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INTERACTION OF GRAPHITE WITH SYNTHETIC MATTE

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Abstract

Graphite blocks are currently used in the concentrate - slag zone in primary PGM smelters, and can possibly be extended to the matte zone. This project evaluates the interaction between synthetic matte and graphite blocks on a laboratory scale. Static crucible tests were performed where graphite crucibles (prepared from standard and high-grade graphite) were filled with synthetic matte (27.7 per cent S – 46.1 per cent Fe – 17.0 per cent Ni – 9.2 per cent Cu) and heated to 1550°C for different time periods (1–5 days). Matte penetration was evaluated using a SEM, while graphite dissolution was evaluated by measuring the carbon content of the matte with a LECO carbon analyser. Matte penetrated into standard grade graphite up to approximately 2 mm, while matte infiltration into the high grade graphite was limited to the immediate hot face. The saturation solubility of graphite in the synthetic matte at 1550°C was 0.43 per cent. Copper, iron, nickel, and sulphur were detected in an accretion that formed in the water-cooled part of the furnace. This accretion consists of mainly Cu-S and Cu-Fe-S based phases.

Keywords: PGM smelter, graphite block, refractory, matte

Introduction

The utilization of carbon-based refractories at the slag-concentrate level¹ is a recent development in the refractory wall design of platinum group metal (PGM) smelters. This design has led to a significant reduction in the corrosion of copper coolers. In a postmortem investigation of a graphite block used for six months in the slag-concentrate zone it was observed that a thin freeze lining (2 mm) formed at the hot face of the graphite block². Penetration of the graphite by the furnace contents was less than 1 mm at the hot face of the graphite block, but significant (depth of up to 10 mm) between the graphite blocks at the matte–slag interface. Base metal sulphides could be observed in this area, deposited on the copper cooler surface, which resulted in chemical reactions between these sulphides and the copper cooler. The mechanism, however, by which the sulphides reached or formed at the cold face of the graphite is not well understood, since no matte concentration gradient was observed from the hot face to the cold face of the graphite blocks. The extension of the graphite blocks to the matte zone is a possibility, but the compatibility between graphite and primary PGM matte must first be understood. This research project therefore examines the interaction between primary PGM matte and graphite on a laboratory scale.

It includes an examination of the influence of graphite grade, matte temperature, and exposure time on the wear of graphite by PGM matte.

Background

PGM matte

Geologically, PGMs associate with base metal sulphides such as pyrrhotite (Fe_{1-x}S), pentlandite ($\text{Fe,Ni}_9\text{S}_8$), chalcopyrite (CuFeS_2), pyrite (FeS_2), and millerite (NiS)³. Prior to smelting, the PGM ore is milled and treated in floatation cells to upgrade the PGM content of the ore³. For sulphide smelting, submerged-arc electric furnaces are employed in which electrodes are buried in a resistive slag, such that when current is applied through the electrodes thermal energy is generated⁴. In sulphide smelting two immiscible fluids, matte and slag, are formed. Matte consists of valuable sulphides (copper, nickel, iron, and cobalt) which serve as collectors for the PGMs. The slag consists mostly of silicates, which are discarded after smelting³. Matte has a higher specific gravity than the slag, which is why separation is achieved by matte settling to the bottom of the furnace and the slag forming the top layer⁴. Matte temperatures can exceed 1500 °C⁶. The liquidus temperature of the smelter slag ranges from 1350°C to above 1600°C depending on the composition of the concentrate⁵.

Furnace sidewall design

The slag zone of a typical PGM smelter is lined with mag-chrome bricks at the hot face and copper coolers at the cold face⁶. Copper coolers provide cooling of the refractory such that a frozen layer of slag (freeze lining) forms at the hot face of the lining. This freeze lining provides protection of the refractory from wear by hot furnace contents⁶. Wear of refractories and copper coolers is more severe in the slag-concentrate zone of PGM smelters. As a consequence, graphite blocks have replaced the mag-chrome bricks in recent PGM furnace lining designs. Utilization of graphite blocks at the slag zone has improved the lining life of the refractory by inhibiting the diffusion of furnace contents towards the copper coolers. Higher penetration of furnace contents is, however, still observed in the slag-matte zone, which is why the matte zone refractory lining design has to be improved².

Graphite has a high thermal conductivity, is not easily wetted by matte, and can withstand high operating temperatures under reducing conditions⁶. Graphite has shown higher resistance to wear at the PGM slag zone furnace lining than mag-chrome bricks. It is envisaged that utilizing graphite blocks in the matte zone of the PGM furnace will improve the service life of the lining.

Graphite

Graphite is carbon that has been processed at temperatures in excess of 3000°C⁷. It is synthesized from carbon-based materials such as anthracite and coke.

Coal-tar pitch is used to consolidate the anthracite or coke particles into a mix, after which the homogeneous mixture is moulded by extrusion, compression, or isostatic pressing to produce the final product. The moulding technique has a great influence on the final properties of the product.

Extrusion produces a non-uniform, anisotropic low-cost material. Extruded graphite has a pronounced anisotropy in properties because the extrusion process tends to align the particles in the direction of extrusion⁷. As a consequence, physical and thermal properties of graphite in the direction of extrusion will vary from properties perpendicular to the extrusion direction⁷.

Compression produces a non-uniform, medium-cost material with edge effects, while isostatic pressing produces a material with great uniformity, isotropic properties, and few defects. Typical stages of the graphitizing process are shown in Figure 17.

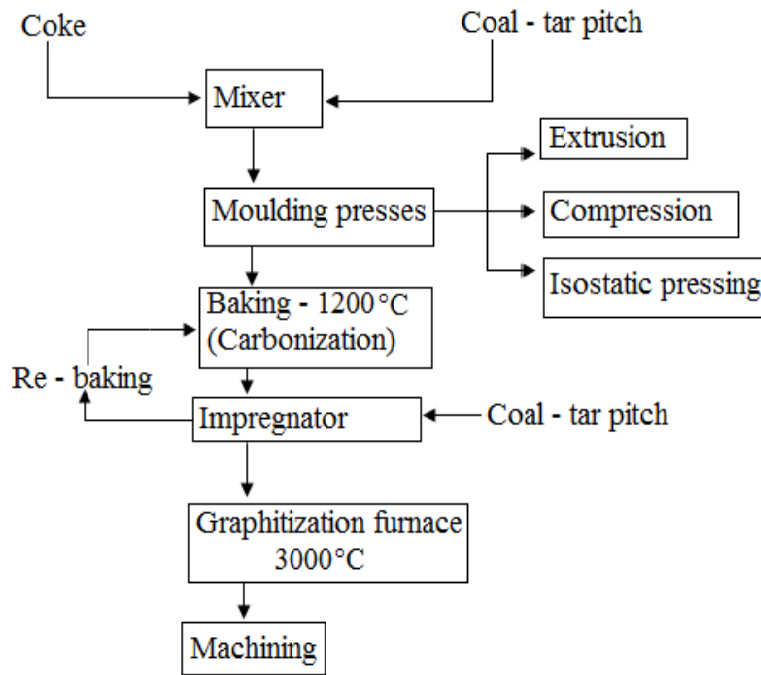


Figure 1-Typical production - process flow diagram for moulded graphite⁷

Baking (carbonization) of the moulded product is performed under reducing conditions between 760°C and 1200°C⁷. Since the baked mould is highly porous, it is further densified by impregnating it with coal-tar pitch, after which it is fired at 3000°C in a resistance furnace to produce a graphitic material (graphite) that has increased resistance to thermal shock and chemical attack⁷.

Experimental

Materials

Two grades of graphite were tested in this work, namely High Grade (HG) graphite and Standard Grade (SG) graphite. HG graphite is denser with higher thermal conductivity, and is less porous compared to SG graphite. Physical and thermal properties of the graphite grades selected for this study are summarized in Table I. These properties were extracted from the supplier's data sheet. A helium gas pycnometer was also used to verify the porosity of the graphite.

The graphite samples were subjected to ICP and LECO sulphur analyses (Table II). The analysed ash and iron contents of the two graphite grades are slightly higher than reported by the supplier (Table I). The aim of varying graphite grade is to identify the graphite grade that is most compatible with matte. The best graphite grade should provide higher resistance towards hot matte penetration and exhibit low solubility in hot matte.

Table I-Physical and thermal properties of Standard and High Grade graphite

Property	HG graphite	SG graphite
Apparent density (g/cm ³)	1.77	1.62
Open porosity (%)	12	24
*Calculated porosity (%)	13.78	21.88
Thermal conductivity (W/m.K)	195	150
Ash content (%)	<0.1	1
Iron content (%)	<0.01	0.5
Manufacturing	Extruded	Extruded
*Calculated using the density, mass, and volume measured with a helium gas pycnometer		

Table II-ICP and LECO sulphur analyses of the graphite

Impurities	S %	Ash %	Cl %	Si %	Ca %	Fe %	Ni %	Cu %
SG graphite	0.04	1.22	0.03	0.14	0.52	0.81	0.11	0.06
HG graphite	0.01	0.30	0.03	0.05	0.32	0.16	0.05	0.05

Synthesis of matte

Synthetic matte was prepared from sulphide powders acquired from Sigma-Aldrich. Starting materials were 12 per cent Cu_2S , 22 per cent Ni_3S_2 , and 66 per cent FeS . The mixture of sulphides was loaded into a silica tube and heated for one hour at 1100°C in a vertical tube furnace. The matte was then air cooled and analysed by ICP and with LECO sulphur and carbon analysers to verify the composition of the synthesized matte. The elemental composition of the synthetic matte is given in Table III. The source of oxygen in the synthesized matte is Fe_3O_4 , which was detected as an impurity in the technical-grade FeS used as a starting material.

Table III-Elemental composition of synthetic matte by ICP and LECO, weight %

S	Fe	Ni	Cu	C	O_2
26.79	44.61	16.41	8.87	0.03	3.28

Furnace set-up

Experiments were performed in a sealed vertical alumina tube furnace which was heated by molybdenum tungsten disilicide elements. The work tube was sealed with water-cooled brass caps. The top brass cap had a gas outlet port and a thermocouple port through which the type S (Pt - Rh10/Pt) thermocouple and SIRO_C700+ oxygen probe fitted. The bottom brass cap had a gas inlet port through which the furnace purge gas entered. Argon used to purge the furnace passed through zirconium turnings at 300°C , which purified the argon to an oxygen partial pressure of approximately 0.004 atmosphere. An alumina tube was fitted inside the work tube to serve as a sample stand. A schematic illustration of the experimental set-up is shown in Figure 2.

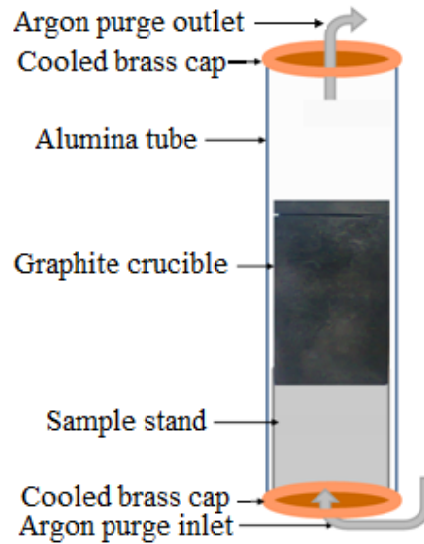


Figure 2-Schematic illustration of the static graphite crucible test set-up

Experimental procedure

Static crucible tests were performed whereby a graphite crucible of known initial dimensions was exposed to synthetic matte at temperature. Synthetic matte was weighed into the graphite crucible and sealed with carbon paste under vacuum. Specimens were further enclosed in a second graphite crucible, which was sealed with carbon paste under vacuum, and then reacted under an argon atmosphere (Figure 2). The specimen was weighed before and after each experiment. After reaction, the specimens were cut axially, mounted in resin, and polished for SEM analysis. The remainder of the sample was milled for ICP, XRD, and LECO analyses.

Examination of the wear mechanisms of graphite by matte

Wear of a refractory material by a liquid can proceed through penetration, dissolution, and erosion^{8, 9}. Penetration of a refractory material by liquid results from physical and mechanical interaction between the liquid and material. Dissolution of refractory by a liquid results from chemical attack of the refractory material by the liquid. Erosion of a refractory material by a liquid is associated with the motion of the liquid⁹. Since only static tests were performed in the current work, erosion of graphite by matte was not a major wear mechanism. Liquid penetration and refractory dissolution are affected mainly by the open porosity and pore size distribution of the refractory material, temperature, refractory material, and liquid composition, as well as the exposure time^{8,9,10-11}.

The matte penetration depth into the graphite and the change in graphite crucible wall thickness was evaluated using SEM analysis. Dissolution of graphite by matte was examined by determining the change in matte carbon content. The carbon and sulphur contents of the matte were determined using LECO analysers.

XRD was employed to determine the crystalline phase composition of the matte and graphite crystal orientation. ICP was used to determine the elemental composition of the matte.

The influence of graphite grade (HG *versus* SG) and exposure time (1 – 5 days) on graphite penetration as well as graphite dissolution into matte at 1550°C was investigated.

Results

Effect of graphite grade on penetration of graphite by matte

Comparative interaction tests were performed on HG and SG graphite crucibles. The specimens were exposed to 1550°C for 1 day, after which they were slow-cooled to 50°C. Matte penetration depth on SG and HG graphite is shown in Figure 3 (a) and (b) respectively. A penetration depth of approximately 2 mm was observed in the SG graphite crucible while matte infiltration into the HG graphite was limited to the immediate hot face (Figure 3b). HG graphite depicted a higher resistance to matte penetration compared to SG graphite. This observation was not surprising, since higher density materials usually exhibit higher resistance to liquid penetration¹² compared with less dense materials. Dissolved carbon in matte was $0.38 \pm 0.03\%$ and $0.33 \pm 0.03\%$ for SG and HG graphite respectively, which is equivalent to 7.4 per cent and 6.7 per cent loss in crucible diameter. Graphite wall thickness change could not be accurately measured since it was only 0.6 mm and 0.5 mm for the SG and HG crucibles respectively. The values given here were calculated from mass of carbon detected in matte, graphite density, and calculated volume of the crucible. Dissolution of SG and HG graphite by matte did not vary significantly since the difference in diameter loss of these crucibles was less than 1 per cent.

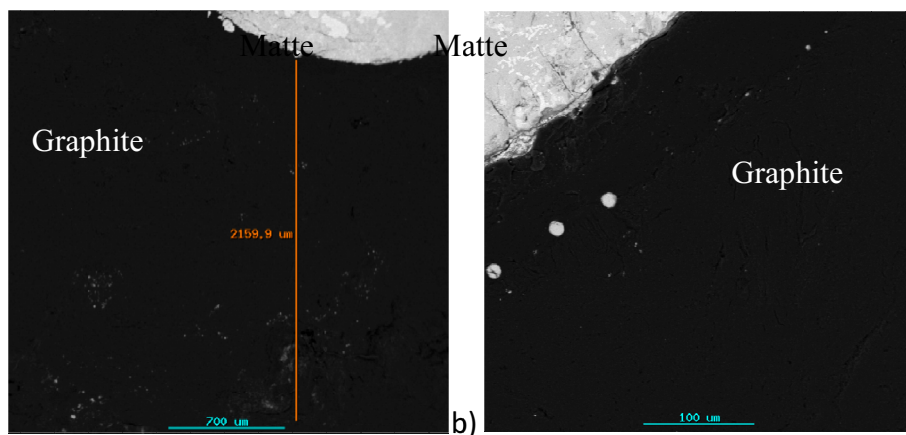


Figure 3-BSE image of matte penetration into the graphite crucibles (a) Penetration up to approximately 2 mm into the SG graphite; b) Penetration limited to the immediate hot face of the HG graphite

An optical microscope image of the sectioned graphite crucible with solidified matte is shown in Figure 4. The convex meniscus of matte on graphite signifies the non-wetting behaviour of graphite by matte^{8,9}. Matte contained in both HG and SG graphite crucibles had convex menisci. The performance of HG and SG graphite exposed to hot matte did not vary significantly, except that HG graphite exhibited higher resistance to matte penetration than the SG graphite.

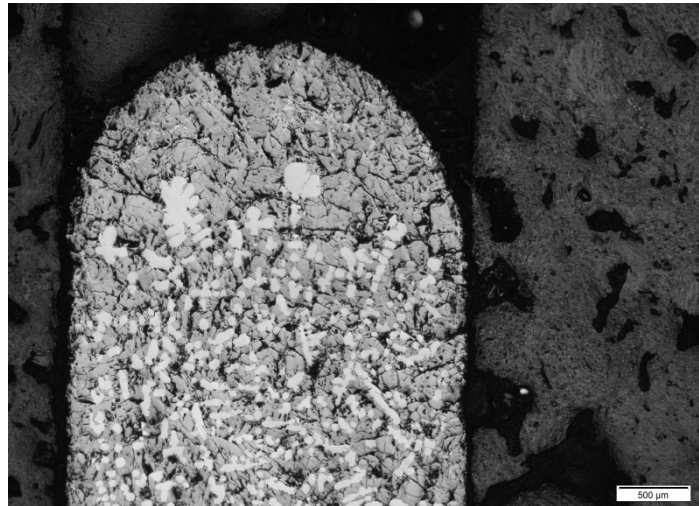


Figure 4-Section of the SG graphite crucible with solidified matte after reaction at 1550°C for 1 day

Effect of exposure time on graphite dissolution and penetration by matte

The effect of temperature and exposure time on graphite-matte interaction was evaluated on SG graphite. The matte-filled graphite crucibles were heated to 1550°C, and reacted for either 1, 3, or 5 days. All specimens were slow-cooled to 50°C.

A matte penetration depth of approximately 2 mm was observed in the graphite crucible (Figure 5). The penetration depth did not increase with exposure time, even after 5 days' exposure the observed penetration depth was approximately 2mm. Matte penetration was not uniform and proceeded mainly through the matrix phase of the graphite crucible. Infiltrated matte consisted of stoichiometric sulphide phases that contained a sulphur-deficient iron-nickel sulphide layer in contact with graphite.

Significant matte loss was observed, increasing from 11 per cent to 20 per cent after 1 and 5 days' exposure respectively. The elemental composition of synthesized and post-mortem matte is shown in Table IV. The percentages of carbon dissolved in the matte at 1550°C after 1, 3, and 5 days were respectively 0.38 per cent, 0.31 per cent, and 0.43 per cent.

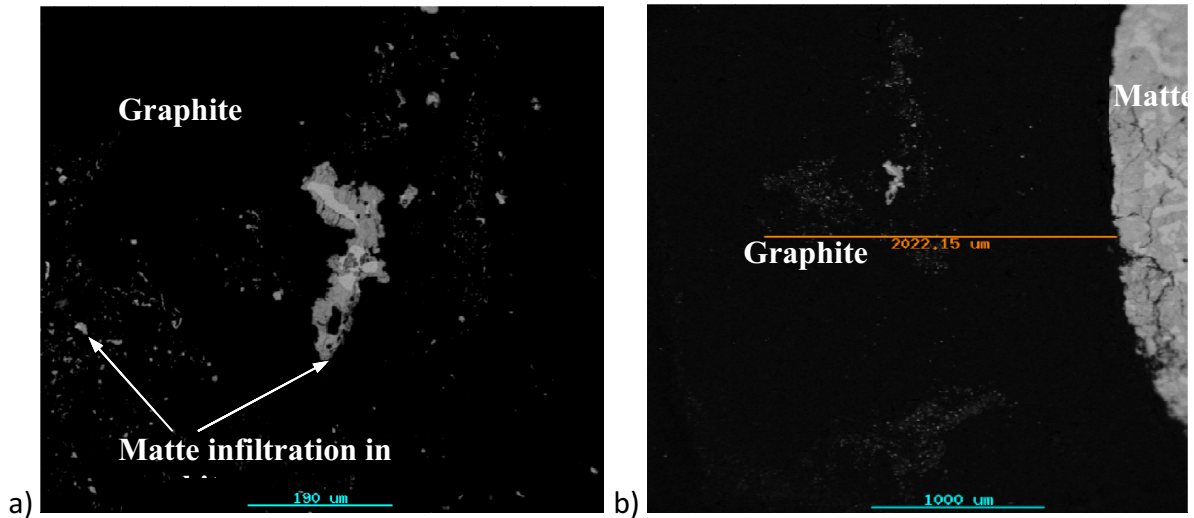


Figure 5-Matte infiltration into the SG graphite at 1550°C for 5 days: a) infiltration detail, b) depth of infiltration of matte into graphite

The three-day exposure test was repeated five times to determine the repeatability of the results. The carbon content of the matte for the five tests had a standard deviation of 0.02 and standard error of 0.01. It is not yet understood why a decrease in carbon dissolution was observed after 3 days.

Table IV-Elemental composition of matte, mass loss of matte and graphite after exposure at 1550°C. weight %

	S (%)	Fe (%)	Ni (%)	Cu (%)	C (%)	O ₂ (%)	Matte loss (%)	Graphite mass loss (%)
Synthesized matte	26.79	44.61	16.41	8.87	0.03	3.28	0.00	-
1 day	25.45	47.01	17.38	9.18	0.38	0.61	11.33	*0.6
3 days	22.52	48.39	19.21	9.57	0.31	**ND	17.02	*1.5
5 days	21.52	51.09	18.99	7.70	0.43	0.27	20.10	*2.0

**ND Not determined

* Calculated from the difference between the mass of graphite before and after exposure. Mass after exposure includes the mass of the matte embedded in graphite due to infiltration

According to Tsymbulov and Tsemekhman¹³ carbon dissolution in a sulphide phase depends on operating temperature, matte sulphur content, and concentration of metal components in the matte. They reported that at 1400°C the solubility of carbon decreases with an increase in sulphur content for a constant Fe:Ni ratio, while at a constant sulphur content the dissolution of carbon increases with an increase in Fe:Ni ratio in the matte. The percentage carbon dissolution associated with the matte composition used in this investigation (0.43 per cent C at 1550°C, (Table) agrees well with the data of Tsymbulov and Tsemekhman,¹³ who found that a matte with nickel content of 20.2 per cent, iron content of 57.6 per cent, and sulphur content of 21.7 per cent dissolves 0.46 per cent carbon at 1400°C. Carbon dissolution into matte has proven to be a mass-transfer controlled mechanism, which is not strongly affected by exposure time but is significantly affected by temperature. It was found that an increase in temperature from 1150°C to 1350°C did not significantly increase the carbon dissolved in the matte, but at 1550°C carbon dissolution and matte loss were significant (Figure 6).

The dissolution of graphite by matte did not increase significantly from 1 to 5 days' exposure. Large quantities of graphite are therefore not expected to be consumed by matte with increasing time of operation. However, matte is constantly tapped and replaced by fresh matte, which implies that after each tap the matte will again dissolve graphite until the matte is saturated with graphite.

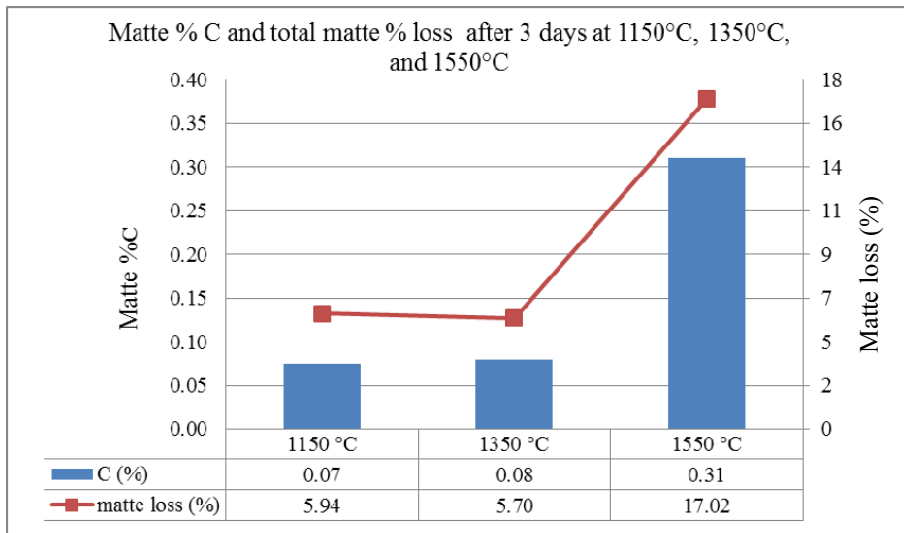
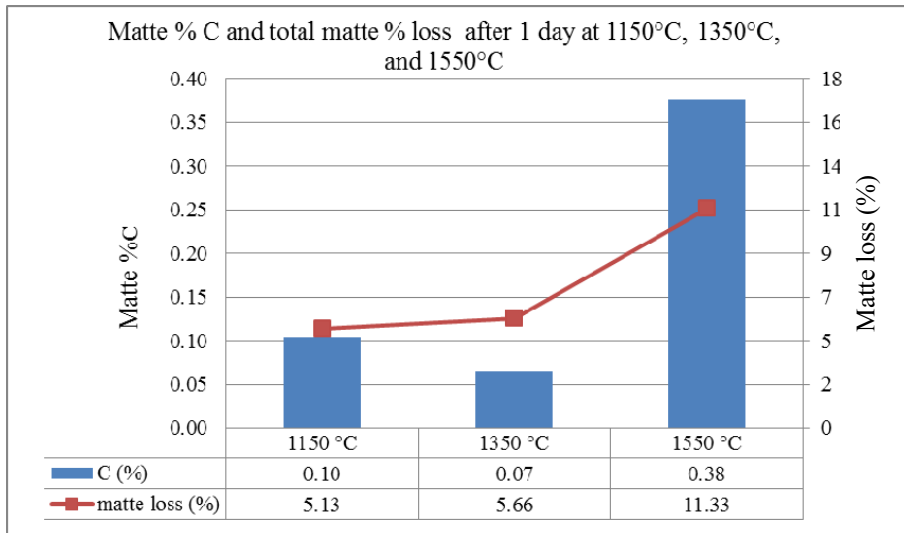


Figure 6-Percentage dissolved carbon in matte and total matte loss as a function of temperature after 1 and 3 days of exposure

Although the examined matte was saturated with carbon at low carbon concentrations, it was observed that exposure time had a major effect on the total mass loss of matte. Average matte mass losses of 10 per cent and 20 per cent were observed for 1 day and 5 days of reaction respectively. This observation was compatible with the matte ICP analysis (Table IV), which indicated that a significant amount of sulphur and copper was lost during 5 days of exposure. The S:Fe ratio and Cu:Fe ratio decreased by 30 per cent and 24 per cent respectively, while the Ni:Fe ratio remained constant at 0.4 per cent.

This agrees with the work of Thomas¹⁴ who observed that the Cu:Fe ratio in copper concentrate decreased with exposure time when a copper iron sulphide concentrate was combusted in the presence of oxygen at temperatures up to 900°C.

It was also observed in the current study that gaseous species from the off-gas precipitated on the top water-cooled brass fitting. XRD analysis indicated that this accretion consists of a mixture of bornite (Cu_5FeS_4), chalcocite (Cu_2S), mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$), covellite (CuS), and chalcopyrite (CuFeS_2) (Table V). These sulphide phases are similar to the product that is observed on the copper cooler surface in industrial PGM smelters². It is believed that these sulphide phases were transported from the crucible to the cold part of the furnace through volatilization at high temperatures. This agrees with the findings of Jorgensen¹⁴, who observed that 41 per cent copper vapourized from a complex copper concentrate (7.4 per cent Zn, 5 per cent Pb and 22.5 per cent Cu) in a nitrogen atmosphere with 1 per cent oxygen at 1400°C.

Vapourization is therefore a plausible mechanism for significant copper loss from matte. The mechanism of sulphide transport from the hot graphite crucible to the cold part of the work tube is still under investigation. This mechanism can, however, be a cause of the deposition of sulphides as is observed at the surface of the copper coolers behind the graphite blocks in industrial primary PGM smelters².

Table V-Semiquantitative XRD analysis of the accretion

Condensate	Weight %	3 σ error
Bornite (Cu_5FeS_4)	25.6	1.08
Chalcocite (Cu_2S)	21.74	1.77
Mooihoekite ($\text{Cu}_9\text{Fe}_9\text{S}_{16}$)	20.58	1.71
Covellite (CuS)	18.32	1.17
Chalcopyrite (CuFeS_2)	13.76	1.41

Conclusions

- Matte penetrated to a higher degree into SG graphite (up to ~2mm) than into HG graphite (limited to the immediate hot face)
- The saturation solubility of graphite into the synthetic matte at 1550°C was 0.43 per cent

- Graphite dissolution into the matte was mainly affected by the matte temperature, and not the interaction time
- Cu, Fe, Ni, and S were detected in an accretion that formed in the water-cooled part of the furnace. This accretion mainly consists of Cu-S – based and Cu-Fe-S – based phases.

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