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# Characterization of a nickel flash smelter refractory material – The effect of thermal gradient

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## ABSTRACT

Magnesia-chromite (MgCr<sub>2</sub>O<sub>4</sub>) spinel-based refractories are applied in nickel and copper flash smelting furnaces, where the refractories experience high temperatures but also thermal gradients due to the cooling of the walls. In the gas space, the refractories are subjected to an aggressive environment with high SO<sub>2</sub> concentrations. Furthermore, the increased use of recycled material streams has introduced new reactive impurities, such as halides, to the process. Therefore, the interactions between the refractories and gaseous species as well as the related reaction mechanisms need to be understood. This study presents a comparison between as-received and spent refractories from a nickel flash smelting furnace to identify the reactive species and shed light on their reaction mechanisms. The thermal gradient over the refractory is expected to affect the microstructure and contribute to the diffusion of elements within the structure. Therefore, special attention was paid to the role of the thermal gradient in the abovementioned interactions.

## KEYWORDS

Flash-smelting, Gas-phase reactions, Thermal gradient, Refractory wear

## INTRODUCTION

The flash smelting process is one of the most widely used methods to extract nickel from sulfide ores due to its cost-effectiveness and environmentally sustainable nature; once initiated, the process is continuous and nearly autothermal [1,2]. In particular, the use of sulfide ore concentrates as feedstock results in high SO<sub>2</sub> concentrations in the gas phase of the smelter, up to 70 vol.% [3,4]. The availability of high-grade sulfidic nickel ores has decreased, and therefore, lower-grade ores with higher amounts of impurities are processed. Nickel-bearing side streams from other processes may be processed to recover valuable metals and they may contain new types of impurities. To protect the structural materials of the smelter interior, it is covered with ceramic refractories, usually based on a magnesia-chromite (MgCr<sub>2</sub>O<sub>4</sub>) spinel. This material is known to possess excellent durability against heat, thermal shocks, and melt erosion forces [5,6]. In addition to the interactions with the reactive gaseous compounds, the refractories experience a thermal gradient of around 1000 °C over the material. Such harsh conditions may result in the gradual degradation of the refractories over time.

The reactions between the phases included in the magnesia-chromite refractories and the flash-smelting environment have been addressed previously in a few fundamental studies [7-10]. However, the aging of refractories in nickel flash smelting furnaces is rarely addressed in the literature. Because of this, very little is known about the degradation of gas-space refractories. Another feature, the effect of which on refractory behavior is unknown, is the significant thermal gradient over the refractory material in the furnace. To better understand the interactions between the gas phase and the refractory material, and how the thermal gradient affects the migration of species into the material, unused refractories and spent refractories sampled from a nickel flash-smelting furnace were analyzed and compared. Furthermore, a comparison was also done with samples in contact with nickel flash smelting slag to elucidate the specific effect of the SO<sub>2</sub>-containing gas phase on the refractory lining.

## MATERIALS AND METHODS

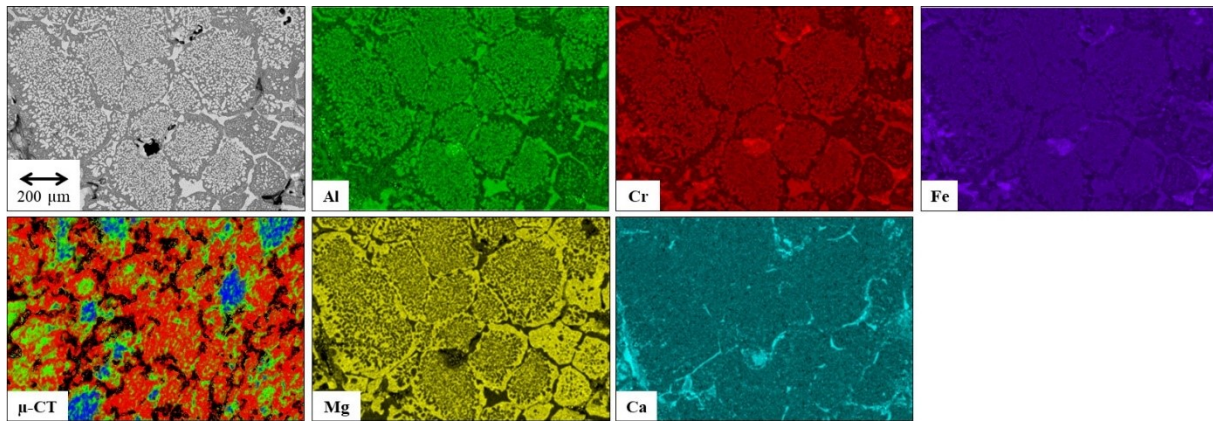
The studied material was a magnesia-chromite product of type MCr50, ISO 10081-2, with a given composition of (in wt.%): 59.5 MgO, 19.0 Cr<sub>2</sub>O<sub>3</sub>, 13.5 Fe<sub>2</sub>O<sub>3</sub>, 6.0 Al<sub>2</sub>O<sub>3</sub>, 1.3 CaO, and 0.5 SiO<sub>2</sub>, with an apparent porosity of 17.0 vol.%. The microstructure of as-received material was analyzed and compared to that of spent refractories from the roof lining of a nickel flash smelting furnace. The characterization was carried out with scanning electron

microscopy (SEM), energy-dispersive spectroscopy (EDS), electron back-scattered diffraction (EBSD), micro-computed tomography ( $\mu$ -CT), and X-ray diffraction (XRD).

Refractory fingers were inserted into a crucible filled with slag in an induction furnace. The hold time at 1450 °C was six hours and during that time an inert gaseous atmosphere was created with argon. After cooling, cross-sectional samples were prepared for microscopy investigation. The main constituents of the slag were 7% MgO, 4% NiO, 31% SiO<sub>2</sub>, and 52% of iron oxides.

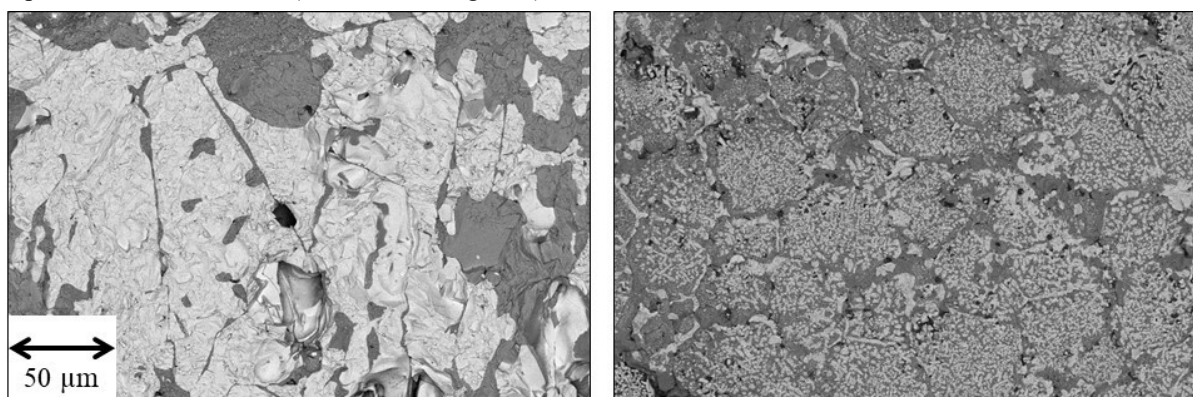
## RESULTS AND DISCUSSION

Two phases were identified in the as-received material with XRD: a MgO (magnesia; periclase) phase and a (Fe,Mg)(Al,Cr)<sub>2</sub>O<sub>4</sub> (magnesia-chromite spinel; picotite) phase. Cross-sectional SEM-EDS examinations supported this observation. In addition, Ca-rich areas were identified in the vicinity of MgO areas with EDS (Fig. 1). The porosity and density distribution of the as-received material was specified with  $\mu$ -CT, revealing the porosity of 10 % and three types of regions with different densities. Based on phase identification and elemental analyses, it was possible to define that low-density areas consisted mainly of MgO, medium-density areas of MgCr<sub>2</sub>O<sub>4</sub> precipitates and (Fe,Mg)(Al,Cr)<sub>2</sub>O<sub>4</sub> embedded in MgO, and high-density areas of larger MgCr<sub>2</sub>O<sub>4</sub> and/or (Fe,Mg)(Al,Cr)<sub>2</sub>O<sub>4</sub> regions. The difference in the porosities given by the manufacturer (17 %) and measured with  $\mu$ -CT (10 %) likely originates from the set threshold values for the  $\mu$ -CT measurement. However, the combinatory characterization of the microstructure and composition of the refractory material by several methods provided novel information regarding the three-dimensional phase and elemental distributions. Furthermore, the results function as a reference point to the characterization of the spent refractories.



**Figure 1.** A cross-sectional SEM image of the as-received material with the corresponding elemental EDS maps. The left image on the lower row is a three-dimensional  $\mu$ -CT density map of the ac-received material.

Regarding the spent refractories, the exposure to high temperatures and a reactive process environment resulted in changes in the microstructure in comparison to the as-received material. Close to the process environment, the morphology of the spent refractory was essentially denser, showing clear signs of sintering (Fig. 2), whereas the microstructure of the material in the colder end of the refractory was similar to that of the as-received material. Based on  $\mu$ -XRF images, the slag had not penetrated the material. Process material had created a separate reaction layer on top of the refractory but no penetration of components into the pores of materials was observed. The only visually observable differences of the colder end were the lower porosity compared to the as-received material and the presence of microcracks (not shown in Figure 2).





**Figure 2.** Two example cross-sectional SEM images of the microstructure of a spent refractory; close to the process environment (left) and towards the colder end of the refractory (right).

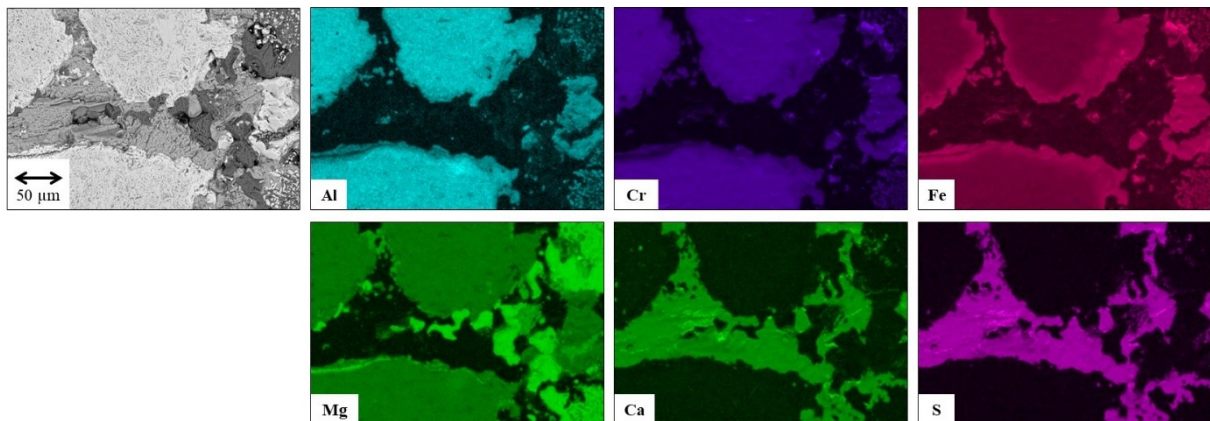
In the elemental maps of the spent refractory, areas rich in Ca, O, and S were identified between the  $(\text{Fe,Mg})(\text{Al,Cr})_2\text{O}_4$  (Fig. 3). This indicates the presence of calcium sulfate ( $\text{CaSO}_4$ ), which may have formed in the reaction with  $\text{SO}_2$  [11]:



or with  $\text{SO}_3$ :

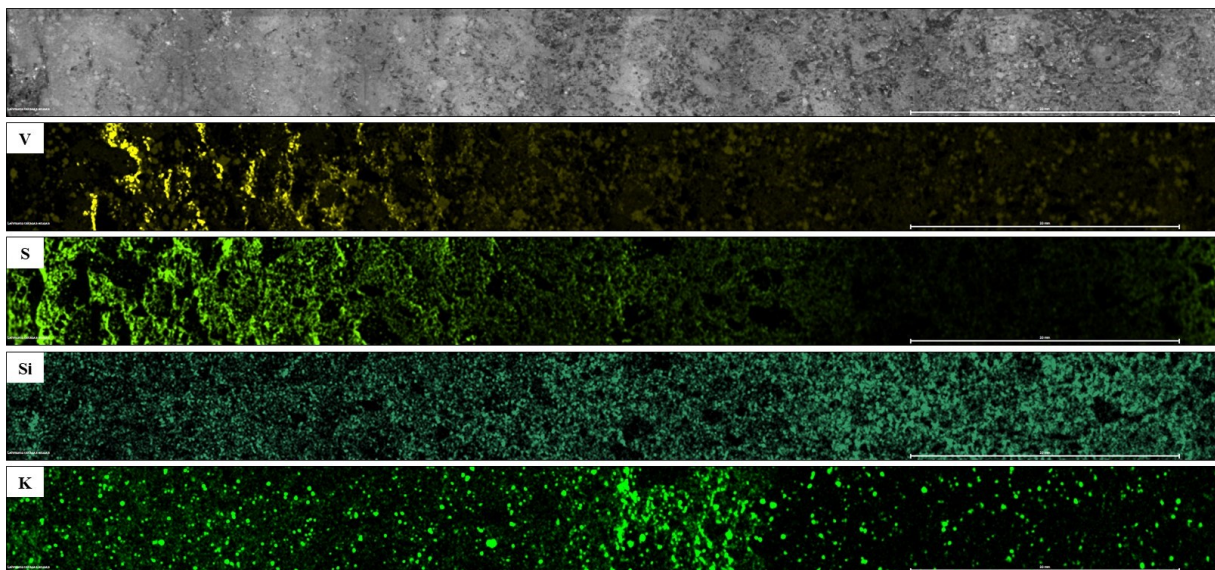


Typical process dust of a nickel flash smelting furnace is known to catalyze the  $\text{SO}_2$ -to- $\text{SO}_3$  conversion [12], so either or both of the sulfur oxides may have reacted with the refractory. The loss of porosity shown in Figure 2 can at least partly be explained by the formation of  $\text{CaSO}_4$ : since the molar volume of  $\text{CaSO}_4$  is roughly three times that of  $\text{CaO}$ , the pores were filled through the increase in the internal volume. However, no extensive microcracking was seen close to the  $\text{CaSO}_4$ -rich areas. Thus, the formation of  $\text{CaSO}_4$  alone does not explain the degradation of the refractory material through cracking.



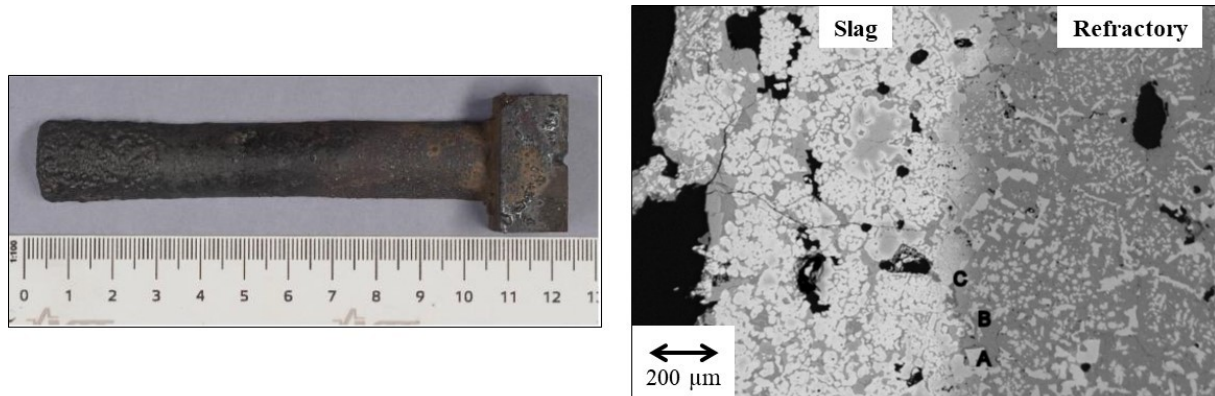
**Figure 3.** A cross-sectional SEM image of the spent refractory material with the corresponding elemental EDS maps.

When analyzing cross-sectional samples of the spent refractories with  $\mu$ -XRF, other elements in addition to S were identified (Fig. 4). The depth of diffusion and the concentration profile depended on the element. Due to the chemical complexity of the flash smelter gas phase, it is still to be clarified, how exactly does the temperature gradient affect the diffusion of different elements and whether the penetration and possible reactivity of these species play a role in the refractory wear. Nonetheless, the identified species indicate that the porosity in the refractory brick is high enough for gaseous species to diffuse into the refractory, possibly affecting the lifetime of the material.



**Figure 4.**  $\mu$ -XRF maps showing examples of the effect of the temperature gradient on diffusion in a spent refractory brick from the roof lining of a nickel flash smelting furnace. The cooler end of the sample is to the left.

In the immersion tests, the slag had evidently reacted with the refractory, for some slag had deposited onto the refractory surface, forming a dense interface between the two materials (Fig. 5). When the chemical composition of the slag was analyzed after the immersion test, it contained higher amounts of Cr and Al compared to the initial composition. Furthermore, Ca had leached into the slag. The dissolution of Cr, Al, and Ca from the refractory provided further evidence of the interaction between the slag and the refractory. This may eventually influence the stability of the phases and contribute to the selection of elements, which are available to react with the gas phase. For example, if no Ca is available,  $\text{SO}_2/\text{SO}_3$  in the gas phase might react with MgO instead, forming  $\text{MgSO}_4$  analogously to Reactions (1) and (2).



**Figure 5.** A refractory sample and an SEM cross-sectional image of the slag/refractory interface after the immersion test.

## CONCLUSIONS

The microstructure of as-received magnesia-chromite ( $\text{MgCr}_2\text{O}_4$ ) spinel-based refractories was compared with similar refractories collected from the gas-phase lining of a nickel flash smelting furnace. The main focus of the comparison lay on the interactions between gaseous species and the refractory material. Special emphasis was put on the role of the prevailing temperature gradient in the diffusion of species into the refractory material. In another set of comparative tests, refractory samples were immersed in nickel flash smelting slag to further clarify, which structural or chemical changes in the refractory originate from the interactions with the gas phase. Based on the results, further conclusions can be drawn:

- The porosity of the refractory allows gaseous species to diffuse deep into the material.
- Temperature gradient affects both the microstructure of the material and the penetration depth of gaseous species.
- Elements such as As, K, Pb, and S were identified inside the refractory. Sulfur had reacted with Ca, forming  $\text{CaSO}_4$ , which led to voluminal changes, and possibly, the formation of internal stresses.
- The possible reactions including other penetrated species need to be studied further. However, their role in refractory wear cannot yet be excluded.
- Similarly to the reactions with the gas phase, interactions with the slag resulted in a densified microstructure.
- Although the reactions between the slag and the refractory material are not considered to be as significant as the gas phase-related reactions, the leaching of Ca from the refractory to the slag may contribute to the formation of  $\text{MgSO}_4$  instead of  $\text{CaSO}_4$  within the refractory.

As for future studies, To better understand the effect of thermal gradient on the diffusion of impurities, controlled laboratory-scale experiments with individual gaseous species should be carried out in the presence of a thermal gradient. Furthermore, modeling on the gas-phase stability and solidification of species would support the interpretation of  $\mu$ -XRF results, for example. Experiments on how the changes in the microstructure and chemical interactions with the impurities affect the mechanical properties of refractories would most likely provide valuable information about the role of cracking, for example, in the wear process.

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