Raw Material Innovations – a Key Success Factor in a Fast Changing Refractories World

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The recent global economic difficulties have resulted in overcapacities in many industries and the refractory industry isn't an exception. In an uncertain environment driven by the slowing Chinese economy and the low crude oil price many industries have slowed down their investments. However, difficult times trigger also new ideas that lead in innovation-friendly companies to renewed product portfolios with materials and services that have a better performance/cost ratio, are more user and environmental friendly, more predictable in their performance and offer more value for the customer. This article gives examples of raw material innovations that target improvements at different steps in the value chain of castables, from the raw materials dry-mix, castable installation, dry-out, to the ultimate performance in service. Efforts to make castable rheology and setting more predictable have resulted in new types of binders and deflocculants and active compounds that achieve a higher robustness against variable parameter in the system. Other developments target the replacement of high-pH shotcrete gelling agents by more health and safety friendly systems. Developments also look at a better compromise between permeability, strength, and the water removal temperature of calcium aluminate bonded dense castables to allow an easier and safer water release. New castable microstructures have been achieved with innovative bond systems that improve the service life of alumina-spinel and alumina magnesia castables. The main driving force behind all these innovations is the never ending request of the steel industry to reduce specific refractory costs and to improve safety and equipment reliability.

1 Introduction

With steel production being the biggest consumer of refractory materials, the refractory industry has gone through a few difficult years as steel production in most western countries was slowing. China, the globally biggest steel producer representing close to 50 % of the global steel production, has seen 3 years without growth in steel production, after a more than a decade long strong increase [1]. Low crude oil prices have slowed down the activities in the oil exploring and transforming industry which resulted in lower demand of steel pipes [2]. In contrast to this slowing trend in major steel producing nations, India's steel production has shown a steady growth over the last 10 years (Fig. 1). Nevertheless, the global steel production capacity utilisation has dropped since the middle of 2014 to very low levels (Fig. 2) which has put steel prices under strong pressure and forced the refractory manufacturer once again to work on cost rather than on performance optimisation. However, with the traditionally used refractory raw materials further saving potentials are limited and when moving to lower quality raw materials typically also performance drops so that overall there is no significant benefit for the refractory costs per ton of produced steel. Total cost might even be higher as maintenance costs might increase.

Therefore the development of new refractory raw materials especially for refractory castables have been in the focus in recent years which resulted in significant innovations driven by the never ending quest of the steel industry for reduced costs per ton of produced steel. Different factors have allowed to make significant progress, the search for solutions with increased performance/cost-ratio but also the quest to make refractory castables more reliable and robust during the installation and commissioning process. Failures that occur during the installation and dry-out phase can have strong impact on the final performance and in some cases even require to repeat the installation and dry-out job if for example an explosive steam spalling has occurred and destroyed the refractory lining even before it could serve its purpose inside a furnace.

This paper will discuss new raw material developments for refractory castables in three different raw material segments:

- Binder
- Additives and active compounds
- Aggregates.

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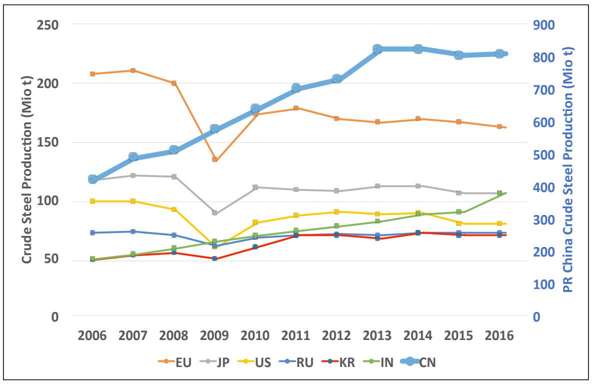

Fig. 1 Annual crude steel production [1]

Fig. 2 Steel production capacity utilization [3]

Increased rheological and setting robustness of castables can save costs at different levels. It allows a more precise planning of the installation, demoulding and commissioning so that these process steps can be done with a minimum of resources. Furthermore it increases the probability that the castable installation will be done with the correct water dosage to achieve the targeted porosity and strength level so that the full performance potential can be exploited.
Newly designed additives and active compounds [4] target to improve the ease of use and robustness of castables and a few examples will be discussed in this paper:

- Deflocculant with better robustness in silica fume containing castables
- Deflocculant for ladle castables that acts at the same time as setting regulator to avoid too long set in winter without making it too reactive in summer
- Permeability enhancing deflocculant that facilitates castable dry-out
- Shotcrete gelling agent for ladle castables.

Another example for a raw material innovation shows that a specifically designed calcium aluminate binder can improve the setting reliability of castables even after long storage time of the castable dry-mix prior to its installation.
Other new binders target the modification of the castable microstructure with the ultimate objective to improve the final performance so that less material is required per ton of produced steel. The positive side effect is that those performance driven products are in most of the cases also more sustainable solutions with a better environmental footprint. Two examples for performance/cost driven binder developments will be discussed in this paper:

- A calcium magnesium aluminate binder for ladle castables with increased corrosion resistance
- A calcium aluminate binder that reduces costs of dry-gunning installations by reducing the amount of material loss caused by re-bound and improves final performance due to reduced water demand.

Also in the field of refractory aggregates new ideas are discussed and example for potential cost savings through weight reduction of the refractory lining with microporous instead of very dense aggregates are highlighted.

2 Additives and active compounds developments

2.1 Robust deflocculant for silica fume containing castable

A major concern with silica fume containing castables is the robust deflocculation and reliable setting and early strength development when the purity of fillers and aggregates varies. Since calcium aluminate hydration is a wet chemical reaction process including dissolution, saturation, and precipitation steps, each modification of the pore solution chemistry by soluble compounds in variable raw materials can impact this mechanism but also the surface interaction between the deflocculant and the powder that needs to be deflocculated.
An active compound, REFPAC® 100 (RP100), has been developed to provide an efficient deflocculant that achieves its performances for a large range of raw material combinations. The term Active Compound refers here to a system that consists of an additive system on a mineral carrier. That allows for example in this case of RP100 a 1 %-addition to the dry-mix which makes dosage easy, reliable and facilitates a homogeneous distribution within the dry-mix. The active compound is a powder that can also been added to the castable dry-mix by means of automatic dosing equipment. Fig. 3 shows the impact of raw material purity on vibration flow of a LCC deflocculated with different additives compared to the active compound. Sodium tri-polyphosphate (TPP) and a specific polycarboxylate ether (PCE) that has been designed for silica fume containing castables show excellent flow after wet mixing (T0) and after 30 min (T30). But this is the case only when the formulation uses a high purity bauxite (BX1) and a high purity silica fume (FS1). When switching to lower quality raw materials (BX2, FS2) the deflocculation efficiency is impacted and a higher water dosage would be required which would negatively impact the final performance during application. Unlike TPP and PCE, RP100 doesn't show this sensitivity to the raw material purity level and also doesn't have negative side effects on the calcium aluminate bonding mechanism so that strength development doesn't get delayed (Fig. 4).

2.2 Robust deflocculant for steel ladle castables

Typically, high purity synthetic raw materials are used to formulate castables that have to resist very high temperatures and direct steel and slag contact for example in steel ladles. These high purity raw materials have a relatively lower impact on calcium aluminate hydration than the medium purity raw materials that are typically used in silica fume containing LCC. Nevertheless one aspect still strongly impacts the setting characteristics of a ladle castable and that's the ambient temperature. Calcium aluminate hydration is a temperature dependent reac-

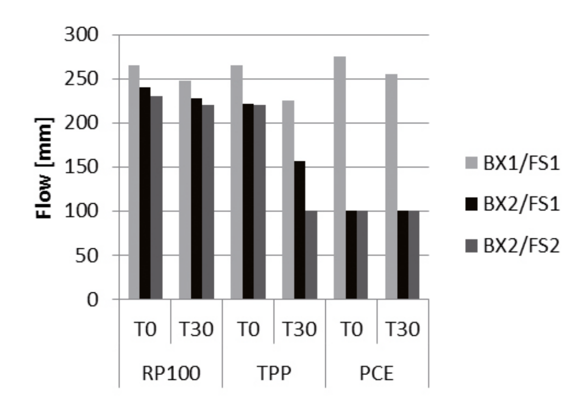

Fig. 3 Initial vibration flow and after 30 min

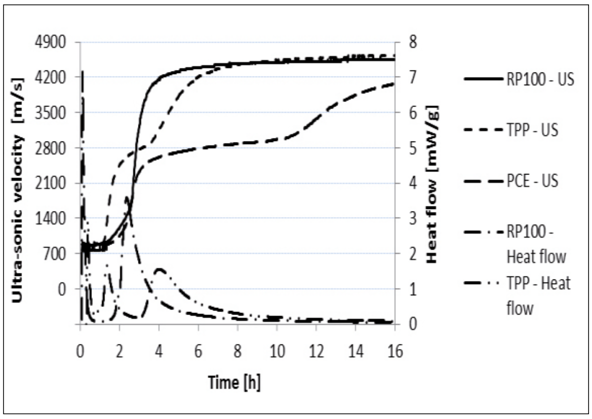

Fig. 4 Ultrasound profile and heat flow

tion, and it is not only the reaction kinetics that change but also the reaction paths. Low ambient temperature favours the precipitation of meta-stabile hydrates as CAH_{10} and C_2AH_8 while high ambient temperature turns the reaction path towards the stable C_3AH_6. The cumulated effect is that at low ambient temperature the setting takes much longer and the strength development is slower than at high temperature. Furthermore, the generally retarding effect of polymer-based deflocculants amplifies the difference between low and high ambient temperature. Fig. 5 shows an example for a castable deflocculated with a PCE (Peramin® AL200) that has been designed for high purity systems. This PCE has a different polymer structure than the PCE that has been used in the previous section for the silica fume containing castables.

A new active compound, REFPAC® 500 (RP500), has been developed that combines a deflocculating organic polymer with a mineral component that triggers calcium aluminate hydration at low temperature without accelerating the hydration at medium and high ambient temperature. Fig. 5 shows the time to reach an ultrasound speed of 4000 m/s which roughly corresponds to the time at which massive calcium aluminate precipitation has occurred (here also called setting time) and which typically creates enough strength to demould and handle the castable. While the efficiency of both deflocculation systems are very little impacted by the ambient temperature it is obvious that the hardening of the castable with the new active compound RP500 is much less temperature dependent. This is a key advantage for the organization of work in precast shops as well as castable installation in steel ladles as the time frame for each step in the process becomes more predictable despite unpredictable ambient temperatures.

2.3 Permeability enhancing and deflocculating active compound that facilitates castable dry-out

Dense castables are difficult to dry and explosive steam spalling can occur when the steam pressure in the pores exceeds the strength of the castable. Polymer fibres are typically added to castables to create small pore channels through which steam can more easily be transported to the surface. However, they cannot change the de-hydration temperature of the calcium aluminate hydrates which occurs mainly in the range between 150–350 °C, in some cases even up to 550 °C.

As higher the de-hydration temperature (change from water bonded in solid phases into steam) as higher the risk of high pressure build up even in the presence of pore channels created by PP-fibres as the steam needs to be transported to the surface first to reduce pressure. When the transport distance to the surface is very long the steam pressure release remains difficult.

A new Active Compound, REFPAC® MIPORE 20 (MP20), has been designed to create three effects:

- Castable deflocculation for most types of castable systems
- Higher gas permeability already at lower temperatures than achievable with PP-fibre
- Modifying the hydration path of calcium aluminate binders and creates calcium aluminate hydrate gel which releases its water at lower temperature than the crystalline hydrates C_2AH_8 and C_3AH_6.

Fig. 6–7 show thermogravimetric measurements of an MCC (AS10) and an LCC (AM6) with temperature measurements in the center of a 10 cm × 10 cm × 10 cm test cube. When employing the MP20, water release occurs at significantly lower temperature which reduces the risk of high pressure build-up. The MCC with MP20 shows a similar TG-

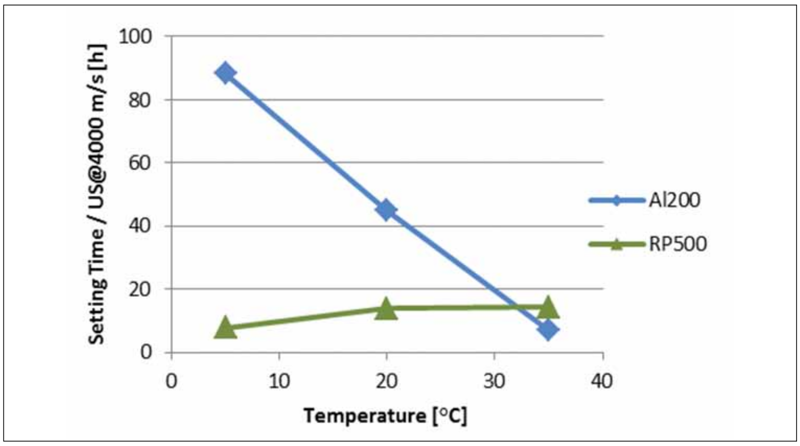

Fig. 5 Time to reach an ultrasound speed of 4000 m/s

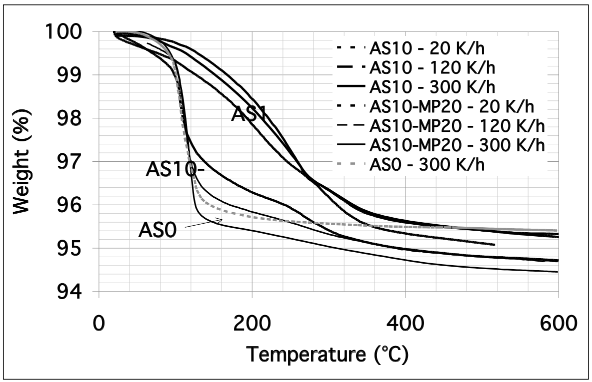

Fig. 6 Macro-TGA of MCC and NCC

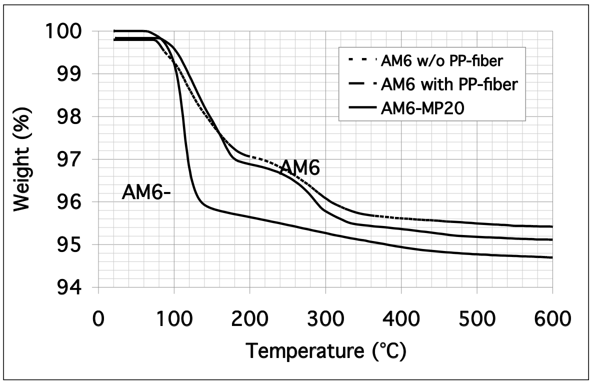

Fig. 7 Macro-TG of LCC (300 K/h)

profile as a silica sol/gel bonded no-cement-castable (AS0) known for its ease of dry-out.

2.4 Shotcrete gelling agent for ladle castables

While extremely efficient deflocculants have brought water demand of ladle castables to very low levels it has become a challenge to flocculate them rapidly when they need to be installed by means of shotcreting. Typically, only very high pH-aqueous solutions are able to stiffen those castables within a very short period of time. A new development has resulted in a solution where a very efficient deflocculant and the flocculant (gelling agent) build components of a system that are well adapted to each other. The result of this development is a gelling agent that no longer requires a very high pH which improves the health and safety at job sites significantly.

3 Binder developments

3.1 Binder with increased stability against aging in a castable dry-mix

Low cement (LCC) or deflocculated castable technology has been widely adopted in the past decades driven by the improved thermomechanical properties and corrosion resistance that these castables display in service.

These improvements have been made possible by the increased sophistication of refractory raw materials and formulations, especially through the introduction of filler and additive systems into the formulations while cement content could be reduced.

However, a negative side effect is frequently observed with LCC's as they tend to be more sensitive to aging during dry-mix storage. This can result in unpredictable castable setting times.

Humidity can either reach the dry-mix by diffusion through the packaging ("external water") or can be packed with the raw materials into the bag ("internal water") as some raw materials like silica fume can contain a significant amount of humidity.

To provide a better stability of the hydraulic calcium aluminate inside a castable dry-mix, a binder with a protective surface, Secar® 712, has been developed [5]. It makes castable setting and early strength development more predictable as shown in Fig. 8–9.

3.2 Binder that increases performance of steel ladle castables

Important parameters for the performance of ladle castables are their magnesium aluminate (MA) spinel content, spinel grain size, and spinel distribution inside the castable to build-in an efficient protection mechanism against slag penetration, structural spalling, and corrosion. Even better performance can be achieved by creating very fine spinel in situ through the reaction of magnesia powder with alumina during the heat-up of the ladle. However while taking advantage of the in situ formation of very fine spinel one needs to put special measures in place to minimize risk related to hydration of magnesia which could potentially negatively influence the casting properties. Magnesia hydration during the dry-out can eventually create cracks. And finally, expansion during spinel formation on the hot side of the castable needs to be well controlled to prevent high stresses in the ladle wall.

A new calcium magnesium aluminate binder, CMA 72, has been developed that consists mainly of microcrystalline MA-spinel

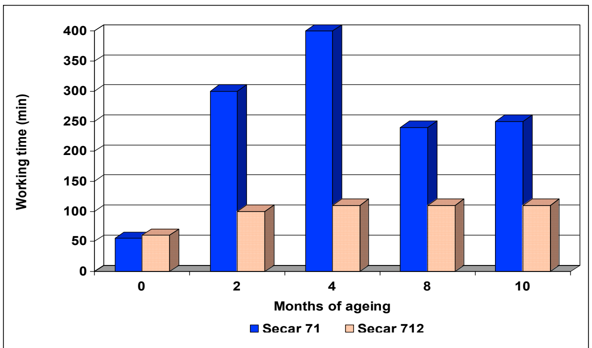

Fig. 8 Working time as function of dry-mix storage time

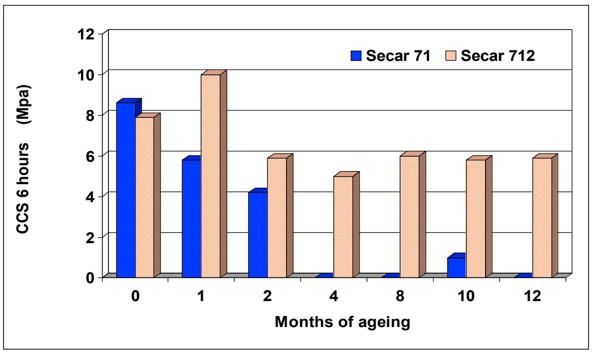

Fig. 9 Early strength development as function of dry-mix storage time

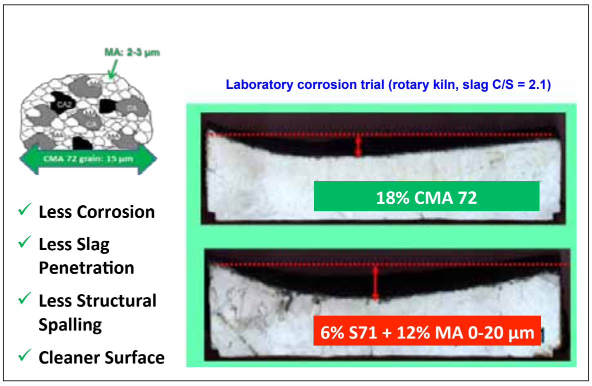

Fig. 10 Samples after rotary slag corrosion test

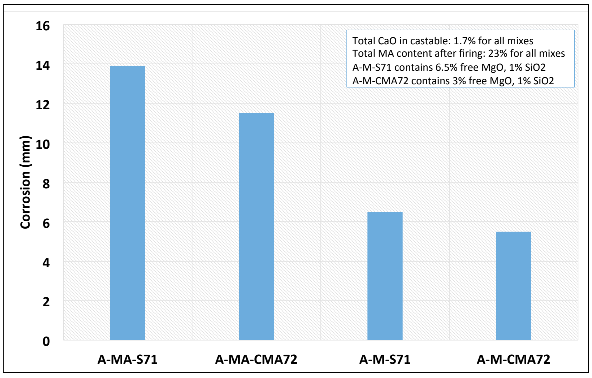

Fig. 11 Corrosion of A-MA and A-M castables

phases and hydraulic calcium aluminate phases. It allows employing homogeneously a high amount of very small spinel particles into the castable with spinel particle sizes similar to those that are formed in situ in alumina-magnesia castables while avoiding the above mentioned inconveniences. Nevertheless, this new binder improves wear resistance of both, alumina-spinel and alumina-magnesia castable as shown in a dynamic slag corrosion test in a rotary kiln (Fig. 10–11). Formulations with the same total amount of spinel after firing and the same amount of CaO have been compared in this case. In the case of the alumina-magnesia castable the amount of free Magnesia could be reduced from 6,5 % to 3 % when CMA 72 was used. CMA 72, due to its microcrystalline spinel content creates a higher strength after firing at equal total CaO content than the reference based on Secar® 71 and added spinel powder. Typical dosage rates of CMA 72 are in the range of 12–18 % for strongly slag loaded applications while addition rates of 8–12 % to alumina-spinel castables are beneficial when thermal shocks are the predominant damage factor. In alumina-magnesia castables also higher contents of CMA72 result in good thermal shock resistance when just a small amount of silica fume is present to control expansion and prevent magnesia hydration [6].

3.3 Binder that improves performance and reduces re-bound of dry-gunning mixes

The dry-gunning method is an established technology despite its inconvenient high rebound rate and relatively high water demand compared to vibrated or shotcreted castable. It allows installation of small quantities of material within a short period of time for example for repairs. Dry-gunning machines are largely available and easy to use. More sophisticated dry-gunning machines have been developed in recent years that also allow the installation of deflocculated castables to achieve lower porosity. Nevertheless, these machines are not so widely spread yet and the technology requires more sophisticated formulations with similar sensitivities as observed with LCC. A new binder has been developed that allows installation of gunning mixes with traditional machines but with reduced rebound rates to minimize material consumption during installation. Furthermore it has a low water requirement that results in low porosity to enable high wear resistance.

4 Aggregates development

Also in the fields of aggregates new developments could lead to further cost optimisations. While for example castables for steel ladle applications use in most of the cases high density aggregates with low porosity, the weakest part of a castable with respect to penetration and corrosion is typically the matrix with much higher porosity than the aggregates. That raises the question if it wouldn't be better to develop micro-porous high temperature resistant aggregates that could result in a weight reduction of a ladle lining. That could not only save refractory material but also energy due to lower thermal conductivity. First attempts into this direction have been made with a synthetic aggregate containing microcrystalline MA-spinel, calcium aluminate phases and micropores. Weight reduction in the range of 10 % have been achieved without big impact on physical properties of the castable since the matrix remained unchanged. Further investigations are running to evaluate the wear resistance with these new aggregates.

5 Conclusions

The steel industry will continue to request refractory solutions with further increased performance/cost ratios per ton of steel. Innovations in the field of refractory raw materials are one important element assisting the refractory industry achieving these targets. Especially in the field of refractory castables the new raw material developments can help improving several aspects in a life of a castable, from more homogeneous and less aging sensitive dry-mixes, over more robust, reliable and repeatable installation and dry-out properties, up to new microstructure designs that enable a longer service life. New active compounds and calcium aluminate and calcium magnesium aluminate binders can play an essential role in this regard. But also innovations in the field of aggregates offer new opportunities for the refractory industry to move the performance/cost ratio to new levels.

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