Physicochem. Probl. Miner. Process., 61(2), 2025, 202839

http://www.journalssystem.com/ppmp

Steel making dust recycling: melting behavior and interactions with refractory bricks

Marko Kekkonen ¹, Diederik van Roemburg ^{1,2}, Lassi Klemettinen ¹, Pekka Taskinen ¹, Mari Lindgren ³, Daniel Lindberg ¹

¹ Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Espoo, Finland

² Brunel, Rotterdam, the Netherlands

³Metso Research Center, Pori, Finland

Corresponding author: marko.kekkonen@aalto.fi (Marko Kekkonen)

Abstract: Stainless steel production generates significant quantities of flue dusts, which are considered as hazardous waste in most industrialized countries as they contain harmful elements, such as heavy metals. On the other hand, the dusts also contain valuable metals, such as steel alloying elements, but the recovery of the valuables is difficult due to the complex composition of the dusts. In this work, the melting behavior of dusts from an Electric Arc Furnace and an Argon Oxygen Decarburization converter were investigated at temperatures 800-1400 °C. In addition, the interaction between a synthetic dust, with high concentrations of potassium, fluorine and chlorine, and selected refractories was studied at 1300 °C mimicking the freeboard conditions of a dust smelting furnace. Melting of the EAF dusts begun in the temperature region of 1250-1300 °C depending on the composition, whereas AOD flue dust, because of its high fluorine content, had a melt fraction of approximately 30 % already at 1200 °C. The present experiments showed that magnesia has good corrosion resistance against potassium vapors at 1300 °C and the penetration depth of potassium into chromium-containing refractories seem to be more susceptible to volume expansion than the other refractories studied, causing cracks through which potassium vapors can easily penetrate deep into the refractory lining.

Keywords: steel dust recycling, melting behavior, electric arc furnace, argon-oxygen decarburization, stainless steel

1. Introduction

The demand for stainless steel (SS) has grown in years 1980-2021 faster than the demand of other major metals, such as copper and aluminum (World Stainless Association, 2022). The growing demand means that the amounts of by-products generated in the steel production process, such as steel dust, also increase. Producing one ton of SS generates 30–70 kg flue dust (Denton et al., 2005), which in addition to zinc contains considerable amounts of other valuable metals, such as alloying elements chromium, nickel, and molybdenum, but also toxic elements like lead and cadmium (de Buzin et al., 2017). Because of the hazardous elements, SS dust is classified as a hazardous waste in most countries and requires treatment before disposal (Ndlovu et al., 2017). There are two main approaches for treating the dust: stabilization prior to landfilling and recycling to recover the valuable metals. The recycling of dusts has become increasingly important as the cost of stabilizing and disposing have increased (de Buzin et al., 2017) and more attention has been paid to environmental issues, sustainability, and circular economy. In addition to the economic benefits due to reduced landfilling waste, reducing the use of virgin raw materials, and lowering environmental impact are the keys to achieving sustainable SS production.

Several recycling processes have been developed for SS dust (Denton et al., 2005; Huaiwei and Xin, 2011; Ndlovu et al., 2017; Liu et al., 2021). They, however, have encountered some problems, like

operational difficulties, poor recovery and high energy requirements. Some of them are also quite complex, requiring auxiliary equipment with high investment and maintenance costs (Lin et al., 2017; Liu et al., 2021). Internal recycling of SS dust into the Electric Arc Furnace (EAF) is an option for recovering the alloying elements. It has been found to be economically viable as well as to improve the recoveries of iron and the alloying elements (Travernier et al., 2004; Takano et al., 2005). Moreover, it improves the value of dust due to increase of the zinc content (Drissen et al., 2002; Travernier et al., 2004). However, the high Zn-content of the EAF dusts also sets limitations for their recycling (Ndlovu et al., 2017). Other problematic elements are alkalis (K, Na) and halogens (Cl, F) (Ma and Garbers-Craig, 2006). It is noteworthy that chlorine content in the dust has increased in recent years because the Cl-containing impurities in the scrap have increased (de Buzin et al., 2017). Volatile components in the dust may penetrate the smelting furnace refractories and result in deterioration of refractory materials, reducing the reactor campaign life and the on-line availability. In addition, the variable composition of the SS dusts makes their recycling demanding and requires well-controlled processes (Kukurugya et al., 2012).

The research on flue dusts has been mainly focused on EAF dust from carbon steel production and less attention has been paid to SS dusts, especially to dust generated by the Argon Oxygen Decarburization (AOD) process. Characterization of SS flue dusts has been carried out through chemical, mineralogical, and morphological analyses (Dominguez et al., 2010; Kukurugya et al., 2012; Omran and Fabritius, 2017; Fan et al., 2017). Moreover, thermogravimetry has been used to study the thermal behavior (Mikhail et al., 1996; Peng et al., 2003; Omran and Fabritius, 2017) as well as reduction kinetics of stainless steel dust (Muvunyi et al., 2023). No studies concerning melting behavior of SS dusts were found in the literature. They would be important for understanding the behavior of dusts at high temperatures and providing guidance for their treatment and recovery of the metal values.

To fill this gap in knowledge, the melting behavior of EAF and AOD-converter dusts and the deportment of elements in different phases were examined in Part I of this study. Alkali metals exit the dust smelting furnace either along with the slag or with the off gas. In Part II, the focus was on alkali vapors since they are especially damaging when they penetrate deeply in the refractories and cause undesirable compound formation (Criado et al., 1981; Scudeller et al., 1990; Lee and Brown, 1995; Dastidar et al., 2018). This may limit the service life of the refractories and lead to costly down time. Thus, the effects of volatile components in SS dusts on different refractory materials were studied for efficient and safe operation of the flue dust smelting and recovery processes.

2. Materials and methods

2.1. Materials and sample preparation

SS flue dusts mainly come from EAF and AOD steps of steel processing. In this study, the melting behavior of AOD dust and two types of EAF dusts (EAF1, EAF2) were investigated. The chemical compositions of the dusts are shown in Table 1. Most of the elements were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES; iCAP 7600, Thermo Scientific, USA) and a CS-2000 (Eltra, Germany) carbon/sulfur analyzer. SiO₂ concentrations were analyzed by decomposing the dust by fusing with sodium hydroxide. The fusion mixture was leached with acidified water and silica was determined spectrophotometrically as molybdenum-blue-silica complex. The halogen (Cl, F) concentrations were determined using Combustion Ion Chromatography (CIC) and a titrimetric method.

The chemical composition of SS flue dust varies considerably depending on the scrap types and other process input materials, the process used and its operating parameters as well as the steel grade produced. Variations can be relatively large even in the same process stage depending on the materials charged into the furnaces, as evidenced by the compositions of EAF1 and EAF2 dusts (Table 1) obtained from two different Electric Arc Furnaces. The main elements in the dusts are iron, chromium, zinc, and calcium oxides. In Table 1 elemental concentrations of Fe and Cr are shown due to the possibility of multiple oxidation states (i.e. FeO or Fe_2O_3) or presence as chromite (FeCr₂O₄) (Kukurugya et al., 2012). There is also a significant amount of silica in the dust. The source of chromium is ferrochrome and SS scrap. Zinc content in the dusts varied between 2 and 26 wt%, depending on the scrap used, and the ratio of galvanized scrap. The relatively high contents of calcium and magnesium in the dusts are due

to the addition of Ca- and Mg-bearing fluxes to the furnaces. In addition to chromium, flue dusts contain also other alloying elements, such as manganese, nickel, molybdenum, and minor amounts of lead and alkali metals (K, Na). Most elements were in the form of oxides, but chlorides, fluorides and sulfides/sulfates were also found in low concentrations.

Element	EAF1	EAF2	AOD
CaO	11.0	22.8	22.8
Cu ₂ O	0.3	0.6	0.3
K ₂ O	1.2	1.3	0.1
MgO	1.7	4.5	2.5
MnO	2.8	3.6	3.9
MoO ₂	0.04	0.4	1.7
SiO ₂	4.8	10.2	7.8
Na ₂ O	1.2	1.1	0.1
NiO	1.2	2.4	4.1
PbO	0.8	0.7	0.2
ZnO	31.6	7.0	3.4
Fe	23.0	16.3	31.8
Cr	2.8	7.4	8.7
С	0.3	2.6	0.4
S	0.3	0.4	0.06
Cl	1.9	0.4	< 0.1
F	0.2	0.5	1.3

Table 1. Chemical composition of the dust samples used (wt%)

For the melting behavior experiments, the dust powders were pressed uniaxially into briquettes weighing approximately 0.2 grams, applying pressure of 5 tons. To investigate the interaction between the dust and the refractory lining material, a synthetic dust having a composition of 50 wt% K₂CO₃, 25 wt% KF and 25 wt% KCl was prepared by mixing K_2CO_3 (Sigma Aldrich, USA; purity: 99.5%), KF (Sigma Aldrich, USA; purity: 99%) and KCl (Alfa Aesar, Germany; purity: 99%) powders thoroughly and grinding in an agate mortar. These compounds were chosen for the synthetic dust due to the high volatilization tendency of (alkali) chlorides and partly also fluorides, see Chapter 3.2. The manufacturers' specifications for the chemical compositions and apparent porosity of the refractory bricks used in the experiments are shown in Table 2.

Table 2. Chemical composition and apparent porosity of the used refractories

		Chemical composition (wt%)							Apparent porosity
Refractory brick	MgO	Al_2O_3	Cr_2O_3	SiO_2	Fe ₂ O ₃	ZrO_2	CaO	Others	(vol%)
Magnesia-chromite (ceramic*)	59.5	6.0	19.0	0.5	13.5	-	1.3	0.2	17.0
Magnesia (ceramic)	97.0	0.1	-	0.6	0.2	-	1.9	0.2	15.0
Alumina-chromia (chemical (fired))	-	64.0	28.0	2.1	-	3.0	-	2.9	15.0
High alumina (ceramic)	-	89.0	-	10.0	0.1	-	-	0.9	15.5

* bonding type by the manufacturer

2.2. Equipment

The experiments were carried out in a vertical tube furnace (Lenton LTF 16/450, UK) equipped with an alumina work tube (38 mm ID, AL23, Friatec AG, Germany). The furnace temperature was controlled by a Eurotherm 3216 PID controller (Eurotherm, UK). Temperature of the hot zone was measured by a

calibrated S-type Pt/Pt-10Rh thermocouple (Johnson Matthey Noble Metals, UK, accuracy of \pm 3 °C) connected to a multimeter (Keithley 2010, USA). The cold junction temperature was measured with a Pt100 resistance thermometer (SKS-Group, Finland, tolerance class B 1/10) connected to another multimeter (Keithley 2000, USA). Temperature data were logged with the LabVIEW software.

The melting behavior experiments were conducted in flowing argon atmosphere and the dust-refractory interaction experiments in a highly reducing atmosphere (90% CO + 10% CO₂) corresponding to an oxygen partial pressure of $10^{-11.6}$ atm at 1300 °C, with a total gas flow rate of 300 mL/min. The gases used (Ar: 99.999 vol%, CO: 99.97 vol%, CO₂: 99.9993 vol%, supplied by AGA-Linde, Finland) were injected from the top of the furnace and the flow rates were regulated by a rotameter (Ar; Kytola Instruments, Finland) and by digital mass flow controllers (CO, CO₂; Aalborg DFC26, USA). For the dust-refractory interaction experiments, the 90% CO + 10% CO₂ atmosphere was chosen to simulate the highly reducing process conditions in the dust smelting furnace.

2.3. The melting behavior experiments

The melting behavior of dusts was investigated at temperatures between 800–1400 °C. In the experiments, a dust briquette weighing approximately 0.2 g was placed in a small platinum crucible. The crucible was attached to Kanthal A1-wire (Kanthal, Sweden) and lifted to the cold zone of the furnace. The furnace work tube was then closed from the bottom with a rubber plug and flushed with argon for 20 minutes before lifting the sample to the hot zone. When the desired contact time was reached, the lower end of the furnace tube was immersed into ice-water mixture, the plug sealing the bottom end of the work tube was removed and the sample-crucible assembly was quenched in ice-water mixture. Details of the technique have been described earlier (Chen et al., 2023).

After quenching, the samples were dried and mounted in epoxy resin, followed by dry grindingpolishing and carbon coating. The microstructures and phase compositions of the samples were analyzed with a Scanning Electron Microscope (SEM; Mira3, Tescan, Czech Republic) equipped with a 30 mm² Energy Dispersive Spectrometer (EDS; Thermo Fisher Scientific, USA). The acceleration voltage was 15 kV, and the beam current approximately 10 nA. The external standards (Astimex, Canada) used for the concentration quantifications are listed in Table 3. The matrix correction was accomplished using Proza-ZAF routine (Bastin and Heijligers, 1990). In addition, image analysis using the Image Pro Plus 6.0 software (Media Cybernetics, USA) was implemented for determining the fractions of phases formed during the annealing.

Element	Standard material and X-ray line analyzed
Ca	anhydrite, K line
Cl	tugtupite, K line
Cr	chromite, K line
Cu	copper, L line
F	fluorite, K line
Fe	hematite, K line
К	sanidine, K line
Mg	magnesium, K line
Mn	manganese, K line
Na	tugtupite, K line
Ni	nickel, K line
0	quartz, K line
Si	quartz, K line
Zn	zinc, L line

Table 3. List of standards used in the EDS analysis for concentration quantifications

Melt formation was studied by fifteen backscattered electron images taken with the SEM from different areas of the sample cross-section to obtain a representative sample structure. The images were obtained at the same brightness, contrast, magnification, and working distance to make them

comparable. These gray scale images were then analyzed with Image Pro Plus 6.0 software to determine the fractions of different phases. A similar method has been used previously for determining the area fractions in heterogeneous phases (Rinne et al., 2022; Chen et al., 2025). The compositions of the phases were determined by EDS to examine the behavior of the elements at the experimental temperatures.

2.4. The interactions between dust and refractory bricks

Dust-refractory interactions were investigated by experiments at 1300 °C. Before the experiments, the refractory bricks were cut into 35 mm × 35 mm × 10 mm (length × width × height) pieces, which were further ground into cylinders. A dense magnesia crucible (Tateho-Ozark Technical Ceramics, USA) was filled with 2.5 g of synthetic dust and a refractory brick cylinder was then placed on top of the crucible. The magnesia crucible was placed inside a molybdenum support crucible, placed on top of an 8 mm diameter alumina rod. The sample-crucible set-up was lifted to the middle of a cold furnace using the alumina rod, after which the CO and CO₂ gas flows were started. Then, the furnace was heated to 1300 °C with a rate of 4 °C/min. The heating cycle was programmed to keep the experimental temperature for 6 h, after which the furnace was cooled down with the same rate. At room temperature, the gas flows were turned off and the sample was removed from the furnace. The lifting set-up in the furnace was like the one describer earlier by Rämä et al. (2018). The sample preparation, microstructural and compositional analyses were carried out as described in the previous section.

2.5. Thermodynamic evaluations

The melting behaviors of iron-free end slags in the reductive smelting of the flue dusts were estimated by thermodynamic simulation using MTOX (vers. 8.2) database of MTDATA (Gisby et al., 2017).

3. Results and discussion

3.1. Part I: Melting behavior of the dusts

Before the actual experiments, a time series was conducted for the EAF2 dust for 1, 2, 4, and 8 h at 800 and 1200 °C. EAF2 dust was chosen because it was estimated to have the highest melting point. The results showed that the EAF2 dust sample sintered, but no melt formation was observed based on SEM-EDS characterization after 2h exposure time. At 1200 °C, increasing the experimental time did not result in significant microstructural changes. Thus, further EAF2 dust melting behavior experiments were conducted at higher temperatures of 1300-1400 °C using 2h contact time. In experiments at 1350 and 1400 °C with EAF2 dust, high fraction of liquid was formed fusing the sample to the crucible and rendering reuse of the crucible impossible. As estimated based on the compositions, this dust had the highest melting point, therefore the fusing issue would most likely have been even more severe with the other dusts at these temperatures. Therefore, only 1200-1300 °C experiments were conducted for the other two dust samples.

3.1.1. Characteristics of the samples

In the case of EAF1 dust, the melt formation started at temperatures above 1250 °C, and at 1300 °C the molten phase constituted already almost 50 area% of the sample, as shown in Fig. 1a. EAF2 dust started to melt at 1300 °C (Fig. 1b), while approximately 30% of the AOD dust was already molten at 1200 °C (Fig. 1c). The high fraction of molten phase in AOD dust already at 1200 °C was due to high fluoride content of the dust (Table 1). Fluorspar (CaF₂) is commonly used as a flux in the reduction step of AOD-process to reduce melting temperature and viscosity of the high-CaO slag.

The relatively low standard deviations presented in Fig. 1 a-b for the area fractions of EAF1 and EAF2 dusts indicate that the phase fractions were quite similar throughout the sample cross-sections. However, significantly higher standard deviations were observed for the AOD dust sample, resulting in higher uncertainties in the phase area fraction determination based on 15 SEM images.

In the case of EAF2 and AOD dusts, the liquid phase consisted of calcium-iron silicates and small quantities of steel alloying elements (point 3 in Figs. 3b, 3c, 4a, 4b, 4c) while in EAF1 dust, the liquid contained also a considerable amount of zinc (point 3 in Fig. 2c). In EAF1 dust, zinc (oxide) was a major

element and in addition to liquid phase, it was also found in two other phases: zincite (~60 wt% Zn, elongated white grains: point 1 in Figs. 2a, 2b, 2c) and zinc ferrite (~25 wt% Zn, light grey particles: point 2 in Figs. 2a, 2b, 2c). The zinc ferrite particles were also rich in steel alloying elements (Cr, Mn, and Ni).



Fig. 1. Phase fractions (area%) in the EAF1 (a), EAF2 (b) and AOD (c) dusts at experimental temperatures in argon atmosphere. The points in the figures represent averages of the 15 analyzed images (standard deviations are shown as error bars). The trend lines are 2nd order polynomial fits

In EAF2 and AOD dusts with low zinc concentrations, two types of spinels were detected. One was rich in chromium (point 1 in Fig. 3a; point 2 in Figs. 3b, 3c, 4c) and the other one relatively low in chromium (point 1 in Figs. 3b, 3c; point 2 in Figs. 4a, 4b). These particles were difficult to distinguish from each other by image analysis or visually due to similar light grey colour. EAF2 dust also contained a small amount of Ni-Cu sulfide particles and AOD dust contained some metallic Fe-Ni particles (point 1 in Figs. 4a, 4b, 4c).

Dicalcium silicate (point 3 in Figs. 2a, 2b; point 2 in Fig. 3a; point 4 in Figs. 3b, 3c, 4a, 4c) was present in all samples and temperatures, although in EAF1 dust at 1300 °C its amount was very low due to the large fraction of melt formed.

There was no chlorine in the AOD dust (Table 1), but in EAF dust chlorine is typically found as zinc, lead, potassium, and sodium chlorides (ZnCl₂, PbCl₂, KCl, NaCl). (Menad et al., 2003; Pickles, 2009; Chen et al., 2011; de Buzin et al., 2017; Lin et al., 2017). Negligible amounts of chlorine were found in



Fig. 2. Microstructures of selected areas in EAF1 dust after heating for 2 h at 1200 °C (a), 1250 °C (b) and 1300 °C (c) in argon

	119.2									
Flomont	12	00 °C (Fig. 2	2a)	12	50 °C (Fig. 2	2b)	13	1300 °C (Fig. 2c)		
Liement	point 1	point 2	point 3	point 1	point 2	point 3	point 1	point 2	point 3	
0	20.3	24.3	36.9	20.2	24.6	34.9	18.7	24.6	27.2	
Ca	3.1	1.2	45.4	2.5	0.8	47.8	1.6	0.7	23.7	
Cr	0.4	5.2	0.01	0.4	5.0	-	0.3	6.0	-	
Cu	-	-	0.2	-	-	0.04	-	-	-	
Fe	14.3	37.7	1.3	14.1	37.9	0.8	14.6	36.6	21.4	
К	0.01	-	0.2	-	0.03	-	0.01	0.01	0.08	
Mg	1.7	1.3	0.06	1.4	0.9	0.06	2.4	1.6	0.6	
Mn	1.9	3.4	0.1	1.8	3.3	0.08	2.3	3.5	1.9	
Na	-	-	0.3	-	-	0.2	-	-	0.7	
Ni	0.7	3.4	0.3	0.8	3.2	0.2	0.8	3.2	0.8	
Si	-	0.03	14.8	-	0.08	15.5	-	0.08	5.8	
Zn	57.7	22.3	-	58.8	23.1	-	59.2	23.1	16.9	
Cl	-	0.02	0.01	-	-	0.01	-	-	0.01	
F	-	0.5	-	-	0.4	-	-	-	-	

Table 4. Phase composition analyses (wt%) of selected points in EAF1 dust. The analysis points are indicated in Fig. 2

the EAF-samples after the experiments, which indicates vaporization of metal chlorides from the flue dusts at experimental temperatures. This is also supported by the fact that no lead and only trace amounts of alkali (Na and K) were found in the samples post the experiments.

Residual potassium and sodium were found mainly in EAF dusts associated with dicalcium silicate particles and in the case of EAF1 dust, also in the liquid oxide phase (point 3 in Fig. 2c). The reason why somewhat higher concentrations of alkali metals were found in the liquid oxide (slag) phase of EAF1 dust compared to EAF2 dust can be explained not only by the lower temperature, but also by the fact that the basicity (CaO/SiO₂) of the liquid (oxide) phase is lower in EAF1 than in EAF2 dust. In order to enhance the removal of alkali metals via slag, a low basicity slag is required. This is due to alkali metals reacting with silica to alkali silicates, which are then removed from the recycling furnace along with slag, whereas excess calcium oxide reacts with silica to form calcium silicates which prevents the formation of alkali silicates (Dastidar et al., 2018). Practically no sodium or potassium residues were found in the AOD dust, as expected due to their low initial concentrations.

Fluorine in the dusts exists primarily as fluorspar (CaF₂) but also as potassium and sodium fluorides (KF, NaF) as well as lead and zinc fluorides (PbF₂, ZnF₂). (Menad et al., 2003; Lin et al., 2017) CaF₂ is a very stable compound and is unlikely to evaporate at the experimental temperatures. However, evaporation of other fluorides is possible if they are initially present in the dust or are formed as a result of reactions with a less volatile fluoride such as CaF₂. Residual fluorine was mainly found in AOD-dust, especially in its liquid phase (point 3 in Figs. 4a, 4b, 4c), due to the higher initial content compared to EAF dusts.



Fig. 3. Microstructures of selected areas in EAF2 dust after heating for 2 h at 1250 °C (a), 1300 °C (b) and 1350 °C (c) in argon

Element	1250 °C	250 °C (Fig. 3a) 1300 °C (Fig. 3b)				1350 °C (Fig. 3c)				
	point 1	point 2	point 1	point 2	point 3	point 4	point 1	point 2	point 3	point 4
0	32.2	35.84	24.4	29.9	28.5	35.9	24.2	25.9	28.4	35.4
Ca	3.0	47.3	1.6	0.9	26.1	47.7	1.5	0.8	27.7	46.5
Cr	26.8	0.02	3.3	29.0	0.7	-	3.1	31.2	1.1	-
Fe	19.7	0.8	36.0	24.0	32.7	0.4	41.8	25.0	29.5	1.0
Κ	0.01	-	-	-	0.03	0.07	-	-	-	-
Mg	6.2	0.07	12.1	5.4	0.5	0.07	8.8	5.9	0.8	0.6
Mn	4.8	0.1	8.4	5.5	3.3	0.2	8.8	5.5	3.5	0.8
Na	-	0.1	-	-	-	0.02	-	-	-	0.06
Ni	4.4	0.1	12.9	2.9	1.7	-	11.4	3.4	1.6	-
Si	0.50	15.3	0.03	-	3.7	15.4	0.04	0.02	4.9	15.4
Zn	0.3	-	0.5	0.6	-	-	-	0.4	0.1	-
Cl	-	-	-	0.02	-	-	0.01	-	-	-
F	0.5	-	-	-	-	-	-	-	0.1	-

Table 5. Phase composition analyses (wt%) of selected points in EAF2 dust. The analysis points are indicated in Fig. 3



Fig. 4. Microstructures of selected areas in AOD dust after heating for 2 h at 1200 °C (a), 1250 °C (b) and 1300 °C (c) in argon

Table 6. Phase composition analyses (wt%) of selected points in AOD dust. The analysis locations are indicated in Fig. 4

		1200 °C ((Fig. 4a)		1250	°C (Fig. 4	łb)		1300 °C (F	ig. 4c)	
	point 1	point 2	point 3	point 4	point 1	point 2	point 3	point 1	point 2	area 3	point 4
0	0.2	23.9	28.7	37.0	0.2	22.6	28.4	0.7	31.8	29.7	35.6
Ca	0.3	8.0	42.6	47.0	0.5	9.0	44.5	0.5	1.1	30.9	48.2
Cr	1.6	3.4	0.04	-	1.6	3.3	0.02	0.9	34.9	0.02	-
Cu	1.8	-	-	-	-	-	-	2.1	-	-	-
Fe	72.9	38.4	10.7	0.3	67.9	36.1	9.2	64.0	13.7	18.3	0.4
Κ	0.03	-	-	-	0.01	-	-	0.03	-	-	-
Mg	-	9.7	0.2	0.01	0.1	9.5	0.3	0.1	5.4	1.2	0.1
Mn	0.3	13.9	0.8	0.07	0.3	17.1	0.8	0.5	5.8	3.5	0.2
Na	-	-	-	0.03	-	-	-	-	-	-	-
Ni	21.9	1.4	0.8	0.03	26.8	1.4	0.7	30.2	0.8	0.9	-
Si	0.1	0.02	6.8	15.2	0.02	0.02	7.2	0.02	0.1	5.5	15.5
Zn	-	0.5	-	-	-	0.4	-	-	0.6	0.2	-
Cl	-	-	-	-	-	-	-	-	-	-	-
F	0.8	0.62	5.0	-	2.4	0.6	5.1	0.6	-	2.2	-

The total chemical analyses of the flue dusts were evaluated for their behavior in the reductive recycling process. The present observations show that halogens are vaporized in inert and reducing atmospheres and iron as well as e.g., nickel and some of the chromium are deporting in the metal alloy, as observed for the AOD dust. The residual slag is a high-melting composition of CaO, MgO, SiO₂, and CaF₂. Fig. 5 shows the solidification equilibria of the EAF and AOD flue dusts post reduction, calculated using MTDATA software (Gisby et al., 2017).



Fig. 5. The solidification equilibria of EAF (2 wt% CaF₂) and AOD (8 wt% CaF₂) flue dusts post metals recovery in a reductive smelting where halides except fluorides have been vaporized from the slag; calculated using MTDATA and MTOX (ver. 8.2) database

The melting points of the formed slags are high, with liquidus close to 1800 °C. The solidus temperatures for both the slags are low, around 1100 °C. In both cases, the slags are within the halite (CaO) primary phase field. It is obvious that for industrial applications, the end slag must be fluxed for lowering the process temperature.

3.2. Part II: Dust - refractory interactions

The experiments in inert atmosphere showed that chlorides and partly also fluorides evaporated from the flue dusts at the experimental temperatures 1200-1400 °C. The compounds may cause excessive wear of the refractory lining, limiting the service life of the refractories and thus decreasing on-line availability. In addition to zinc, alkali (e.g., K₂O, Na₂O, K, and Na) vapors are very damaging to refractories because they can penetrate deep into pores and cracks in the refractories and cause localized melting, densification and/or undesirable compound formation with volume expansion (Scudeller et al., 1990).

The refractory interaction experiments focused on volatile potassium compounds with different refractory materials (bricks) under reducing conditions in flowing CO - 10% CO₂ atmosphere. The reactions of a synthetic dust, containing high concentrations of potassium, fluorine, and chlorine, on four types of refractories were studied at 1300 °C.

3.2.1. Characteristics of the samples

3.2.1.1. Magnesia-chromite

The microstructure of magnesia-chromite refractory material before the experiment is shown in Fig. 6 a. It consists of two main phases, periclase (MgO) and chromium spinel ($(Mg,Fe)(Cr,Al,Fe)_2O_4$), with periclase appearing as the dark gray phase and chromium spinel as the light gray phase.

Post annealing (Fig. 6 b), chromite was present as isolated (large crystals) primary chromite, as secondary chromite on periclase grain boundaries (bonding phase), and as exsolutions in the periclase grains (Supplementary Fig. S1). Potassium was found in large amounts in aluminum-rich spinel near the bottom of the refractory sample and smaller amounts in the magnesium-rich spinel, and especially in periclase (Supplementary Fig. S1 a, b). This is consistent with the work of Zhao et al. (2018) who found that among the five common refractory mineral components (MgO·Cr₂O₃, MgO·Al₂O₃, Al₂O₃, MgO, and Cr₂O₃), MgO has the best resistance against potassium vapors.



Fig. 6. Cross-section of magnesia-chromite refractory brick as-received (a) and after a contact time of 6 h at 1300 °C in CO-10% CO₂ atmosphere (Chr = chromium spinel, Per = periclase) (b). The 5 squares represent areas where EDS-characterization was performed (Supplementary Fig. S1)

The potassium content gradually decreased when going deeper into the refractory and at a penetration depth of over 5 mm (Supplementary Fig. S1 c-e) only negligible amounts of potassium could be found. This is probably due to volume expansion as a result of formation of a potassium aluminate K_2O ·Al₂O₃ (Criado et al., 1981; Hayashi et al., 1983) at the bottom of the refractory sample, which leads to closing of the pores to some extent and prevents penetration of potassium vapors deeper into the material. The cross-section of the magnesia-chromite brick (Fig. 6 b) as well as microstructures from different levels (Supplementary Fig. S1) also show that the top was more porous than the bottom part, which was in direct contact with the volatile components of the synthetic dust.

3.2.1.2. High-alumina

The high-alumina refractory material consists of coarse grains surrounded by a fine textured matrix (Fig. 7), the main phases being corundum (Al₂O₃) and mullite (3Al₂O₃ 2SiO₂). Potassium reacted primarily with mullite, while the reaction with corundum was moderate, which agrees with earlier studies (Scudeller et al., 1990; Stjernberg et al., 2013; Li et al., 2017; Li et al., 2018). The potassium content of the corundum particles (dark gray) decreased gradually deeper in the brick, and at a penetration depth of more than 5 mm no potassium was found in the corundum particles (area 3 in Supplementary Fig. S2 c), while mullite needles (light gray) with high potassium concentration could be found even in the upper part of the brick (Supplementary Fig. S2 e). High potassium concentration was also found in the particles rich in molybdenum (presumably evaporated from the support crucible) near the bottom of the refractory sample (Supplementary Fig. S2 a).

The formation of potassium aluminate $(K_2O \cdot Al_2O_3)$ because of a reaction between potassium vapor and corundum, as well as kalsilite $(K_2O \cdot Al_2O_3 \cdot 2SiO_2)$ and leucite $(K_2O \cdot Al_2O_3 \cdot 4SiO_2)$ as a consequence

of reactions between potassium vapors and mullite, causes high volume expansion (Criado et al., 1981; Hayashi et al., 1983; Scudeller et al., 1990; Stjernberg et al., 2013). This was also observed in the present experiments. Cracks, formed in the samples because of volume expansion, enhance the penetration of vaporized potassium deeper into the brick, resulting in formation of mullite particles with a high concentration of potassium also in the upper part of the refractory sample. Because of the considerable volume expansion, SiO₂ in the refractory lining must be limited to a small fraction.



Fig. 7. A cross-section of high-alumina refractory brick as-received (a) and after a contact time of 6 h at 1300 °C with the synthetic dust in CO-10% CO₂ atmosphere (b). The 5 squares represent areas where EDS-characterization was performed (Supplementary Fig. S2)

3.2.1.3. Alumina-chromia

The alumina-chromia brick, shown in Fig. 8, is a mixture of alumina (Al₂O₃, dark regions) and aluminachromia solid solution (Al₂O₃-Cr₂O₃, brighter regions) phases. Potassium was found in large amounts in the Al₂O₃-Cr₂O₃ solid solution phase, near the bottom of the refractory sample (areas 3 and 4 in Supplementary Fig. S3 a, b). The potassium content gradually decreased when going deeper into the brick and at a penetration depth of over 4.5 mm (Supplementary S3 d) only trace amounts of potassium were found.

As can be seen in Supplementary Fig. S3 c, the alumina particles were surrounded by a rim, presumably formed by diffusion of Cr_2O_3 into Al_2O_3 grains. This layer seems to hinder the corrosion of the alumina particles, as only negligible amounts of potassium could be found in the alumina particles compared to the surrounding zones.

3.2.1.4. Magnesia

The microstructure of magnesia brick is characterized by coarse magnesia grains connected through fine-grained magnesia (Fig. 9). In addition to direct MgO-MgO bonding, there is also a light gray bonding phase between the magnesium grains, which was analyzed to be dicalcium silicate (point 3 in Supplementary Fig. S4 b, c).

High potassium levels were found in the particles rich in molybdenum throughout the refractory sample (Supplementary Fig. S4 a, c, d). However, only trace amounts of potassium were found in the periclase particles (Supplementary Fig. S4), indicating that magnesia refractory has a good corrosion resistance against potassium vapors. This is consistent with thermodynamic calculations and

experimental results by Zhao et al. (2018). The sample also retained its physical shape well and the structure remained porous even in the bottom part. Although magnesia has good corrosion resistance to potassium vapors, the porous structure allows also other gases to penetrate the refractory material, potentially causing deterioration of the refractory lining.



Fig. 8. Cross-section of alumina-chromia refractory brick as-received (a) and after a contact time of 6 h at 1300 °C with the synthetic flue dust in CO-10 % CO₂ atmosphere (b). The 4 squares represent areas where EDS-characterization was performed (Supplementary Fig. S3)



Fig. 9. Cross-section of magnesia refractory material as-received (a) and after a contact time of 6 h at 1300 °C with synthetic flue dust in CO-10% CO₂ atmosphere (b). The 4 squares represent areas where EDS-characterization was performed (Supplementary Fig. S4)

4. Conclusions

SS flue dusts contain hazardous elements, but also valuable metals, such as steel alloying elements, which makes their recycling attractive. The chemical and structural characterization of SS dust is an

important step in assessing the feasibility of recycling. Their characterization has been the subject of intensive studies, but the melting behavior of SS has not received attention so far. However, it is an important factor for understanding the behavior of dust at high temperatures, also for providing guidance on dust recycling by high-temperature techniques.

The melting behavior of flue dusts from EAF and AOD-converter as well as the distribution of elements in different phases were examined. Melting of the EAF dusts in inert atmosphere started in the temperature range of 1250-1300 °C, depending on the composition of the dust. The AOD dust had a molten fraction of approximately 30 area% already at 1200 °C because of its high fluoride (CaF₂) content. In the EAF1 dust, the steel alloying elements deported in zinc ferrite phase. In EAF2 flue dust, the alloying elements were found in spinel phases and in AOD dusts they were in spinel and metallic ferronickel alloy phases.

Based on the total chemical analyses of the dusts, thermodynamic calculations were performed to offer insights on the behavior of the residual slag in a smelting furnace after reduction of iron, nickel and some of the chromium into a metal alloy phase. It is evident that fluxing is required in order to keep the slag molten at industrial operating temperatures.

The melting behavior experiments showed that chlorides and partly also fluorides evaporated at the experimental temperatures in inert conditions. Since alkali vapors (e.g., K₂O, Na₂O, K, and Na) are especially damaging to ceramic refractories, the focus in the second part of the study was on the interactions of volatile potassium compounds with different refractory bricks and their phases in reducing conditions i.e., in the freeboard of a smelting furnace.

The refractory – dust interaction experiments in reducing conditions showed that magnesia has good corrosion resistance to potassium vapors. The penetration depth of potassium into chromium-containing refractory materials was limited to the vicinity of the gas-refractory surface. Silicate-bonded alumina refractories were sensitive to corrosion by potassium vapors because of their susceptibility to volume expansion compared with the other refractories studied. The volume expansion is mostly due to the reaction between potassium and mullite. Potassium vapors can penetrate deeply into these refractories through the open pores and cracks and result in deterioration of refractory materials. Thus, SiO_2 in the refractories must be limited to a small fraction.

The obtained results increase the knowledge of the melting behavior of SS flue dusts with different compositions and offer insights into elemental deportments between condensed and gaseous phases. This information is useful in designing high-temperature recycling processes for the dusts in order to recover valuable elements. The present work also provides information related to selection of suitable refractory materials in the freeboard of a smelting furnace, although the dust-refractory interaction experiments were limited to potassium-containing oxide, chloride and fluoride compounds. In future work, the experiments should be expanded to cover a wider variety of volatile compounds as well as prolonged contact times.

Acknowledgments

Outokumpu stainless steel plant (Tornio, Finland) is acknowledged for providing dust samples for the experiments.

The study received financial support from Business Finland funded SYMMET project (grant number 3891/31/2018) and utilized the Academy of Finland's RawMatTERS Finland Infrastructure (RAMI), based jointly at Aalto University, GTK Espoo and VTT Espoo.

References

BASTIN, G.F., HEIJLIGERS, H.J.M., 1990. Quantitative Electron Probe Microanalysis of Ultralight Elements (Boron-Oxygen). Scanning, 12(4), 225–236.

- CHEN, M., SUKHOMLINOV, D., TASKINEN, P., HAMUYUNI, J., TILJANDER, M., LINDGREN, M., LINDBERG, D., 2025. Adoption of Hydrogen as a Climate-Neutral Reducing Agent for Recovering Metals from Copper Slag. Metall. Mater. Trans. B, https://doi.org/10.1007/s11663-025-03444-8.
- CHEN, M., SUKHOMLINOV, D., TASKINEN, P., TILJANDER, M., LINDBERG, D., JOKILAAKSO, A., 2023. *Phase relations of the MgO-SiO*₂-CrO_x system at 1600°C in air and reducing atmospheres. J. Am. Ceram. Soc. 106(10), 6230-6243.

- CHEN, W-S., SHEN, Y-H., TSAI, M-S., CHANG, F-C., 2011. Removal of chloride from electric arc furnace dust. J. Haz. Mater. 190, 639-644.
- CRIADO, E., MOYA, J.S., DE AZA, S., 1981. Alkalines Vapour Attack on a High Alumina Refractory. Ceram. Int. 7, 19-21.
- DASTIDAR, M.G., SARKAR, B.K., MITRA, M.K., DEY, R., 2018. Effect of alkali on different iron making processes. Material Sci. & Eng. 2, 304-313.
- DE BUZIN, P.J.W.K., HECK, N.C., VILELA, A.C.F., 2017. EAF dust: An overview on the influences of physical, chemical and mineral features in its recycling and waste incorporation routes. J. Mater. Res. Technol. 6, 194-202.
- DENTON, G.M., BARCZA, N.A., SCOTT, P.D., FULTON, T., 2005. *EAF Stainless Steel Dust Processing*. In: John Floyd International Symposium on Sustainable developments in metals processing, July 3-6, 2005: Melbourne, Australia, 273-283.
- DOMINGUEZ, M.I., ROMERO-SARRIA, F., CENTENO, M.A., ODRIOZOLA, J.A., 2010. *Physicochemical characterization and use of wastes from stainless steel mill*. Environ. Progr. Sust. Energy, 29, 471-480.
- DRISSEN, P., KUEHN, M., JUNG, H.P., TAVERNIER, H., GRISVARD, C., 2002. Recycling of EAF dust into the EAF especially from high alloy steelmaking. Metall. Res. Techn. 99, 341-347.
- FAN, Y., ZHANG, L., VOLSKI, V., VANDENBOSCH, G.A.E., BLANPAIN, B., GUO, M., 2017. Utilization of Stainlesssteel Furnace Dust as an Admixture for Synthesis of Cement-based Electromagnetic Interference Shielding Composites. Scientific Reports, 7, 15368.
- GISBY, J., TASKINEN, P., PIHLASALO, J., LI, Z., TYRER, M., PEARCE, J., AVARMAA, K., BJÖRKLUND, P., DAVIES, H., KORPI, M., MARTIN, S., PESONEN, L., ROBINSON, J., 2017. *MTDATA and the Prediction of Phase Equilibria in Oxide Systems: 30 years of Industrial Collaboration*. Metall. Mater. Trans. B, 48(1), 91-98.
- HAYASHI, T., NISHIO, H., AYUZAWA, N., 1983. *The Behaviour of Alkali to Alumina*. Interceram, Special issue, 68–71.
- HUAIWEI, Z., XIN, H., 2011. An overview for the utilization of wastes from stainless steel industries. Res. Conserv. Recycl. 55, 745-754.
- KUKURUGYA, F., HAVLIK, T., KEKKI, A., FORSÉN, O., 2012. Chemical and structural characterization of different steelmaking dusts from stainless steel production. In: Kammel's Quo Vadis Hydrometallurgy 6, 4-7.6.2012, Herlany, Kosice, Slovakia, 93-101.
- LEE, K-H., BROWN, J.J., 1995. Corrosion of Alumina-Chromia Refractory by Alkali Vapors 2: Experimental Approach. Korean J. Ceram. 1, 86-90.
- LI, N., VAINIO, E., HUPA, L., HUPA, M., ZABETTA, E.C., 2017. High-Temperature Corrosion of Refractory Materials in Biomass and Waste Combustion: Method Development and Tests with Alumina Refractory Exposed to a K₂CO₃-KCl Mixture. Energy & Fuels, 31, 10046–10054.
- LI, N., VAINIO, E., HUPA, L., HUPA, M., ZABETTA, E.C., 2018. Interaction of High Al₂O₃ Refractories with Alkaline Salts Containing Potassium and Sodium in Biomass and Waste Combustion. Energy & Fuels, 32, 12971–12980.
- LIN, X., PENG, Z., YAN, J., LI, Z., HWANG, J.Y., ZHANG, Y., LI, G., JIANG, T., 2017. Pyrometallurgical recycling of electric arc furnace dust. J. Clean. Prod. 149, 1079-1100.
- LIU, P., LIU, Z., CHU, M., TANG, J., GAO, L., YAN, R., 2021. Green and efficient utilization of stainless steel dust by direct reduction and self-pulverization. J. Haz. Mater. 413, 125403.
- MA, G., GARBERS-CRAIG, A.M., 2006. A review on the characteristics, formation mechanisms and treatment processes of Cr (VI)-containing pyrometallurgical wastes. J. South. African Inst. Mining Metall. 106, 753-763.
- MENAD, N., AYALA, J.N., GARCIA-CARCEDO, F., RUIZ-AYÚCAR, E., HERNÁNDEZ, A., 2003. Study of the presence of fluorine in the recycled fractions during carbothermal treatment of EAF dust. Waste Management, 23, 483-491.
- MIKHAIL, S.A., TURCOTTE, A.M., AOTA, J., 1996. *Thermoanalytical study of EAF dust and its vitrification product*. Thermochim. Acta, 287, 71-79.
- MUVUNYI, R.A., ZHENG, D., LI, J., MA, G., OWUSU-ACHEAW, Y., ZHANG, X., 2023. Kinetics of Carbothermal Reduction of Electric Arc Furnace Dust from a Stainless Steel Plant. JOM, 75, 1137–1147.
- NDLOVU, S., SIMATE, G.S., MATINDE, E., 2017. Waste Production and Utilization in the Metal Extraction Industry (1st ed.) CRC Press.
- OMRAN, M., FABRITIUS, T., 2017. Effect of steelmaking dust characteristics on suitable recycling process determining: Ferrochrome converter (CRC) and electric arc furnace (EAF) dusts. Powder Technology, 308, 47-60.

- PENG, J., PENG, B., YU, D., TANG, M., 2003. *Thermo-analytical study on stainless steelmaking dust*. J Cent. South Univ. Technol. 10, 301–306.
- PICKLES, C.A., 2009. Thermodynamic analysis of the selective chlorination of electric arc furnace dust. J. Haz. Mater. 166, 1030-1042.
- RINNE, T., KLEMETTINEN, A., KLEMETTINEN, L., RUISMÄKI, R., O'BRIEN, H., JOKILAAKSO, A., SERNA-GUERRERO, R., 2022. Recovering Value from End-of-Life Batteries by Integrating Froth Flotation and Pyrometallurgical Copper-Slag Cleaning. Metals, 12, 15.
- RÄMÄ, M., NURMI, S., JOKILAAKSO, A., KLEMETTINEN, L., TASKINEN, P., SALMINEN, J., 2018. *Thermal Processing of Jarosite Leach Residue for a Safe Disposable Slag and Valuable Metals Recovery*. Metals, 8, 744.
- SCUDELLER, L.A.M, LONGO, E., VARELA, J.A., 1990. Potassium vapor attack in refractories of the alumina-silica system. J. Am. Ceram. Soc. 73, 1413–1416.
- STJERNBERG, J., OLIVAS-OGAZ, M.A., ANTTI, M-L., ION, J.C., LINDBLOM, B., 2013. Laboratory scale study of the degradation of mullite/corundum refractories by reaction with alkali-doped deposit materials. Ceram. Int. 39, 791–800.
- TAKANO, C., CAVALLANTE, F.L., DOS SANTOS, D.M., MOURÃO, M.B., 2005. Recovery of Cr, Ni and Fe from dust generated in stainless steelmaking. Mineral Process. Extr. Metall. 114, 201-206.
- TRAVERNIER, H., GRISVARD, C., JUNG, H.P., DRISSEN, P., 2004. Foaming of the slag and recycling of stainless steel dusts by injection into the electric arc furnace for stainless steels. European Commission, Directorate-General for Research and Innovation, Publications Office.
- WORLD STAINLESS ASSOCIATION, 2022. Stainless Steel in Figures 2022.
- ZHAO, Y., CHENG, G., LONG, F., LIU, L., DONG, C., WANG, X., ZHAO, J., 2018. Analysis and Prediction of Corrosion of Refractory Materials by Potassium during Biomass Combustion-Thermodynamic Study. Materials, 11, 2584.

Supplementary material



Element	area 1	area 2	area 3	area 4
0	28.9	29.6	43.3	36.5
Al	5.9	6.7	20.1	18.8
Κ	2.0	2.9	31.2	25.6
Na	0.2	0.2	-	0.1
Ca	0.6	0.6	2.2	2.0
Cr	14.7	14.7	0.5	3.7
Fe	10.6	10.2	0.05	2.3
Mg	37.2	35.2	0.4	8.9
Мо	-	-	0.3	0.4
Si	0.01	0.1	2.0	1.9
Cl	0.03	-	0.1	0.01





Element	point 1	area 2	area 3	
0	27.6	28.7	41.3	
Al	9.1	2.5	15.9	
Κ	4.6	1.9	23.2	
Na	0.2	1.0	0.3	
Ca	1.7	0.4	1.6	
Cr	28.7	3.9	2.3	
Fe	6.7	11.6	2.4	
Mg	21.2	50.1	10.4	
Мо	-	-	0.6	
Si	0.1	0.02	2.0	
Cl	0.01	0.03	0.03	

Element	area 1	point 2	area 3
0	27.5	28.1	30.0
Al	4.9	1.0	0.8
Κ	0.6	0.3	0.5
Na	0.2	0.2	1.0
Ca	0.3	0.2	0.7
Cr	15.5	31.1	4.0
Fe	10.7	6.1	12.1
Mg	40.3	23.9	51.0
Si	0.03	0.2	0.04
Cl	0.01	-	-

50 µn

Element	point 1	point 2	area 3
0	25.0	29.5	28.0
Al	9.5	9.7	0.7
К	0.1	-	0.1
Na	0.3	0.4	0.7
Ca	0.17	0.1	0.2
Cr	35.6	32.1	4.2
Fe	7.0	5.8	12.4
Mg	22.2	22.4	53.5
Si	0.2	-	0.1
Cl	0.02	-	-

Element	area 1	area 2	area 3
0	28.0	27.6	27.6
Al	1.4	1.5	9.3
К	-	0.04	0.03
Na	0.7	0.8	0.3
Ca	0.2	0.2	0.9
Cr	4.6	4.5	33.7
Fe	14.3	12.0	10.9
Mg	50.8	51.7	17.1
Si	0.02	0.1	0.2
Cl	0.02	0.02	0.01

Fig. S1. Microstructures and phase analyses (wt%) of magnesia-chromite refractory material in areas 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e) marked in Fig. 6 of the manuscript text



Element	area 1	area 2	area 3	point 4
0	40.6	38.5	38.5	28.4
Al	17.5	49.8	49.5	4.6
Si	16.9	0.4	0.4	0.7
Κ	23.6	10.5	1.0	24.8
Na	-	0.2	0.2	0.3
Ca	1.5	-	0.6	1.4
Cr	-	0.03	0.02	-
Mg	-	0.4	0.3	-
Мо	-	0.2	0.4	39.5
Cl	-	-	-	0.3

(d)



Element	point 1	point 2	area 3
0	35.6	29.4	39.5
Al	16.9	18.4	55.4
Si	24.4	28.3	2.8
Κ	15.9	18.4	1.6
Na	0.1	0.03	0.3
Ca	1.1	1.1	0.02
Cr	0.01	0.1	
Mg	-	0.03	0.4
Cl	0.04	-	0.04
F	6.1	4.4	-



Element	point 1	point 2	area 3
0	34.3	35.7	40.8
Al	17.5	16.9	58.5
Si	29.6	28.2	0.1
Κ	14.9	15.0	0.02
Na	0.02	0.2	0.2
Ca	1.6	1.5	0.03
Cr	0.1	0.02	-
Mg	0.3	0.3	0.4
F	1.7	2.2	-



Element	point 1	point 2
0	35.2	41.5
Al	17.3	14.2
Si	29.2	30.6
К	14.4	11.6
Na	1.3	0.09
Ca	1.3	1.0
Cr	0.1	0.1
Mg	0.5	0.5
Cl	0.02	0.01
F	0.8	0.5



Element	point 1	point 2
0	40.8	39.2
Al	14.7	15.9
Si	32.1	32.2
К	9.2	9.5
Na	0.3	0.3
Ca	1.3	1.4
Cr	-	0.1
Mg	0.8	0.7
Cl	0.03	-
F	0.8	0.7

Fig. S2. Microstructures and phase analyses (wt%) of high-alumina refractory material in areas 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e) marked in Fig. 7 in the manuscript text







Element	area 1	area 2	area 3	area 4
0	41.0	41.7	33.5	35.4
Al	58.1	57.5	29.9	33.2
Cr	0.03	-	16.3	17.2
К	0.03	0.03	12.6	8.6
Na	0.2	0.2	0.2	-
Ca	-	0.03	1.3	-
Mg	0.5	0.4	1.3	1.0
Р	-	-	3.3	2.7
Si	0.2	0.1	1.7	1.9
Cl	-	-	0.02	0.01
F	-	-	0.01	-

50 µn

Element	area 1	area 2	area 3	area 4
0	39.5	40.5	38.6	32.6
Al	59.3	58.4	48.9	31.0
Cr	0.2	0.2	7.1	30.6
К	0.1	-	2.6	2.8
Na	0.3	0.2	0.04	0.02
Ca	-	0.02	-	0.5
Mg	0.4	0.5	0.5	0.5
Si	0.2	0.2	2.3	2.1
Cl	0.01	0.01	0.01	-



Element	point 1	area 2	area 3
0	25.15	31.7	33.6
A1	20.10	24.6	28.1
AI	-	24.0	36.1
Cr	0.7	43.45	27.9
Κ	0.02	0.01	0.01
Na	0.03	0.02	0.02
Ca	0.06	0.02	-
Mg	0.02	0.1	0.3
Si	-	0.2	0.1
Cl	0.02	-	0.01
Zr	74.0		
Zr	74.0	-	0.01

Fig. S3. Microstructures and phase analyses (wt%) of alumina-chromia refractory material in areas 1 (a), 2 (b), 3 (c) and 4 (d) marked in Fig. 8 in the manuscript text



Element	area 1	area 2	area 3	area 4	
0	33.5	32.3	32.6	24.8	
Mg	63.5	64.8	64.9	1.3	
Κ	-	-	0.04	27.4	
Na	0.6	0.6	0.6	0.05	
Al	0.2	0.2	0.2	0.07	
Ca	2.1	2.0	1.6	1.6	
Cr	0.03	0.02	-	-	
Si	0.1	0.04	0.1	-	
Cl	0.01	-	-	0.28	
F	-	-	-	0.2	
Мо	-	-	-	44.3	

(c)

50 µm 32)



Element	area 1	area 2	point 3
0	30.3	32.0	34.0
Mg	68.2	66.1	0.3
Κ	-	0.01	0.3
Na	0.7	0.6	0.04
Al	0.3	0.2	0.04
Ca	0.4	0.9	49.0
Cr	0.01	-	0.01
Мо	-	-	0.7
Si	0.1	0.1	15.7
Cl	-	0.02	-



Element	area 1	area 2	point 3	area 4
0	32.1	31.1	31.2	26.0
Mg	66.8	67.2	0.2	1.6
Κ	-	0.03	0.1	26.7
Na	0.6	0.7	-	0.08
Al	0.2	0.2	0.2	0.07
Ca	0.2	0.6	51.2	1.6
Cr	0.04	0.07	0.1	-
Si	0.08	0.06	17.2	0.06
C1	-	-	-	0.3
F	-	-	-	0.08
Мо	-	-	-	43.5



Element	area 1	area 2	area 3	area 4
0	32.5	32.6	30.6	26.6
Mg	64.9	66.1	67.9	0.5
Κ	-	-	-	26.8
Na	0.6	0.6	0.7	0.1
Al	0.2	0.2	0.2	0.2
Ca	1.6	0.4	0.5	1.6
Cr	0.1	-	0.1	-
Si	0.1	0.1	0.1	-
Cl	-	-	-	0.3
F	-	-	-	0.2
Мо	-	-	-	43.7

Fig. S4. Microstructures and phase analyses (wt%) of magnesia refractory material in areas 1 (a), 2 (b), 3 (c) and 4 (d) marked in Fig. 9 in the manuscript text

(b)