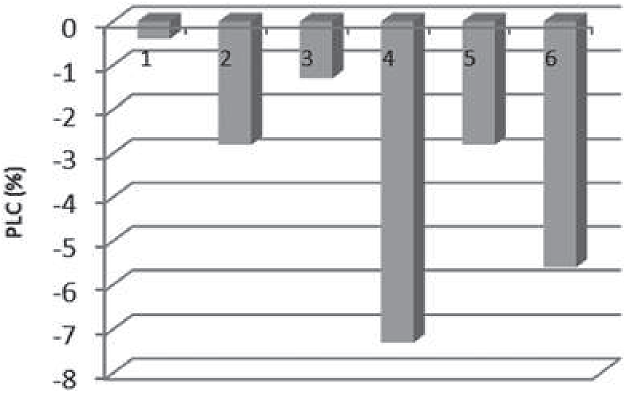



*Fig. 2: Permanent linear change of the gunning mixes after firing at 1550°C / 3h.*

show inferior performance in application when compared to mix 1.

The cold crushing strength (CCS) after firing at 1550°C / 3h is always higher with silica fume plus soft clay when compared to CT10SG (Fig. 3). However, this higher cold strength is caused by the formation of a glassy phase during firing which reduces the hot strength at application temperatures as shown in (Fig. 4).

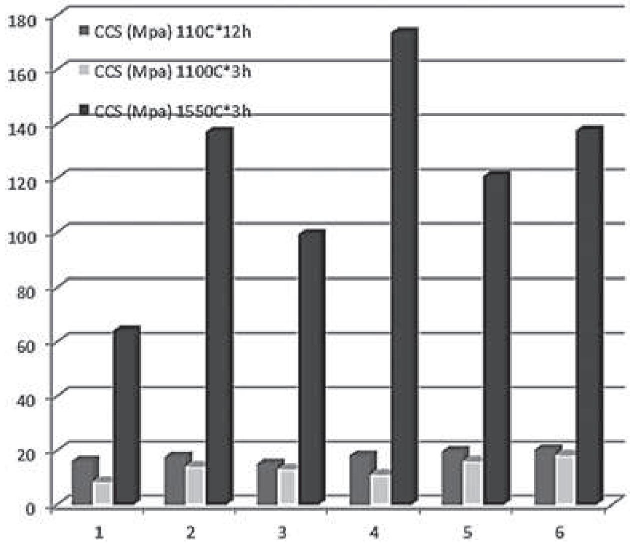



*Fig. 3: Cold crushing strength (CCS) of gunning mixes 1 to 6 at different pre-firing temperature.*

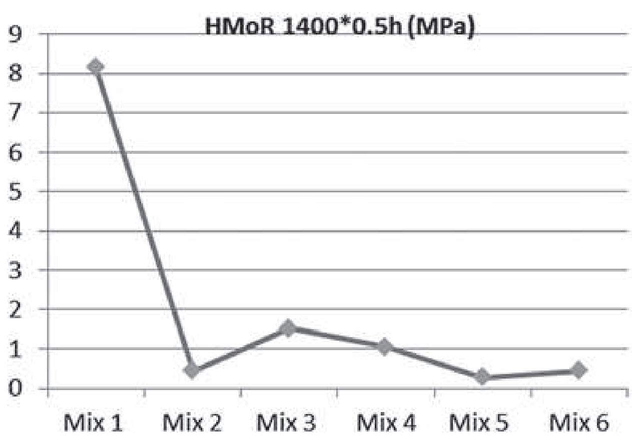



*Fig. 4: Hot modulus of rupture (HMoR) of gunning mixes 1 to 6 at 1400°C.*

The BFA and bauxite based gunning mixes 3 and 5 with CT10SG also show higher CCS after firing at 1550°C when compared to mix 1. Here, the impurities of the BFA and bauxite fines -45 micron ($SiO_2$, etc.) also cause some glassy phase formation which is proved by the low HMoR as well. The CCS of mix 1 of 60 MPa after firing at 1550°C is considered sufficient for the application and higher CCS values do not provide an advantage because they
5 come along with low HMoR values. Gunning mix 1 based on tabular alumina and CT10SG clearly shows the best hot strength (HMoR 8 MPa at 1400°C) because it provides high chemical purity for both aggregate and matrix.

Sample bars of mix 1 and mix 2 were taken for further analysis on XRD as shown in Fig. 5. Besides corundum as the main phase, only high melting calcium aluminates are formed during firing of gunning mix 1: calcium dialuminate ($CA_2$, melting point 1765°C), and calcium hexaluminate ($CA_6$, melting point 1850°C). Conversely, low melting calcium aluminate silicate phases such as gehlenite ($Ca_2Al_2SiO_7$) are formed in mix 2 with silica fume plus soft clay.

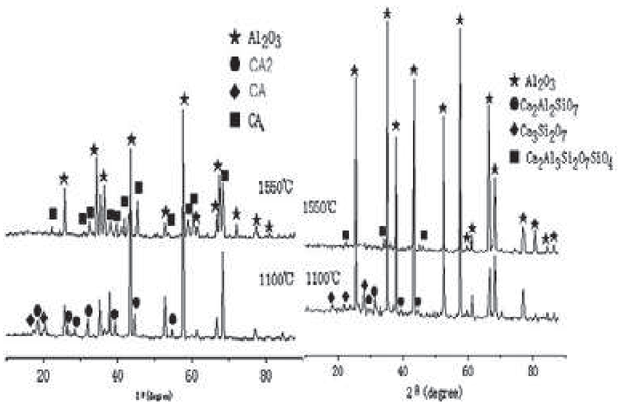
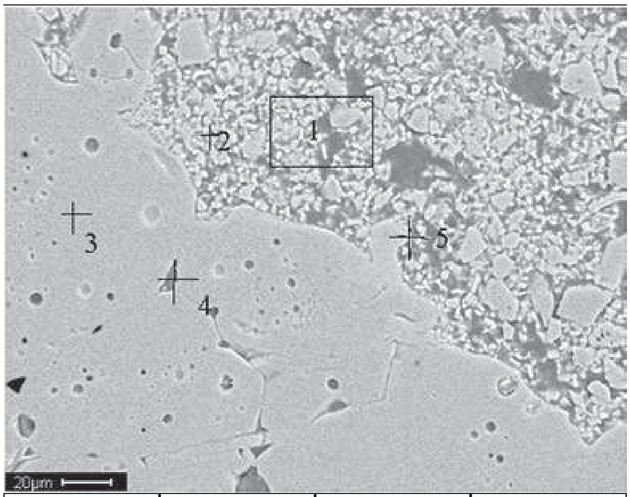



*Fig. 5: XRD of sample bars from mix 1 and mix 2 fired at 1100°C and 1550°C.*

In order to investigate the microstructure of mix 1 and 2, scanning electronic microstructure (SEM) analysis was conducted on the sample bars as shown in Fig. 6 and Fig. 7. The EDS for elements detection is attached to the images. Mix 2 has much larger pores when compared to mix 1. This indicates a pore size growth by liquid phase sintering in mix 2 during firing at 1550°C. A smaller pore size is advantageous with regard to slag infiltration resistance because large pores can be penetrated much easier. Silica containing phases are found by EDS in mix 2. They show at the grain boundaries and pores between the corundum crystals. They are molten phases at application temperatures and act like a lubricant in the material, thus reducing the hot strength as previously discussed (Fig. 4).

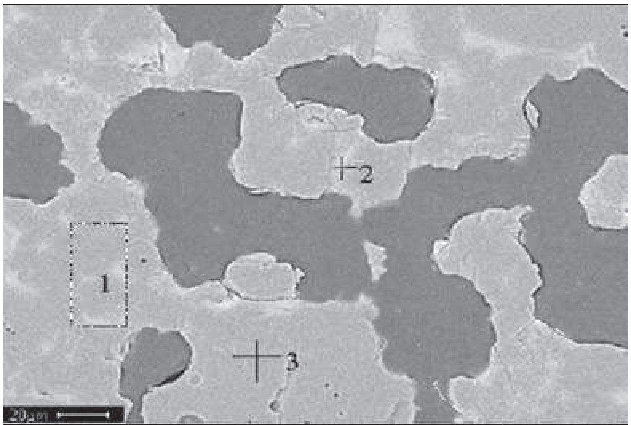
The slag resistance of the gunning mixes was tested in an induction furnace. The furnace wall was lined with gunning mix sample bars. 10kg steel scraps and 200g powder from steel ladle slag from the RH degassing processing route were put into the furnace. The slag composition is given in table 2. After melting of the furnace charge, the temperature (1680°C) was hold for half an hour before the furnace was cooled down and sample bars were taken out of the lining. Afterwards the bars were cut to measure the slag infiltration.

The infiltration depth is lower for all gunning mixes with CT10SG when compared to silica fume plus clay (table 3). The bauxite based mixes 5 and 6 show the worst slag infiltration when compared to the tabular and BFA mixes.




| spot | O | Al | Ca |
|---|---|---|---|
| 1 | 37.57 | 39.71 | 22.72 |
| 2 | 36.96 | 50.78 | 12.27 |
| 3 | 36.66 | 63.34 | |
| 4 | 33.34 | 37.07 | 29.49 |
| 5 | 51.79 | 28.75 | 21.46 |

*Fig. 6: SEM and EDS of mix 1 sample bar pre-fired at 1550°C/3h; dense tabular grain in lower left side and matrix in upper right side; dark areas are pores.*




| spot | O | Al | Ca | Si |
|---|---|---|---|---|
| 1 | 34.92 | 40.45 | 19.07 | 5.56 |
| 2 | 23.51 | 9.02 | 49.16 | 18.29 |
| 3 | 35.60 | 64.40 | | |

*Fig. 7: SEM and EDS of mix 2 sample bar pre-fired at 1550°C/3h; dark areas are pores; brighter silica containing phases around the corundum crystals.*

Tab. 2: Steel ladle slag (RH degassing) for slag test

| | MgO | $Al_2O_3$ | $SiO_2$ | CaO | $Fe_2O_3$ |
|---|---|---|---|---|---|
| wt.% | 5.47 | 30.8 | 5.03 | 51.09 | 5.89 |

Tab. 3: Infiltration depth in slag test

| | Mix 1 | Mix 2 | Mix 3 | Mix 4 | Mix 5 | Mix 6 |
|---|---|---|---|---|---|---|
| Slag Infiltration depth (mm) | 1.6 | 5.8 | 2.2 | 4.1 | 11.2 | 13.6 |

Fig. 8 shows cross sections of test bars from mix 1 and 2 after the slag test. The deeper infiltration in mix 2 is clearly visible. It is interesting to mention that the apparent porosity after firing at 1550°C is higher for mix 1 with CT10SG when compared to mix 2 with silica fume plus clay (32% vs. 22%). Nevertheless, the pore size in mix 1 is significantly lower than in mix 2 as can be seen in the SEMs (Fig. 6 and 7). Therefore mix 1 provides a better slag resistance in spite of higher apparent porosity, because larger pores can be infiltrated much easier. In addition the silica containing low melting phases in the matrix of mix 2 support the penetration of slag. For dry gunning mixes the normal range of apparent porosity after drying is around 30%. Lower porosities after firing at high temperature indicate liquid phase sintering reactions which lead to shrinkage (cracking), pore size growth (slag infiltration), and low hot strength (e.g. HMoR) and which deteriorate the performance of the gunning mix in the application.

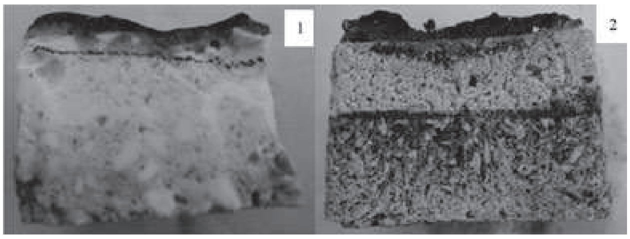



*Fig. 8: Sample bars of mix 1 and mix 2 after induction furnace slag test; infiltration depth clearly higher in mix 2.*

## INDUSTRIAL GUNNING TRIAL

A practical trial was performed using mixes 1 and 2 to see if these results would be comparable to those done in the laboratory. A gunning machine with a pie-type rotor, feeding at a rate of 12 rpm, was used to convey 227 kg of mix through 30.5 m of hose. A double bubble 38 mm nozzle was used along with a 8-hole water ring. 1% of pre-dampening was used for the CT10SG mix where 1.5% was used for the mix containing clay/fume. Results are summarized in table 4.

Water content was determined to be less than what was needed in the laboratory mixes, with mix 2 using about 1% less water than mix 1. Mix 2 did slightly clog in the nozzle on a couple of occasions therefore more water may have been more beneficial. Rebound data was similar for both mixes, at approximately 10%. Strengths followed a similar trend as in the laboratory mixes. The fume containing mixes displayed higher cold strength than the mix containing CT10SG, although the CT10SG containing mix proved to be able to provide more than adequate dried and fired strength. Mix 2 again displayed significantly higher shrinkage after being fired to 1550 °C.

This successful trial along with the accompanying data shows that CT10SG can be used as a replacement for clay/fume-containing mixes where higher hot strength are desired.

## CONCLUSION

The special calcined alumina CT10SG as a new plasticiser provides suitable rheology properties for gunning mixes as demonstrated in the matrix slurry tests. It reduces the firing shrinkage of gunning mixes when compared to traditional plasticisers such as soft clay and silica fume, thus providing a higher volume stability and refractoriness. The slag resistance is improved with CT10SG in the gunning mix matrix. The tabular alumina based gunning mix with CT10SG performs best in terms of permanent linear change, hot modulus of rupture, and slag corrosion resistance. In this mix the high chemical purity of aggregate and matrix composition prevent the formation of low melting silica containing phases which would deteriorate the high temperature properties. An industrial trial of CT10SG confirmed the findings of the initial investigation.



Tab. 4: Industrial gunning trial results

| | | **Mix 1** | **Mix 2** |
|---|---|---|---|
| | | | |
| **Panel Water Content %** | | 9,3 | 8,3 |
| | | | |
| **REBOUND (%)** | | 10,2 | 9,4 |
| | | | |
| **CMoR (MPa)** | **Dried** | 3 | 6 |
| | **Fired 1100°C** | 3 | 6 |
| | **Fired 1550°C** | 16 | 24 |
| | | | |
| **CCS (MPa)** | **Dried** | 26 | 48 |
| | **Fired 1100°C** | 17 | 35 |
| | **Fired 1550°C** | 89 | 134 |
| | | | |
| **Density (g/cm³)** | **Dried** | 2,54 | 2,58 |
| | **Fired 1100°C** | 2,45 | 2,55 |
| | **Fired 1550°C** | 2,49 | 2,93 |
| | | | |
| **PLC (%)** | **Fired 1100°C** | +0.32 | -0.25 |
| | **Fired 1550°C** | -0.20 | -4.70 |
| | | | |
| **Porosity (%)** | **Dried** | 28 | 25 |
| | **Fired 1100°C** | 32 | 30 |
| | **Fired 1550°C** | 33 | 18 |

## ACKNOWLEDGEMENTS

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