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Development of Basic Gunning Mixes: Comparison of Laboratory Trials, Thermochemical Calculations and Steel Plant Trials

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INTRODUCTION

The strategy of maintenance or relining of vessels like Basic Oxygen Furnaces (BOF), Electric Arc Furnaces (EAF) Ladles and RH degassers play a major role in determining steel plant efficiency[1]. The decision of the used repair mix and choosing the optimum maintenance method together with the related equipment depend on the general plant strategy. Nowadays basic refractory gunning mixes are indispensable for the efficient maintenance of steel producing units. The performance of these mixes is based on optimized grain size distribution, binder combination and selection of raw materials and is highly influenced by the producer. Customer requirements are very complex but the focus is always on a product that is easy to use, long-lasting and cheap in price. In order to meet the constantly increasing demands on the quality of innovative mixes and the rapid implementation of new developments, various approaches to increase the speed of development are being discussed in this paper.

DEVELOPMENT OF HIGH-QUALITY GUNNING MIXES

Conventional basic gunning mixes manufactured with low cost raw materials and common bonding agents can no longer fulfill the new requirements concerning easy workability, stability during processing and service life in operation. But in the end, it is always the customer who decides which philosophy of vessel-maintenance is advantageous for them. However, it has to be clear that lower prices force the manufacturer into applying inexpensive, low-quality raw materials and a less sophisticated production technology. Along with the decreasing quality of the mix, the frequency of the gunning repairs increases[2]. Apart from the higher mix consumption, the overall costs rise due to the restricted production capacity. A better approach is the improvement of gunning efficiency. High-quality gunning mixes and a modern gunning technique allow more efficient maintenance of the vessels without a major cut in production capacity. The creation of an optimum grain size distribution, the composition of the ideal binding agents together with the appropriate additives and the perfect composition of the raw materials used are the basis for the development of modern gunning mixes. Manufacturing according to the highest standards of the production plant is another important component in this process.

Grain size distribution

Grain size distribution has a major influence on the processing and initial adhesion of the material to be applied. Therefore, when developing new products, particular importance is given to individual customer and system requirements. For many years, the distribution according to Dinger-Funk was largely responsible for the development of new products. This is partly due to the fact that the processing technology in earlier times hardly permitted throughputs of more than 100kg/min. High-performance application systems deliver up to 400kg/min of optimum mixed spray mass, which is applied from distances lower than 1.8m to the surface to be maintained. This causes the loss of valuable components of the spraying mixture due to rebound which reduces the overall maintenance efficiency and leads to considerable losses of partially more than 30% of the mix applied. It is therefore important to keep the rebound as low as possible. This is achieved by increasing the proportion below 60µm. Positive in this context was also the reduction of the upper grain size limit to 3mm. With regard to rebound optimization, the amount of >1 mm must also be taken into account. If this exceeds a limit value of approx. 55%, an increased coarse grain rebound is to be expected with certainty. If, on the other hand, the fine fraction of smaller than 0.063mm is too low, the plasticity and thus the primary adhesion during spraying are reduced.

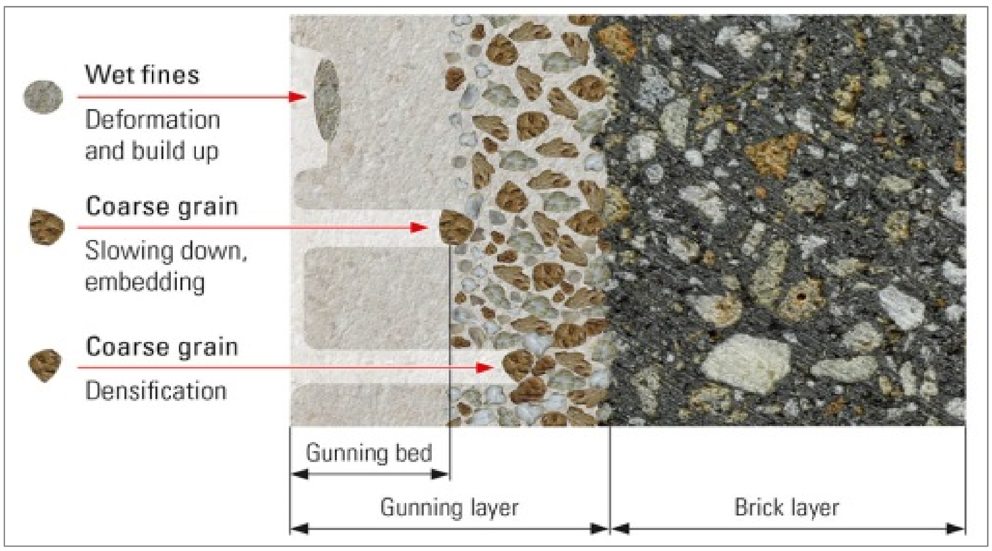

Figure 1. Formation of a gunning bed

The fines improve the plasticity required for adherence, but may not exceed a certain limit as the mix will otherwise spall during drying, or the gunned layer will become too unstable.

The fines-water slurry incorporates the grains. Coarse grain fractions stabilize and densify the gunning layer whose bulk density should be approximately 2.6g/cm³ (after drying), and increase corrosion resistance. Too much coarse grain, however, causes increased rebound rates and thus material loss.

Binder combination

The gunning mixes in general must have properties such as quick wettability, water compatibility and excellent adhesion. The lack of adhesion when applying the material to a hot or cold wall is the most common deficiency during application. When attempts have been made in the past to correct this lack by increasing the amount of binder in a refractory mix, it has been shown that the mixture has other serious disadvantages. Considerable amounts of binders, e.g. sodium silicate, reduce the refractoriness of the composition to an undesirable level, reduce the strength of the material after heating or during operation, interfere with the formation of a dense, pore-free matrix and increase clogging problems in the gunning hose or spray lance. Regardless of the binder concept used, the basic prerequisites such as the best possible adhesion, rapid stiffening and curing, sufficient strength of the mixture over the entire temperature range of the chemical bond and minimized reduction of wear resistance, must be taken into account for every new development.

Nowadays, there are 2 typical systems which are used in gunning mixes: silicate bond and phosphate bond, whereby combinations of the two are also often used. Also worth mentioning are sulfate-bonded products for special applications because they hardly form low-melting alkali phases but the initial adherence is negatively influenced due to reduced adhesiveness.

Silicate bond

This bonding system is based on the use of water-soluble alkali silicates, is relatively inexpensive and, due to its moderate curing speed, more suitable for the application using a hand-held lance. The wettability of the mixtures, the water absorption and the setting speed are very well fulfilled by the use of water glass, as the speed of dissolution is rather high.

The dissolution rate of the water glass is strongly dependent on the SiO_2/Na_2O modulus. The higher this modulus, the less easily soluble the water glass is. The type of silicate used depends on the gunning system and the moment of water addition. If the maintenance mixture is applied with a 10m long hand lance, the mixture has more time to react with water than with an automated renovation system where the water is added just before it leaves the lance. After extensive test series, water glass with a modulus of 2.0 to 2.7 is nowadays mainly used.

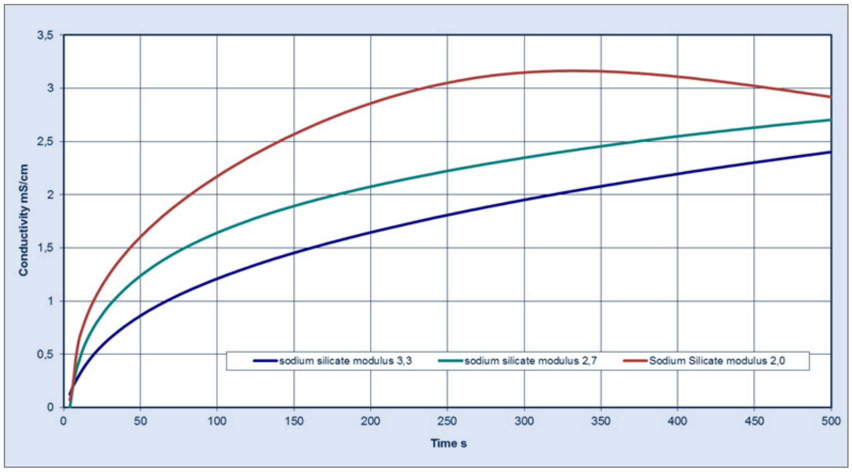

Figure 2. Rate of dissolution of sodium silicates in water at 20°Celsius

Phosphate bond

This kind of chemical bonding is characterized on the use of different phosphates with different acid contents and different degrees of polymerization. When common phosphates such as sodium metasilicate (Na-O -[NaPO3]x - Na) are used without the addition of further additives, the gunning layer does not stabilize quickly and sufficiently. However, this is necessary to ensure stiffening of the applied layer and also to incorporate and embed the coarse fractions of the applied mixture. Therefore the effect is used that phosphates react faster with basic raw materials the more acidic they are.

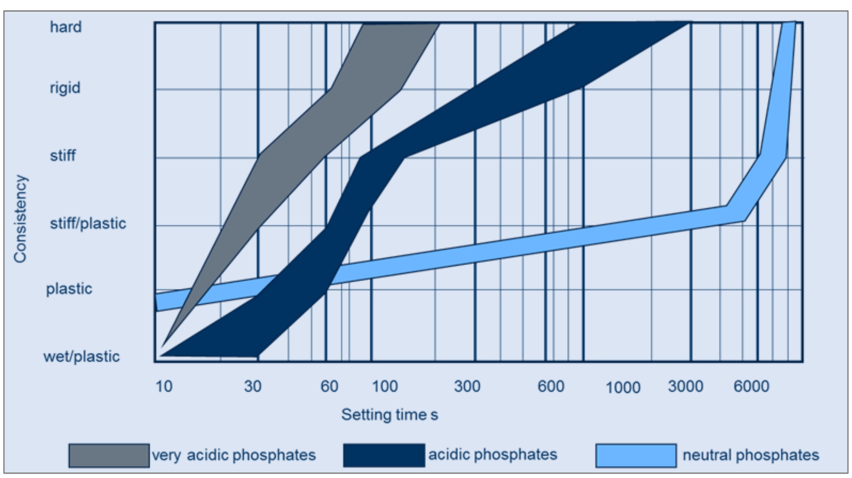

Figure 3: Setting speed of phosphate bonded gunning mixes at 22°Celsius

In principle, the setting rate may not drop below a certain level because the risk of clogging in the lance increases and the formation of a jellylike structured gunning bed is not possible. This would be the situation, for example, if high-acid phosphates such as monoaluminium phosphate ($Al[H_2PO_4]_3$) or urea phosphate ($CO[NH_2]_2 \cdot H_3PO_4$) were used[3]. The purpose of using this binder is therefore to adjust the setting rate by adding additives, such as finely distributed lime-rich powders (e.g. $CaCO_3$ as micro powder < 3 µm) or by combining different phosphates in such a way that the above-mentioned properties can be adjusted in the applied matrix. Furthermore, the influence of low-melting eutectics, which would reduce the refractoriness during use, should also be considered during the development of new gunning mixes.

Selection of raw materials

The refractoriness of unshaped basic mixes is highly influenced by the choice of the optimum raw material or raw material combination. The chemical binder [4] guarantees the necessary intermediate strength until the ceramic bond is formed at more than 1300°C. From that time onwards, the blend of the used dead burned magnesia is responsible for the superior sinter ability and for the high refractoriness. For the development of high-quality gunning mixes, low-iron sintered magnesia with more than 90% MgO and a high CaO/SiO_2 ratio is used as the preferred raw material. In addition to the prerequisite of a high CaO/SiO_2 ratio, it must also be ensured that the sum of oxides like Fe_2O_3 and Al_2O_3 does not exceed a maximum limit of 1.5%. In order to achieve the best results in practice with regard to refractoriness, high-quality gunning mixes are additionally treated with lime-rich additives, so that the formation of bonding phases with high melting points such as tricalcium phosphate or dicalcium silicates can be generated. A further advantage can be generated by the use of Alpine sinter magnesia as it has a high lime/silica ratio in order to avoid the formation of refractoriness-reducing low melting phases such as merwinite ($3CaO\ MgO\ 2SiO_2$) and monticellite ($CaO\ MgO\ SiO_2$). Developers and manufacturers of basic gunning mixes are often forced to follow the sometimes very low market prices. As a result, many different raw material combinations are used, with a very wide spectrum ranging from recycling material to olivine.

	Grade 1	Grade 2	Grade 3	Grade 4	Grade 5	Grade 6
	%	%	%	%	%	%
MgO	94,5	75-85	91	96	94	92
CaO	0,5	5-20	2,1	2	3	2
SiO_2	1,3	1,5	0,5	0,7	2,5	4
Fe_2O_3	2,1	5,5	5,7	0,2	0,4	1

Figure 4. Chemical analysis of commonly used DBM grades

WEAR SIMULATION

In order to achieve ideal comparability between laboratory results and trials at the customer site, the same material combinations as described below were always used for subsequent investigations.

	chemical analysis					DBM grade			bonding system	
Version	MgO	SiO2	CaO	Fe2O3	Al2O3	94-95%	alpine	alternative	Phosphate	Silicate
Mix A	66,5	1,4	23,0	3,8	0,5		x		x	
Mix G	88,1	6,2	4,4	0,6	0,5	x		x		x
Mix H	86,8	4,8	4,7	0,5	0,5	x			x	
Mix B	85,7	5,0	5,0	0,6	0,5	x		x	x	
Mix D	72,5	4,5	17,0	3,8	1,3		x			x
Mix I	67,2	4,7	13,5	1,1	1,1	x		x	x	
Mix F	67,3	5,9	13,1	1,1	1,2	x		x		x
Mix E	88,6	6,3	3,5	0,6	0,7	x				x

Figure 5. Trial mix overview

Physical characteristics

To determine the physical values of test specimens, the mixture was enriched with 4% special oil, since water causes cracks during drying and preheating. About 15 minutes after mixing, the bulk density (BD) of the test cylinder was measured. Due to the sometimes high lime content of some mixtures, cracks nevertheless formed during the tempering process. Therefore, the bulk density could not be measured directly after drying at 250°C and had to be calculated from the BD of the original cylinders by subtracting the added oil. At temperatures of 1000°C and more, however, values could be determined if the test cylinders were placed in the hot furnace immediately after setting at ambient temperature (22°C). Values gained at 1600°C are of highest interest as they are most relevant in practice.

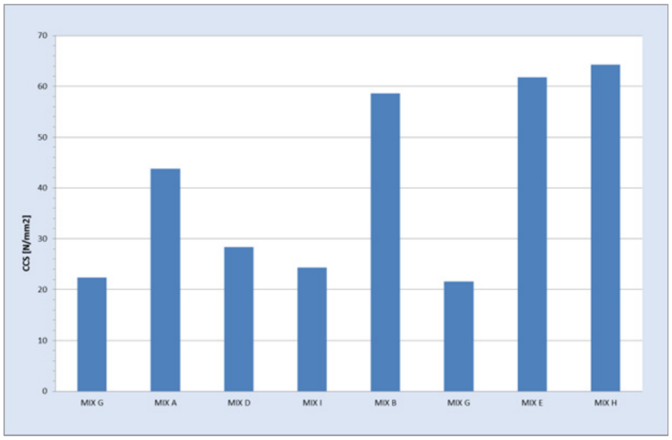

Figure 6. Comparison, Cold Crushing Strength, 1600°C, 4h, ox

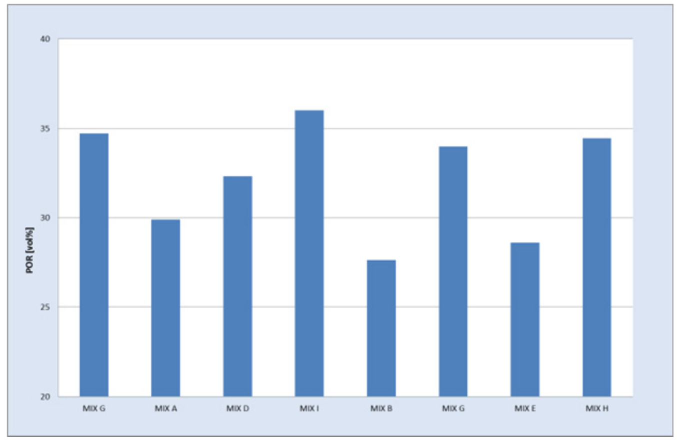

Figure 7. Comparison, Porosity, 1600°C, 4h, ox

Resume

A closer look at the results in Figure 6 and Figure 7 leads to the conclusion that a comparison of the key indicators is not related to a generally valid statement. A high CCS should result in a low porosity, because the space between the pores is greatly reduced by sintering. Comparing Mix H and Mix G in detail, it becomes clear that a direct correlation of the values is not given. A generally valid statement about a possible correspondence with a practical correlation cannot be reliably derived on the basis of this data.

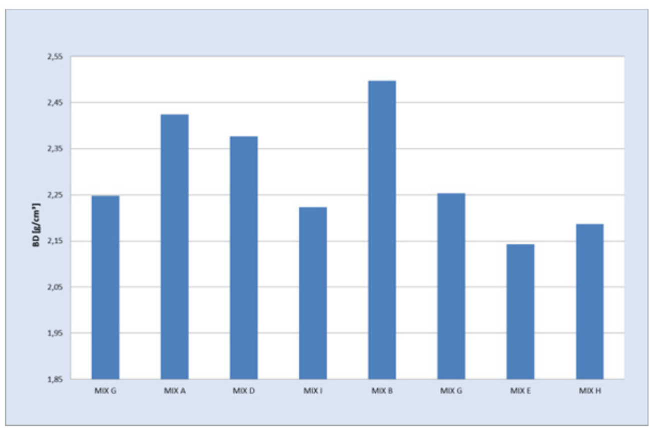

Figure 8. Comparison, Bulk Density, 1600°C, 4h, ox

FactSage

Thermochemical modeling is a proven method to calculate the interactions between process slag (e.g.: BOF or EAF slag) and the basic wear or gunning lining material. Since these calculations are based on theoretical equilibrium calculations, the results do not consider any kinetic modeling, mass transfer or abrasion effects. The general modeling approach of the thermochemical calculations using FactSage is based on the calculation of the phase distribution in an infiltrated layer with a mixture of lining material (gunning mix) in contact with slag defined by mass ratio.

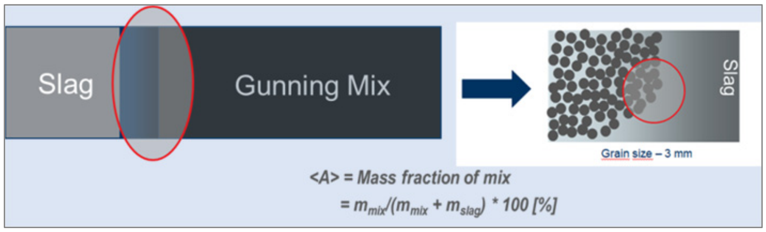

Figure 9: FactSage modeling approach for corrosion process

Based on this modeling approach, the interaction of a typical EAF and BOF slag with different standard gunning mixes should be evaluated. The calculations show the influence on the refractoriness at the interface (transition) between the individual gunning mixes and the EAF/BOF slag. For the calculations the total amount of liquid phase was calculated for varying amounts of slag <A> addition in combination with the gunning mix <100-A>. Due to the fact that the slag is liquid at the desired temperature of 1650°C, the amount of liquid refractory material refers to the total amount of formed liquid phases minus the added amount of (liquid) cover powder. This amount of liquid phase represents the liquid material coming directly from the refractory material. The results of this calculation are illustrated in the diagrams below.

Thermochemical simulation of interaction between a basic gunning mix and EAF slag

For the interaction of different gunning mixes with a typical EAF slag the mixes displayed in Figure 4 were used. The used slag was taken from one of our customers, analyzed in our laboratory and shows an average chemical analysis of the EAF process.

MgO	CaO	SiO_2	FeO	Al_2O_3	MnO
[%]	[%]	[%]	[%]	[%]	[%]
8,9	47,1	22,3	11,2	6,9	2,9

Figure 10. EAF slag used for calculation

As seen in Figure 11 those gunning mixes were brought into contact with the EAF slag and the wear of refractory was calculated for a slag amount of 10%, 20% and 30%.

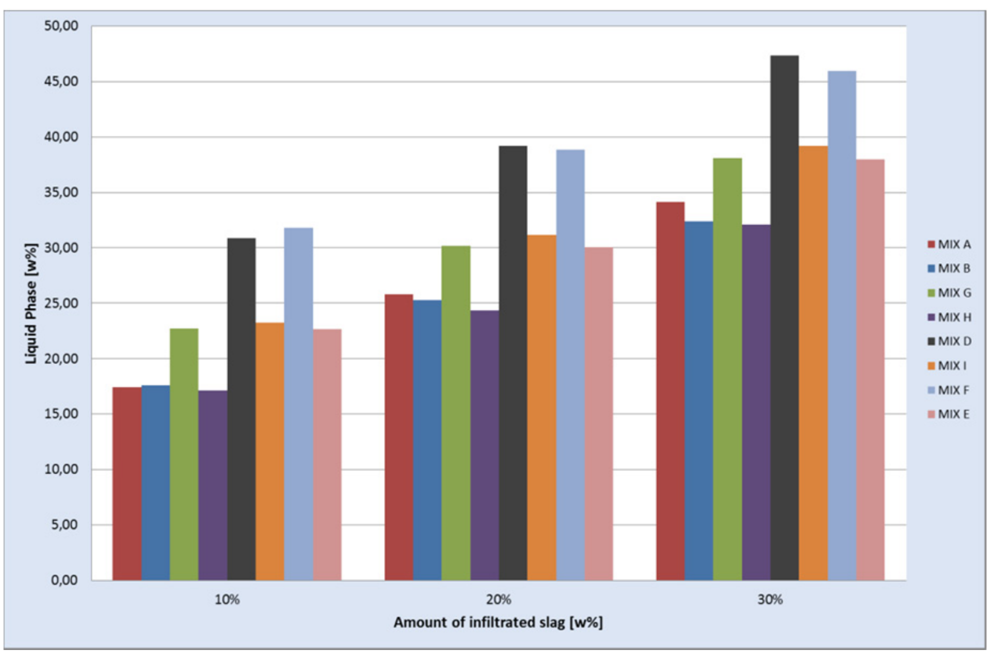

Figure 11. Liquid phase formation from refractory material for a slag content of 10%, 20% and 30%

To indicate the influence of the binder (phosphate or sodium silicate bonded mixes) on the refractoriness, mixes with a same raw material concept were compared in the FactSage calculation.

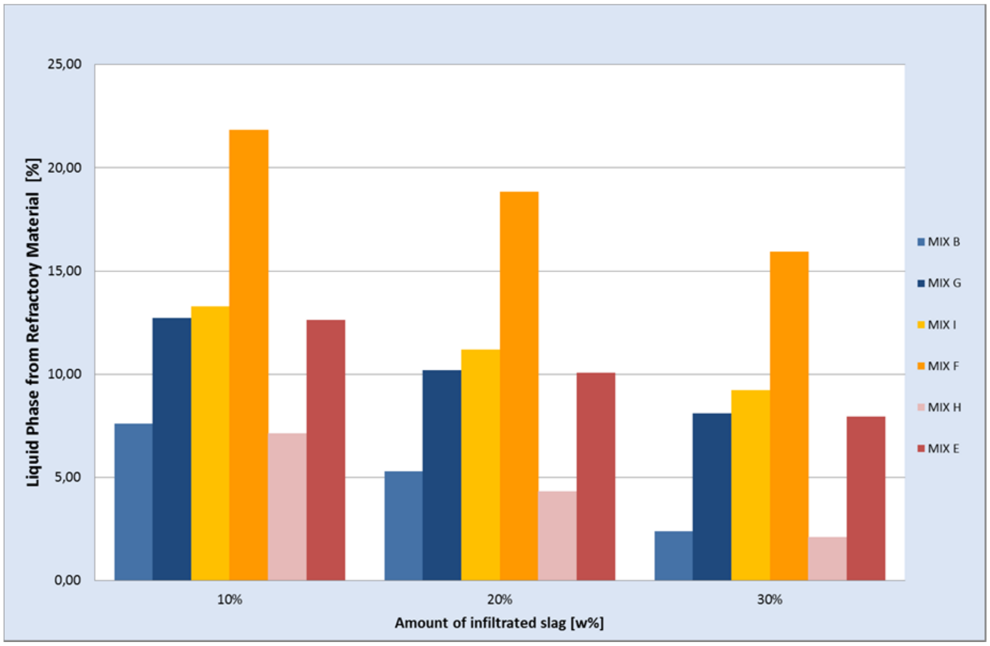

Figure 12. Comparison of phosphate and silicate bonded mixes for a slag content of 10%, 20% and 30%

Results

The results of the thermochemical simulation and the reaction between the gunning mix and the EAF slag can be summarized as follows:

- Generally CaO-rich mixes are favorable for this type of slag compared to SiO_2-rich mixes
- Mixes using a phosphate bonding show advantages compared to the sodium silicate bonding for the same raw material concept
- Sodium silicate bonded mixes in combination with high amounts of CaO and SiO_2 show the highest wear rate and with that the lowest refractoriness (Mix F and Mix G)
- The highest refractoriness is achieved with phosphate bonded mixes based on low-iron sintered magnesia (Mix H and Mix B).

STEEL PLANT TRIALS

The evaluation of the performance of a gunning mix is mostly subject to personal expert opinion. For this test, an automatic gunning robot was used in the EAF steel plant to minimize the human influencing factor. The refractory wear was measured with a fixed installed laser measurement system.

Trial Setup

To obtain a data-based overview of the tested gunning mixes the trials were conducted under defined guidelines. The refractory wear was measured with a laser scanner before gunning, after gunning and additionally 4 heats after gunning to record measured and absolute values of the mix performance. Moreover, the production parameters were collected from the steel plants Level-2 system to highlight their influences on the mix performance.

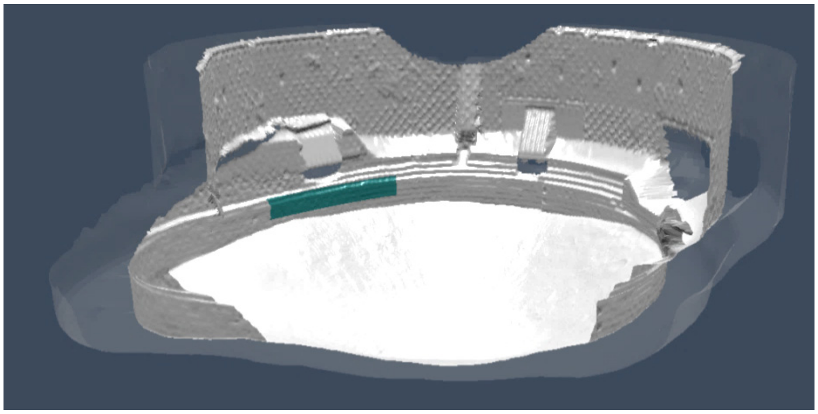

Figure 13: Comparative area in EAF

Figure 5 represents an overview of the tested mixes whereas Figure 13 represents the area (2.65 – 2.90m depth and 195 – 255°) in the EAF where the trial mixes were applied and compared.

Trial conclusion

Figure 14 highlights a part of Figure 15 in order to explain the trial results in detail. Generally speaking, it summarizes the minimum refractory wear thickness in the above defined area in mm over heats/events. White vertical lines indicate the points in time where laser measurements were applied, whereas the green bold bars at the bottom indicate the appliance of gunning maintenance. The measured minimal thickness of the mix trial area over all heats is described by the black bold line. In order to distinguish between the appliances of the different mixes the areas are colored with one background color per mix. The red line depicts the refractory gradient from the beginning to the end of the usage of one specific mix. The absolute gradient per mix is denoted in the value wear during operation in mm. Additionally, key parameters like tapping temperature, tap-to-tap time, power-on time as well the amount of heats in operation and amount of mix applied is added. Finally KPIs like mix/heat ratio and wear/heat ratio are calculated and denoted at the bottom of the analysis.

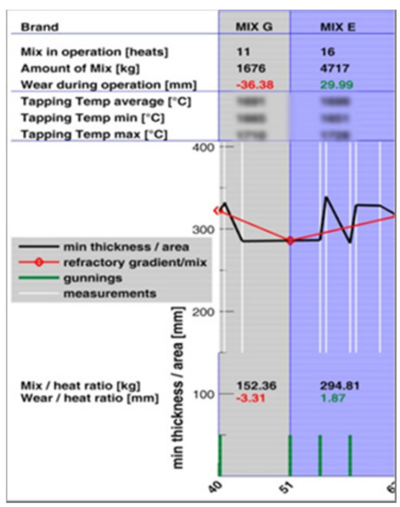

Figure 14: Wear behavior based on applied gunning mix

By evaluating Figure 15, one can see that during usage of MIX E the lining thickness (wear during operation) increased the most (16.19mm), apart from MIX B, but only 16 heats were produced with 4717kg of gunning mix, resulting in a mix/heat-ratio of roughly 295kg/heat. This can be assessed as moderately high, but with regard to the high average tapping temperature of 1699°C, this value can be positively highlighted. Moreover, MIX B showed a mix/heat ratio of 122kg/heat with a lining growth of 44.84mm during 40 heats of operation. MIX I also performed very well, indicated through very slight lining growth during 41 heats. MIX A showed moderate performance with a wear/heat ratio of -0.42mm, but still performed better than MIX D and MIX F, but clearly outperformed MIX G and MIX H.

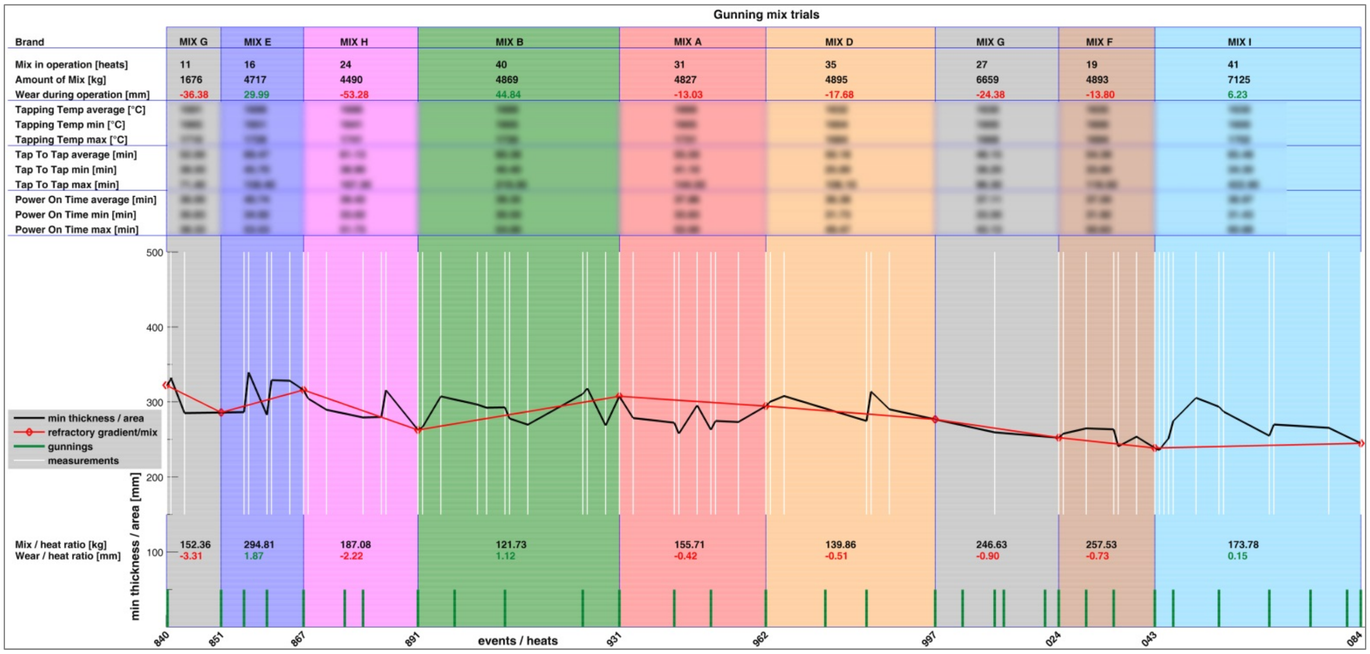

Figure 15: Overview of wear behavior during usage of all tested mixes

The statistical deviation of the tapping temperature applied during each mix is shown in Figure 16 as a representational example of the covered production process parameters. In detail, Figure 16 shows that during the operation of MIX E, MIX H and MIX B the applied tapping temperatures were really high on average. Nevertheless, MIX E and MIX B showed the best performances. As the performance of MIX H was the worst compared to the others, it could be argued that this mix was at times exposed to the highest tapping temperatures. All important production process parameters were evaluated during this trial and their results were considered while concluding and ranking this mix trial series.

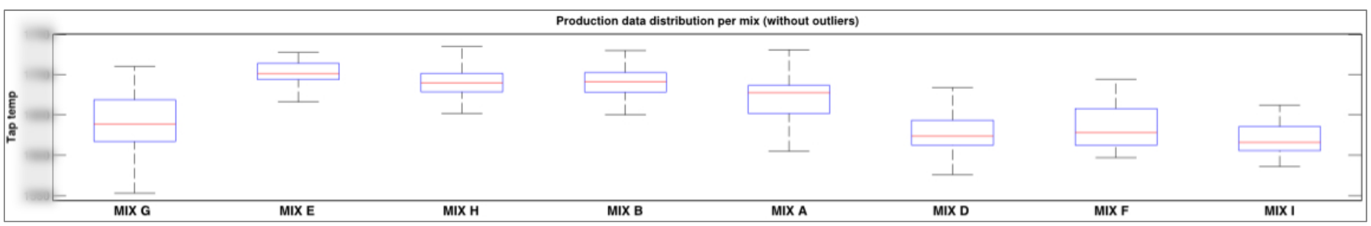

Figure 16. Boxplot tapping temperature, data distribution per mix

Trial ranking

Summing up, MIX B shows very promising results during the trial. MIX B performance results are better than the results of MIX I, which still showed a very stable performance, followed by MIX A. The best performance was achieved by MIX E, which resulted in noteworthy lining growth. However, it must be said that the mix/heat ratio was very high since only 16 heats were produced while 4717 kg of gunning mix was applied. The current result of the MIX G performance was sobering since the lining thickness decreased more than during the appliance of the other mixes, except for MIX F, whose performance was almost equal. Concluding the trials, the poor performance of MIX H was obvious due to the fact of the most loss of lining thickness in all areas.

Ranking	Type of Mix
1	Mix E
2	Mix B
3	Mix I
4	Mix A
5	MixD / Mix F
6	Mix G
7	Mix H

Figure 17: Performance ranking of tested mixes

CONCLUSION

Many companies are working hard to shorten the time to market for newly developed products. When developing refractory bricks for the lining of various furnaces, it is easy to determine physical properties. Values such as chemical analysis, density, porosity or the modulus of rupture at different temperatures can be used as an indicator for the expected performance under real conditions. The expected lifetime can therefore be predicted with sufficient accuracy in a given field of application, based on the physical and chemical properties of the brick and the premise that a competent bricklayer will install it professionally. This approach is very different when it comes to the development of semi-finished products, such as basic gunning mixes. Not all eventualities that occur during practical application can be taken into account during development. The performance hereby depends very much on the local conditions. Internal factors such as grain size distribution, bonding system rheological properties that can be influenced by the researcher do not allow a direct correlation with actual practical suitability. Also the calculation of the phase distribution, with or without the influence of slag, by FactSage, does not correlate conclusively with the practical efficiency. These calculations show at least tendencies and confirm generally known theses. As described above, no meaningful link could be established between laboratory tests, FactSage and field trials. The most significant influence on the performance is the on-site processing by the personnel including the selected processing technology. Therefore, the so-called external factors, such as the spraying system used – manual or automatic, water injection – high pressure, binary nozzle or conventional, throughput of the mass in relation to the distance of the lance from the lining or metallurgical influences, to name only a few, are the really decisive influencing factors for the performance of a newly developed mix. Ultimately, the entire development chain is always about the appropriate practical application and the route via real-life trials with new products should therefore be accelerated.

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