SUSTAINABLE ALUMINA SPINEL CASTABLES:
A Cr_2O_3-CONTAINING ALTERNATIVE FOR THE FERRA-ALLOY INDUSTRY

Minghua Zhang, Micael Larsson, Edina Alibasic, Ronald Robles, Hanna Landell
Höganäs Borgestad AB, Bjuv, Sweden

ABSTRACT
Low-cement-bonded alumina-chromia castables are used in the ferroalloy industry. However, the presence of Cr_2O_3 in these refractories can lead to the formation of water-soluble hexavalent chromium-containing alkali chromate salts, which are carcinogenic and pose environmental and health hazards.
Alumina-spinel castables, which combine alumina and spinel/MgO, offer a balance of properties including good thermal shock resistance, corrosion resistance, and mechanical strength. These materials are widely used for steel ladles.
Four alumina spinel castables were developed and tested in the laboratory, including three low-cement-bonded castables and one non-cement-bonded castable.
The low-cement-bonded castables had higher compressive strength and porosity compared to the non-cement castable.
This study demonstrates that alumina spinel castables are a viable alternative to alumina-chromia castables.
Subsequently, both low-cement and non-cement castables were field-tested.
The results showed that the non-cement castable did not exhibit the expected service life, whereas the low-cement-bonded castable with calcium magnesium aluminate cement showed promise as a replacement for the alumina-chromia castable.

INTRODUCTION

The ferroalloy industry is crucial in the production of a wide range of steel and other metal alloys. The manufacturing processes in this industry necessitate extremely high temperatures, often exceeding 1600°C, and involve exposure to highly corrosive molten materials, such as slag and metal. Consequently, the selection of refractory materials for lining furnaces, launders, and other ferroalloy production equipment is of utmost importance.
Chromium oxide (Cr_2O_3) has been a popular choice for refractory materials in the ferroalloy industry due to its exceptional thermal stability, resistance to chemical attack, and ability to maintain structural integrity at elevated temperatures. However, the use of Cr_2O_3-containing refractories has raised environmental and health concerns, particularly regarding the potential release of hexavalent chromium (Cr(VI)), which is a known carcinogen[1-3].
In response to these concerns, the ferroalloy industry is actively seeking alternative refractory materials that can match the performance of Cr_2O_3 without the associated environmental and health risks. One promising alternative is the use of alumina spinel castable[1-5], a Cr_2O_3-free refractory material composed of aluminum oxide (Al_2O_3) and spinel or magnesium oxide (MgO).

Castable Materials and Corrosion Test

– Castable Materials

Four alumina spinel castables were developed and tested in the laboratory, comprising three low-cement-bonded castables and one non-cement-bonded castable.
Those four castables, along with a competitor Cr_2O_3-containing castable (D8), underwent corrosion cup tests.

Table 1. Cr_2O_3-containing Castable D8 Composition:

D8	Al_2O_3	Cr_2O_3	SiO_2	CaO	Fe_2O_3
wt%	88.5	8	1.6	1.4	0.1

Table 2. Overall composition of four alumina spinel castables. LC, low cement castables; NC, no-cement refractory castable.

wt%	LC-1	LC-2	LC-3	NC
Tabular 0--6 mm	69	69	69	68
Spinel AR 78 0-1mm	18	14.25	12	20
Alumina Fines	8	6	6	8
Calcium Aluminate Cement 70	5			
Amorphous Alumina Binder				3
Calcium Magnesium Aluminate Cement		10	12.25	
MgO content%	3.71	5.21	5.15	4.16
CaO content%	1.45	1.00	1.23	0.00
water %	4.5	4.6	4.5	4.25

– Sample Preparation and Characterization

The dry components were mixed using a stand mixer for five minutes. Water was then added, and the castable was wet-mixed for an additional five minutes. Vibration flows were measured after five minutes of wet mixing using the flow cone described in ASTM C230 (height 50 mm). The flow value represents the percentage increase in diameter measured 30 seconds after removing the cone and vibrating for 30 seconds at a frequency of 50 Hz. The molds were kept at 20°C for 24 hours before demolding.
The cold crushing strengths (CCS) were measured after drying or fired at different temperatures. Cylindrical specimens ("cup") were used in the static corrosion cup test. The corrosion media included two metals, Metal A and Metal B, and a Slag A, from a ferroalloy plant (Table 3 and 4). The dimensions of the cups were: external diameter 100 mm, height 100 mm, and central inner cavity 50 mm in diameter and 50 mm in depth. After casting, the samples were kept in the molds for 24 hours, then demolded and dried at 110°C for 24 hours. Before the corrosion resistance test, the cups were fired at 800°C for 5 hours.

Table 3. Chemical Composition of the Industrial Produced Slag A

Slag A	Al_2O_3	CaO	Cr	Fe	K_2O	MgO	MnO	Na_2O	NiO	S	SiO_2	TiO_2	BAS
wt %	24	2.9	2.3	0.5	0.1	40	0.1	0	0	0.2	31	0.3	1.8

Table 4. Chemical Composition of the Industrial Metals

Metal %	C	Cr	Cu	Fe	Mn	Ni	P	S	Si	Si Me	Ti	V	Slag	Al
Metal A	6.5	66	0	24	0.2	0.4	0	0	1.4	1.4	0.1	0.1		
Metal B	6.3	67	0	27	0.2	0.4	0	0	1.3	1.4	0	0.1	-0.9	- 0.9

For the static corrosion resistance test, pre-heated cups were filled with cold metals and slag, then fired at 1700°C for 1 hour. After cooling, the cups were cut open for further examination.

RESULTS AND DISCUSSION

– Static Corrosion Cup Test Results

Figures 1 depicts the cross-sections of the corroded samples by Metal B. Figures 2 shows the cross-sections of the corroded samples by Slag A+Metal A.

Based on a visual inspection of Figure 1: there does not appear to be a distinct visual difference in the corrosion among the five samples. However, the low cement castables LC-2 and LC-3 do seem to exhibit relatively slightly better corrosion resistance compared to the other samples. This suggests that, under exposure to Metal B, the low cement LC-2 and LC-3 castables demonstrate marginally improved corrosion performance over the other materials tested.

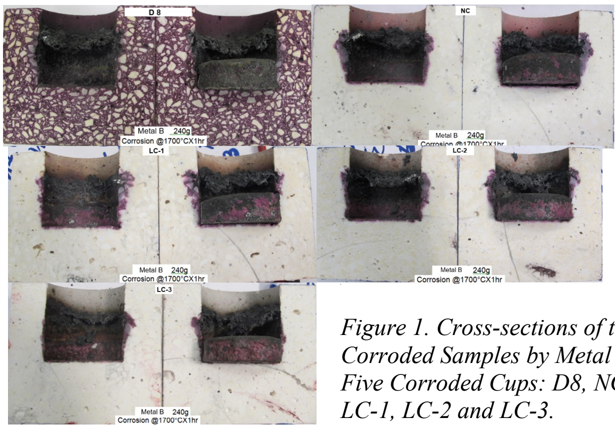

Figure 1. Cross-sections of the Corroded Samples by Metal B. Five Corroded Cups: D8, NC, LC-1, LC-2 and LC-3.

The visual assessment indicates there may be subtle differences in the corrosion behavior between the various castable formulations when subjected to Metal B.

Overall, this corrosion cup testing provides initial insights into how the castable materials respond to certain corrosive environments.

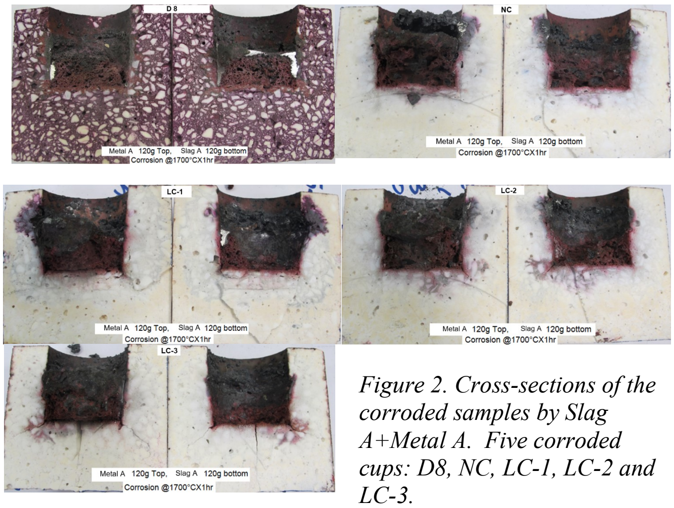

Figure 2. Cross-sections of the corroded samples by Slag A+Metal A. Five corroded cups: D8, NC, LC-1, LC-2 and LC-3.

Observations on Figure 2 cup samples (corroded by Slag A + Metal A): All the samples in Figure 2 demonstrate more infiltration compared to the samples in Figure 1 (corroded by Metal B). The non-cement castable NC, as well as the low cement castables LC-1 and LC-2, exhibited the most extensive infiltration. The infiltration level for the D-8 sample is difficult to estimate due to the ambiguous color.

It is undoubtedly that the viscosity of the molten slag and the liquid formed during the interaction between the slag and the refractory body significantly influences the infiltration. The higher the viscosity, the more difficult it is to infiltrate the refractory. It is generally accepted that Cr_2O_3 can increase the viscosity of slag.

Additionally, the low cement castables LC-3 and D-8 display deep cracks at the bottom of the samples. This cracking behavior is likely attributed to microstructural changes in these refractories. The microstructural changes could lead to weakening of the grain boundaries and overall structural integrity. In contrast, the NC and LC-1 samples did not exhibit cracking, potentially due to their lower MgO content matrices being more resistant to microstructural changes.

These observations highlight the importance of the refractory material composition and its interaction with the corrosive slag environment in determining the infiltration resistance and structural integrity during service.

– Castables' Placement and Mechanical Properties

Table 5 reveals that the non-cement castable NC exhibited improved flow behavior and required a lower water addition compared to the other castable formulations.

Table 5. Overall placement properties of four alumina spinel castables.Low cement castable(**LC**); Non-cement castable(**NC**).

wt%	**LC-1**	**LC-2**	**LC-3**	**NC**
Water	4.5	4.6	4.5	4.25
Wet-out time Sec.	30	45	50	50
Wet Mixing Time, min.	5	5	5	5
Vibrating Flow % T_0	128	105	115	158
Vibrating Flow % T_{30}	114	100	89	159
Vibrating Flow % T_{60}	102	90	88	154
Workability,hrs	14.5		7	
Setting time, hrs	17.5	10	9	10

Table 6. Overall physical properties of three low cement castables. Two castables, LC-2 and NC, were selected for industrial trials and compared with competitor' Cr_2O_3-contining castable, D8.

Physical Properties	**LC-2**	**NC**	**D8**
110°C CCS MPa	49.39	66.9	100
110°C Density, g/cm^3	2.98	3.11	3.15
110°C Porosity, %	13.2	7.3	
800°C CCS MPa	81.1	51.19	70
800°C Density, g/cm^3	3.02	3.06	3.1
800°C Porosity, %	16.6	15.8	19
800°C PLC,%	-0.01	-0.03	-0.4
1200°C CCS MPa	92.01	23.76	80
1200°C Density, g/cm^3	2.99	3.05	
1200°C Porosity,%	16.6	15.8	
1200°C PLC,%	0.03	0.013	-0.1
1400°C CCS MPa	74		
1400°C Density, g/cm^3	2.94		
1400°C Porosity,%	16		
1400°C PLC,%	-0.05		
1600°C CCS MPa	105.4	86.48	100
1600°C Density, g/cm^3	3	3.08	
1600°C Porosity,%	16.9	16	
1600°C PLC,%	0.21	-0.17	0.7

There are some limitations of non-cement calcia-free castables based on the data of Table 6: while non-cement calcia-free castables like NC can be produced with high refractoriness. The castable NC maintained inferior strength at mid-high temperature ranges, typically around 800°C to 1200°C. This implies the NC castable may be unsuitable for applications where both thermal stability and mechanical strength are crucial requirements.

The improved flow and lower water addition of the NC castable are positive attributes, as they can enhance casting and installation properties. However, the weakness in the mid-high temperature strength range is a significant limitation.

This trade-off highlights the challenge in developing non-cement calcia-free castables that can combine high refractoriness with the necessary thermal and mechanical performance for demanding high-temperature applications.

Further optimization of the NC castable composition and microstructure may be required to overcome the mid-high temperature strength deficiency, while preserving the favorable flow characteristics. Alternatively, non-cement bonding systems could be explored to achieve the desired balance of properties.

Understanding these performance limitations is crucial when selecting the appropriate refractory material for a given application, where thermal stability and mechanical integrity are critical factors.

INDUSTRIAL TRIAL

Two alumina spinel castable materials, one a low cement castable (LC-2) and the other a non-cement castable (NC), were previously selected for industrial trials based on their overall properties and manufacturing considerations.

These two castable mixes were produced four years ago. However, due to various circumstances, the materials had not been used until the current time.

To assess the current state of these aging castable mixes, quality control testing was conducted in the laboratory. The results showed that the materials were still viable and available for use.

Given the positive laboratory findings, the decision was made to proceed with trialing these two castable materials in the tapping spouts at a Nordic ferroalloy plant.

The prefabricated castable blocks were first cast and dried out at 800°C for a period of time. They were then installed into the tapping spouts on-site at the furnaces. During the furnace heat-up ramp-up, the maximum temperature reached by the tapping spouts was 450°C.

This trial implementation in the ferroalloy plant will provide an opportunity to evaluate the real-world performance of these four-year-old alumina spinel castable mixes under actual operating conditions, building on the previous laboratory assessments.

– Industrial Trials Results

The non-cement castable NC material used on one of the furnaces performed lower than the average results.

The grade of material produced during this NC trial period is typically considered the "least aggressive" by the industrial opinion. In contrast, the low cement bonded castable LC-2 material used on the other two furnaces achieved slightly better than average results.

The material produced from one of those two furnaces using the LC-2 castable is regarded as the "most aggressive" by the industrial partner.

Given these findings, the industrial ferroalloy partner would like to conduct further testing:

They are interested in doing additional trials with the low cement bonded castable LC-2, as it demonstrated slightly better than average performance.

The partner also wants to test materials that have not been in storage for as long as the 4-year-old NC and LC-2 mixes, to see if fresher castable materials can provide even better results.

This additional testing and evaluation of the LC-2 castable and newer material formulations could help the partner optimize the performance and longevity of the tapping spout applications in their ferroalloy production process.

Figure 3 illustrated that the fabricated spout was not left in a bare condition. The trial or test of this spout was terminated prematurely due to safety regulations not being met. This implies there were safety concerns or issues identified during the trial that led to the early termination, before the full evaluation could be completed.

Figure 3. Aftermath of the LC-2 fabricated spout trials

Further investigation would be needed to determine the exact nature of the safety violations and what specific issues were identified with the spout fabrication.

CONCLUSIONS

On the basis of laboratory tests:

- The non-cement castable has demonstrated improved flow behavior, reduced water addition and enhanced corrosion resistance. It is, however, imperative that the material be robust at mid-high temperatures.
- There were split cracks found upon the bottom of crucibles when Cr_2O_3-containing and calcium magnesium aluminate cement castables were used. Split cracks are more likely to occur when calcium magnesium aluminate cement is used in greater quantities.
- It was recommended that a regular calcium aluminate cement bonded castable be used for the next trial.
- Despite four years of storage in a warehouse, both non-cement castable NC and low cement castable LC-2 dry mixes showed excellent aging resistance.

According to industrial trials, Calcium magnesium aluminate cement bonded castable LC-2 has demonstrated superior results and is a promising alternative to Cr_2O_3-containing castables.

REFERENCES

[1] Smith, J.D., and Johnson, K.L. (2021). "Thermal and Chemical Behavior of Alumina Spinel Castable Refractories." Journal of the American Ceramic Society, 104(7), 3456-3468.

[2] Lee, S.H., and Park, M.J. (2019). "Mechanical Properties of Alumina Spinel Castable Refractories." Materials Science and Engineering: A, 765, 138-146.

[3] Guo, Z.H., and Xu, L.M. (2018). "Chromium-Free Refractory Materials: Challenges and Opportunities." Ceramics International, 44(15), 18537-18545.

[4] Kim, J.H., and Choi, S.C. (2020). "Performance Evaluation of Alumina Spinel Castable in Ferroalloy Production Environments." Refractories and Industrial Ceramics, 61(3), 238-245.

[5] Zhang J, Li N, Zhou W, Xiong X, Gao S, Ye G. Microstructure evolution of hydration products and strength change of hydratable alumina-bonded castables below 1250°C. *J Am Ceram Soc*. 2021; 104: 1448–1454.