

D. Gregurek, T. Prietl, S.B. Breyner, A. Ressler, N.M. Berghofer

INNOVATIVE MAGNESIA-CHROME FUSED GRAIN MATERIAL FOR NON-FERROUS METALS REFRACTORY APPLICATIONS

D. Gregurek	RHI AG, TC Leoben
T. Prietl	RHI AG
S.B. Breyner	RHI AG, TC Leoben
A. Ressler	RHI AG, TC Leoben
N.-M. Berghofer	RHI AG

Abstract

The complexity of metallurgical processes in the non-ferrous metals industry, especially changes in the process conditions in combination with a diversity of metal processing furnaces, requires a precise knowledge of the system for the selection of refractory products. However, particular importance is still focused on the specific refractory consumption being as low as possible.

The addition of recycling material with a high amount of impurities and the increase of low-grade ore concentrates used in the base-metals industry also entails a significant change of slag chemistries, process temperatures, etc., which influence the performance of already approved linings.

This acknowledgement of process changes with decreased brick lifetimes provided the motivation for RHI AG to develop high-performance refractory bricks especially for non-ferrous metals applications. The internal laboratory tests with fayalitic slag showed very promising results compared with our approved magnesia-chromite bricks for this application.

In order to identify suitable refractory products and to improve the life of the refractory lining, innovative product development has to be undertaken. In addition, the practical corrosion testing methods and facilities available within the RHI Technology Center, such as the induction furnace and the rotary kiln test equipment, allows the best possible understanding of brick wear at a laboratory scale. Based on the results of the test work, the optimal refractory solution can be recommended for a field trial at the customer's site.

Introduction

The complexity of metallurgical processes in the non-ferrous metals industry, and especially changes in the process conditions in combination with the diversity of metal processing furnaces¹, requires a precise understanding of each individual system for the selection of refractory products². In addition to this, particular importance is paid to the specific refractory consumption being as low as possible.

Another important aspect results from the global shortage of resources, which forces companies to invest in recycling processes. In the base-metals industry, recycling operations provoked significant changes; for example, operating with changing slag basicities and process temperatures will influence the performance of previously suitable linings. The raw material mix for primary smelters has also changed, e.g. higher levels of secondary raw materials in the smelter feed are used. Also, in the platinum group metals (PGM) industry the slag composition has changed due to the higher Cr content in the concentrate, thus resulting in higher solidus temperatures of the slag accelerating the chemical corrosion mechanism at the slag/refractory interface.

In order to improve the lining life for specific non-ferrous metals applications, test procedures have to be developed to simulate the various demanding service conditions. The RHI Technology Center in Leoben, Austria, combines practical corrosion testing methods and equipment (e.g. an induction furnace and rotary kiln) with various microscopy facilities to enable a comprehensive understanding of brick wear following pilot-scale trials³⁻⁶. Based on the test results, optimal refractory solutions can be recommended for field trials directly at the customer's site.

Development work, testing facilities, and analytical procedure

The new magnesia-chromite brick RADEX VFG consists of newly-developed fused magnesia-chromite smelter material. Chrome ore (low in silica) was added additionally to increase the resistance to corrosion and thermal shock. The microstructure of the newly developed brick brand is presented in Figure 1.

Figure 2 shows the smelter plant (pilot plant at the TCL) in which the fused magnesia-chromite material was produced. After positive chemical, physical and mineralogical material characterization of the first melting blocks (up to 400 kg) the RHI Radenthein plant started with industrial production of that material. The first successful brick production at the Radenthein smelter plant was completed in July 2011 after numerous laboratory and industrial scale trials.

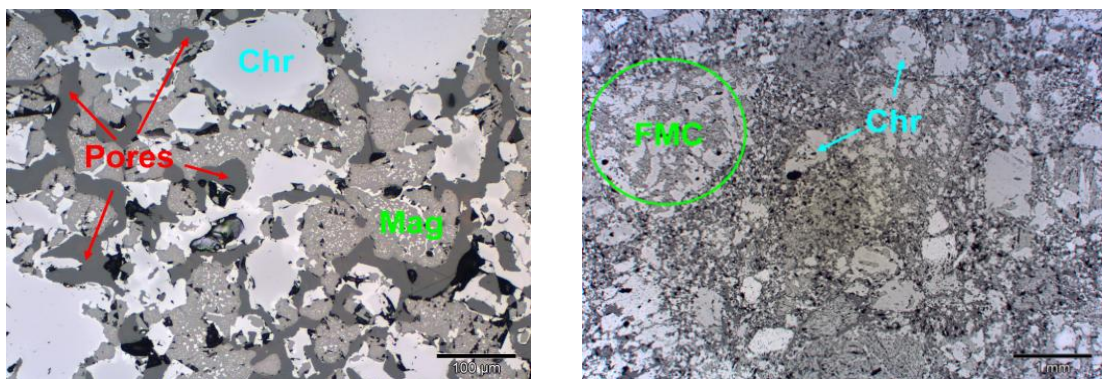


Figure 1-Microstrutural overview/detail. Microstructure of RADEX VFG with newly developed fused magnesia-chromre smelter (FMC) and chromite (Chr). Pores filled with preparation resin



Figure 2- Raw material synthesis at TC Leoben

Rotary furnace and induction furnace tests were carried out at the RHI Technology Center to determine the corrosion resistance of the newly-developed magnesia-chromite brick to fayalite-type process slag. A typical chemical analysis of a slag used for the test is shown in Table I. The results were compared with the standard magnesia-chromite and alumina-chrome brands.

Table I-Typical chemical composition of a slag used for the test trials

MgO	Cr ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	CaO	SiO ₂	SO ₃	CuO	NiO	PbO	SnO ₂	ZnO
0.6%	0.2%	2%	49%	0.7%	25%	1%	5%	0.7%	7%	2%	7%

Four magnesia-chromite brands (i.e., RADEX OX6, RADEX BCF-F23, RADEX FG, and RADEX VFG) and one alumina-chromia brand (i.e., RESISTAL RK10) were tested in both furnace tests. RADEX OX6 is a high-quality magnesia-chromite brick (type MCr 50, ISO 10081-2) based on magnesia-chromite co-clinker (i.e., OXICROM sinter) and chrome ore. RADEX BCF-F23 and RADEX FG are also high-quality magnesia-chromite bricks (types MCr60 and MCr50, respectively) based on fused magnesia-chromite and chrome ore. The newly developed RADEX VFG contains fused magnesia-chromite and has a higher Cr₂O₃ content⁷. RESISTAL RK10 is an alumina-chromia brick (type ACr80/5 ISO 10081-4) based on fused alumina and chromium oxide.

The rotary furnace is relatively small (92 mm in diameter); however, up to six different brick brands can be installed and tested simultaneously (Figure 3). Trials are usually performed within a temperature range of 1400–1700°C. The furnace is heated using a propane-oxygen gas mixture. During the test, 3–5 kg of slag is used per cycle. The specific analysis described in this paper was carried out for 20 cycles at 1600°C. The rotation of the furnace also results in a dynamic testing procedure.

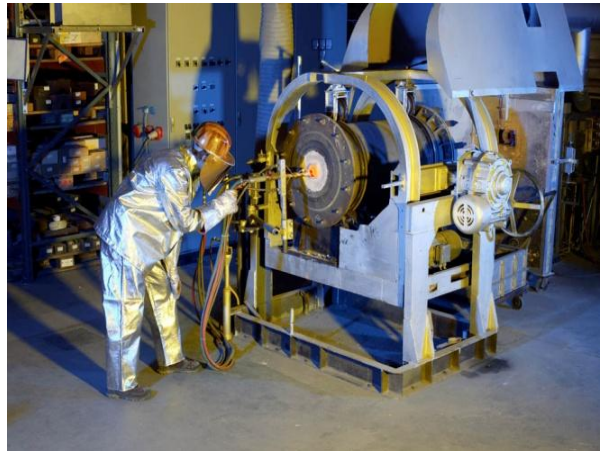


Figure 3-Rotary kiln test

Up to 16 different grades can be used to line the induction furnace (Figure 4). The furnace is 250 mm in diameter and operates in a temperature range of 1500°C to 1750°C (1650°C for the tests described). During the practical test, up to 60 kg of metal and 1.5–2 kg slag are used per cycle, and the slag is changed every 0.5–1.5 hours. The test described here was run for approximately 6 hours.



Figure 4-Induction furnace test

The macroscopic overviews of all the tested bricks, in cross section, are shown in Figures 5 and 6. Table II summarizes the results of both trials, including the evaluation of the wear area/depth in terms of the final cross-sectional profile. The mineralogical investigations were performed on polished sections using a reflected light microscope and a scanning electron microscope combined with an energy-dispersive X-ray analyser (Figures 7 to 9).

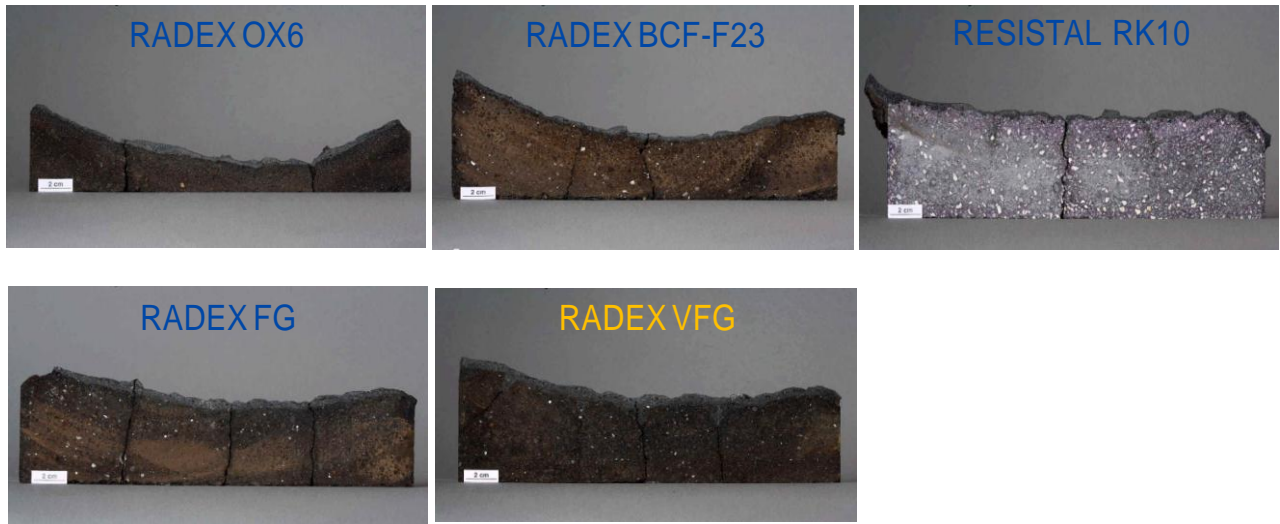


Figure 5-Magnesia-chromite RADEX OX6, RADEX BCF-F23, RADEX FG, RADEX VFG, and alumina-chromia RESISTAL RK10 bricks after the rotary kiln test

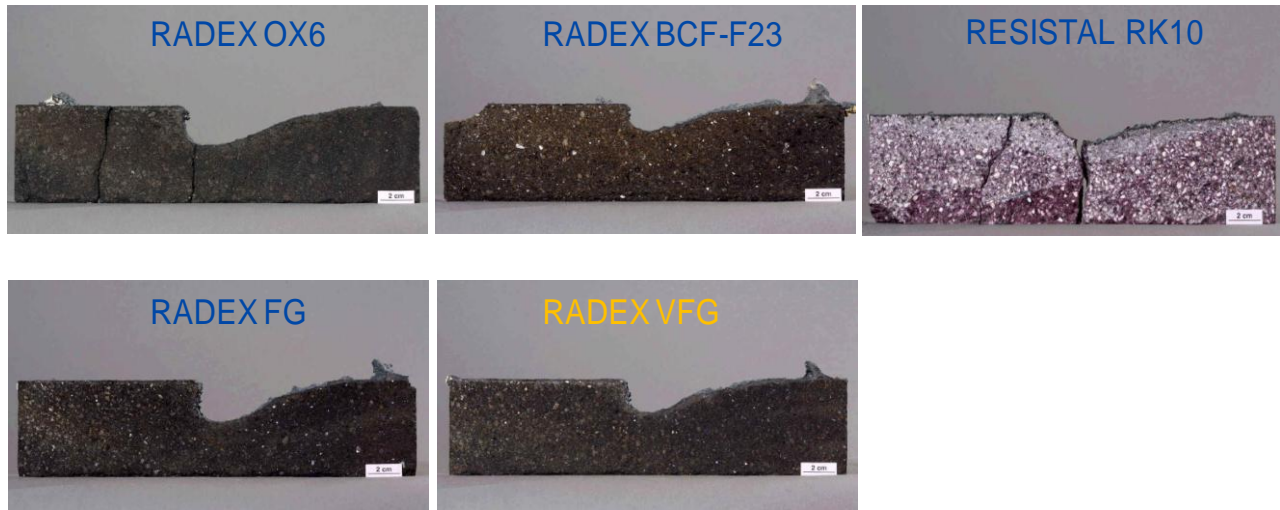


Figure 6-Magnesia-chromite RADEX OX6, RADEX BCF-F23, RADEX FG, RADEX VFG, and alumina-chromia RESISTAL RK10 bricks after the induction furnace test

Table II-Results of the rotary kiln and induction furnace tests

Brick brand	Rotary kiln test (1600°C)		Induction furnace test (1650°C)	
	Wear area*	Wear depth*	Wear area*	Wear depth*
	(cm ²)	(mm)	(cm ²)	(mm)
RADEX OX6	109	57	15	27
RADEX BCF-F23	70	39	8	16
RADEX FG	38	24	13	25
RADEX VFG	33	21	10	21
RESISTAL RK10	28	16	9	15

*based on macroscopic investigation and wear evaluation from the final cross-sectional profile

Experimental results

Macroscopic appearance

According to the macroscopic appearance (cross-sections), the best performing bricks, in terms of the wear area and wear depth, were RADEX VFG and the alumina-chromia brick RESISTAL RK10. The highest wear was observed for RADEX OX6.

Mineralogical investigation

The main microstructural changes of the investigated magnesia-chromite bricks after the rotary kiln and induction furnace tests are summarized below.

The immediate brick hot face was covered with a thin reaction zone of 3–5 mm. Behind the reaction zone, an infiltrated and corroded brick microstructure could be observed. The infiltration depth varied between 2–17 mm. The lowest infiltration of the brick microstructure was exhibited by RADEX VFG and RADEX FG (approximately 3 mm). The highest infiltration depth was observed for RADEX OX6 (up to 17 mm), which showed complete infiltration over the entire polished section.

At the transition between the reaction zone and the infiltrated brick microstructure there was dissolution of the magnesia brick component, leaving relics of primary and secondary chromite precipitations. Due to diffusion phenomena, the chemical composition of the chromite was also altered, becoming enriched with mainly Fe-oxide at the rims. This was also observed for primary and secondary chromite precipitations.

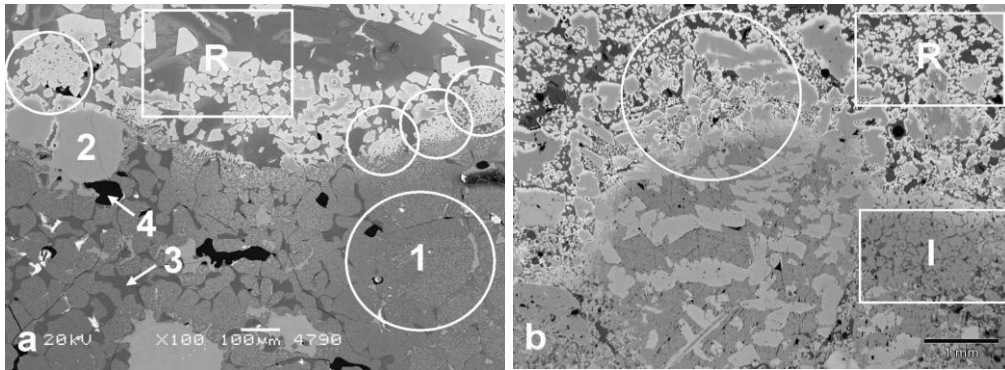


Figure 7-Microstructural overview/detail, immediate brick hot face. (a) RADEX OX6, (b) RADEX VFG. Reaction layer (R), infiltrated and corroded brick microstructure (I), relics of chromite precipitations (circles) after the corrosion and dissolution of magnesia within the OXICROM sinter (1), chromite (2), forsterite (3), pore (4)

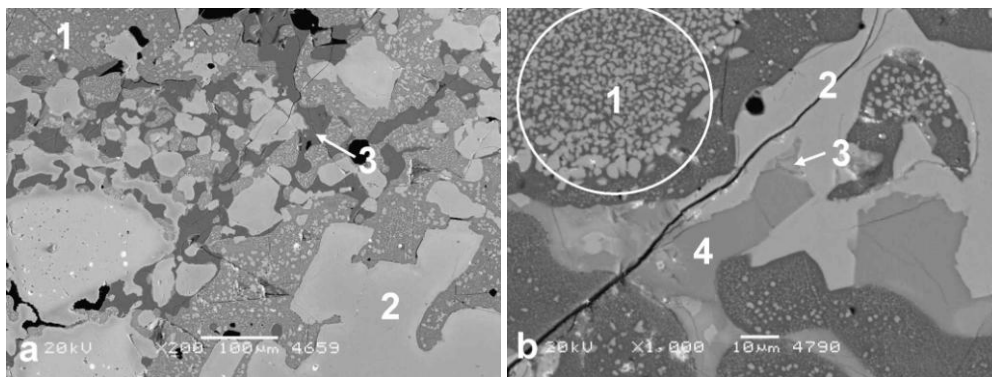


Figure 8-(a) RADEX VFG, microstructural detail, approx. 1 mm from the brick hot face. Infiltrated and corroded brick microstructure. Fused MgCr-grain (1), chromite (2), forsterite (3). (b) RADEX OX6. Microstructural detail, approx. 20 mm from hot face. OXICROM sinter (1), chromite (2), corrosion of the interstitial phase dicalcium silicate (C₂S) (3), merwinite (4)

In the infiltrated brick microstructure, due to corrosion of the magnesia brick component, the main reaction product was Mg-silicate forsterite (M₂S). In addition, the interstitial phase of the magnesia component, especially the dicalcium silicate (C₂S), was corroded. The main reaction product was monticellite (CMS).

The alumina-chromia RESISTAL RK10 brick showed an infiltration depth of approximately 5–10 mm. At the transition between the reaction zone and the infiltrated brick microstructure, fused alumina Mg-Fe-Al-Cr-oxide was formed due to corrosion of the main brick component. In the infiltrated brick microstructure the second main brick component, namely Zr-mullite, was also corroded. Within the infiltrated brick area the Cr-corundum bearing matrix had recrystallized.

The alumina-chromia RESISTAL RK10 brick showed an infiltration depth of approximately 5–10 mm. At the transition between the reaction zone and the infiltrated brick microstructure, fused alumina Mg-Fe-Al-Cr-oxide had formed due to corrosion of the main brick component. In the infiltrated brick microstructure the second main brick component, namely Zr-mullite, was also corroded. Within the infiltrated brick area the Cr-corundum bearing matrix had recrystallized.

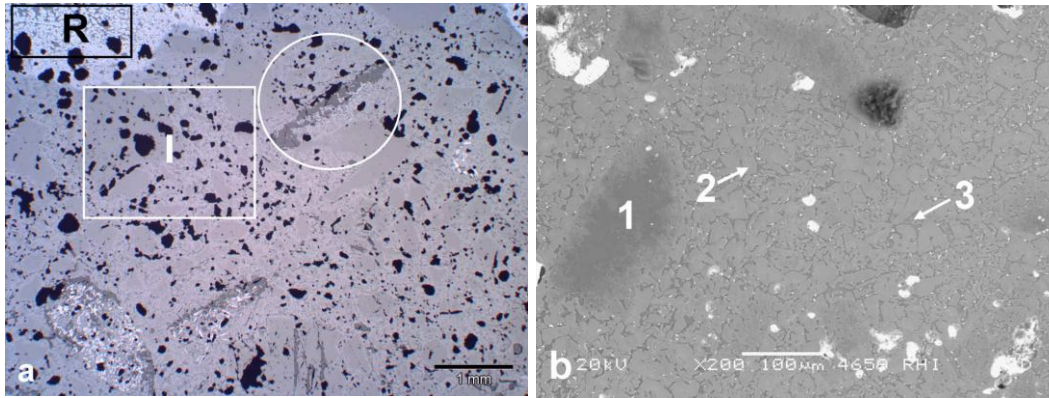


Figure 9-(a) Microstructural overview, immediate hot face. (b) Microstructural detail, approx. 5 mm from hot face. Reaction layer (R), infiltrated and degenerated brick microstructure (I), corroded Zr-mullite (circle), white fused alumina (1), Cr-corundum (2), phosphorus-bearing glassy phase (3)

Conclusion

The results obtained from the pilot-scale trials indicate that the newly-developed magnesia-chromite RADEX VFG brick exhibited the lowest wear among the tested basic bricks. The mineralogical analysis showed that all the basic brick brands experienced very similar corrosion phenomena, but each had a different infiltration depth.

Similar to RADEX VFG, the alumina-chromia brick RESISTAL RK10 also showed very low wear at a macroscopic level. Nevertheless, the infiltration depth was slightly higher compared to the basic brick brands comprising fused magnesia-chromite and chrome ore.

A comparison of the rotary kiln and induction furnace test results showed minimal differences in the wear levels of the individual brick brands. The RADEX BCF-F23, RADEX VFG and RESISTAL RK showed similar performance in terms of corrosion resistance. There was only a minor difference between RADEX OX6 and RADEX FG, both of which showed the highest wear.

Currently, various field trials at different smelters (primary and secondary smelters) are planned, and a number are already in progress. RADEX VFG will be tested in high-wear areas, especially in slag linings of primary and secondary smelters, tuyere surroundings, tap-hole areas, and the end-walls of short rotary furnaces for copper and lead treatment. The details will be presented as soon as they are available.

An additional advantage of the RADEX VFG magnesia-chromite brand is the lower Fe_2O_3 content (<10 wt.%), providing increased resistance under reducing conditions. The increased abrasion and corrosion resistance will also be an additional advantage of this brand in pyrometallurgical vessels with high bath agitation in combination with aggressive corrosion attack.

References

1. Davenport W.G. et al. Extractive Metallurgy of Copper. Elsevier Science, Kidlington, Oxford, UK, 2002. p. 432.
2. Routschka, G. Refractory Materials. Essen, Vulkan-Verlag GmbH, 2004. p. 512.
3. Nilica, R. Variations of fused magnesia-chromite material. Internal report, RHI Technology Center, Leoben, Austria, 2010.
4. Jörg, S. Rotary slag test on newly developed fused magnesia-chromite material and RADEX FG. Internal report, RHI Technology Center, Leoben, Austria, 2010.
5. Jörg, S. Rotary slag test on fused magnesia-chromite and OC4 alternatives. Internal report, RHI Technology Center, Leoben, Austria, 2011.
6. Gregurek, D. and Ressler, A. Investigation of basic and non-basic bricks after the rotary- and induction furnace tests. Internal report, RHI Technology Center, Leoben, Austria, 2011.
7. Breyner, S. Fused magnesia-chromite based fired basic bricks. Internal report, RHI Technology Center, Leoben, Austria, 2010.

The Author



Dr. Dean Gregurek, *Mineralogical department*, RHI AG Technology Center Leoben

1996 finished study of petrology at KFU University of Graz

1999 finished PhD study at University of Leoben

1999-2001 worked for Luzenac Europe (talc business)

2001- RHI AG (Technology Center Leoben -mineralogical department)

specialized in post mortem studies of refractories in the NFM industry