

# PROCEEDINGS



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# STUDY ON SLAG DESIGN OF FAYALITIC BY-PRODUCTS AS AN OXIDE RAW MATERIAL FOR SOLAR HEAT ABSORBER AND STORAGE MEDIA

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## Introduction

Concentrated Solar Power (CSP) and thermal technology has become a focus of research due to the general increase in demand for sustainable and resource-efficient energy production. <sup>1</sup> Furthermore a higher potential of generating energy with CSP technology was announced within the integration of thermal energy storage (TES) systems to compensate an off-sun condition and besides being able to produce energy independently from the weather or daytime conditions<sup>2</sup>. Therefore, several approaches are currently under research to find more environmentally friendly solar heat absorbers and storage media with better properties to be more efficient comparing to the currently used salt mixtures<sup>3,4</sup>. As a result, the focus of research is on the modification and use of oxide residues as high temperature resistant ceramic particles for solar heat absorbers and storage media<sup>1,2</sup>. This study investigates the engineering of fayalitic slag as a secondary residue investigating different melting and cooling strategies. The general aim is to produce a material with a high crystallinity, a high heat capacity, temperature stability up to 1000°C and good abrasion resistance. <sup>1,2,5</sup> Therefore, in order to understand and maximise crystallisation in the fayalitic system, as a first step different cooling strategies are systematically varied in laboratory scale experiments. In a second step, various oxidic doping agents will be tested to determine whether they enhance the desired properties.

## Materials and Methods

The investigations in this study are carried out with an fayalitic slag aligned with the copper route, similar to previous studies from Alkan *et al.*<sup>1</sup>. The composition of the slag, focusing on the main components, is shown in Table 1 and was measured by using an X-ray fluorescence spectrometer (XRF, PANalytical WDXRF spectrometer Axios).

**Table 1:** Composition of the synthetic fayalitic slag

Compound	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	CuO	ZnO	PbO
wt%	0.37	1.49	3.20	26.26	0.86	2.69	62.48	1.44	0.89	0.33

The fayalitic slag which is used in this study is shown in Figure 1. The slag is produced synthetically at IME Aachen. For handling further trials and to ensure homogeneity, the slag was granulated using a water quenching method.



**Figure 1:** Synthetic fayalitic slag, granulated

The trials are carried out in a resistance heated chamber furnace. The material is fed into a 0.2 L alumina crucible. For each trial 200 g of slag is used. The furnace is heated up with 250°C/h up to 1200°C. This temperature is maintained for 1 h to ensure the entire slag is melted and homogenised in the crucible. The whole process is performed under an argon atmosphere, therefore 1 L/min is supplied into the resistance heated furnace. Different cooling strategies are tested, ranging from quenching the molten slag at cooling rates from 300°C/h to 10°C/h.

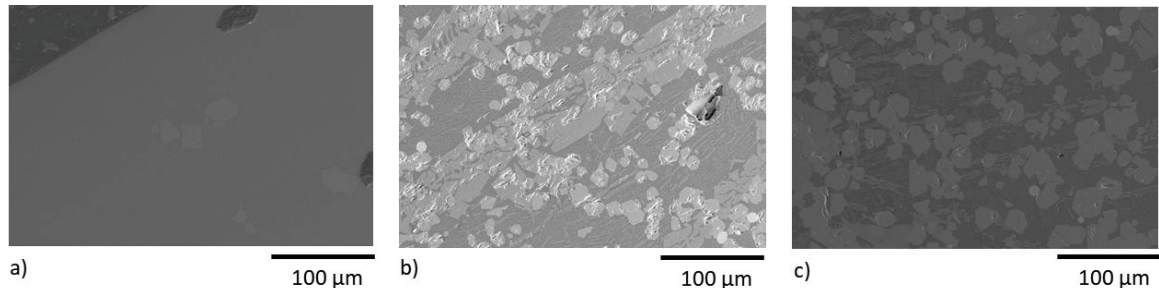
Microstructural and chemical analysis of embedded and coated cross sections is performed by scanning electron microscopy (SEM Ultra 55, Zeiss, Wetzlar, Germany) and energy dispersive spectroscopy (EDS; UltiMate, Oxford, Abdingdon, United Kingdom). For the cross-sectional analysis, samples are embedded in commercial epoxy resin. The phase components are analysed with X-ray powder diffraction (XRD; D8 Advance, Bruker AXS, Karlsruhe, Germany). Measurements were made using a diffractometer with Cu-K $\alpha$  configuration, with having a closer look at 2 $\theta$  in between 10° and 80°.

## Results and Discussion

The melting trials conducted in this study aimed to investigate various cooling strategies for the quenching of molten slag and cooling rates ranging from 300°C/h to 10°C/h. The entire process within the furnace is performed under an argon atmosphere to prevent potential reactions with ambient air.

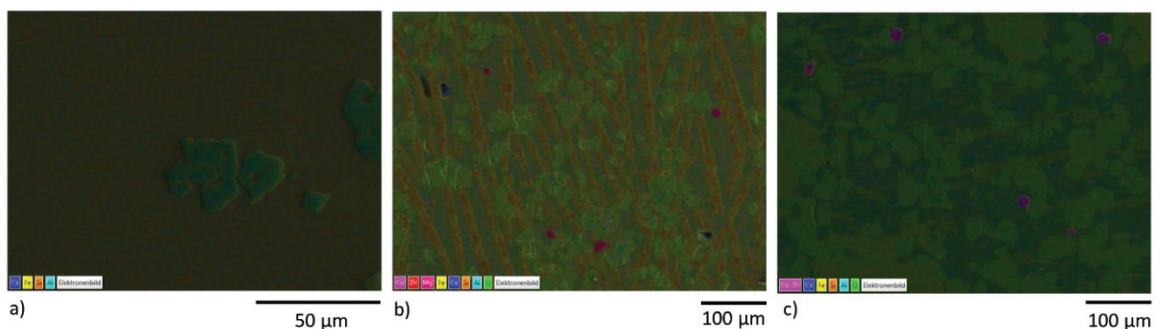
Figure 2 presents SEM recording of the three edge parts of the samples from the performed experiments. In case of the quenched sample, as illustrated in Figure 2 a), an amorphous structure is observed, characterized by minimal crystallization. Conversely,

when trials were executed at slower cooling rates relative to the quenched slag, a decrease in amorphous content and increase in crystallinity were noted (see Figure 2 b) and c)). By comparing the quenched case to a cooling rates of 300°C/h and 10°C/h, it can be established that the growth of larger grains is associated with a reduction in the cooling rate.



**Figure 2:** SEM pictures of: a) quenched slag; b) cooling rate 300°C/h; c) cooling rate 10°C/h

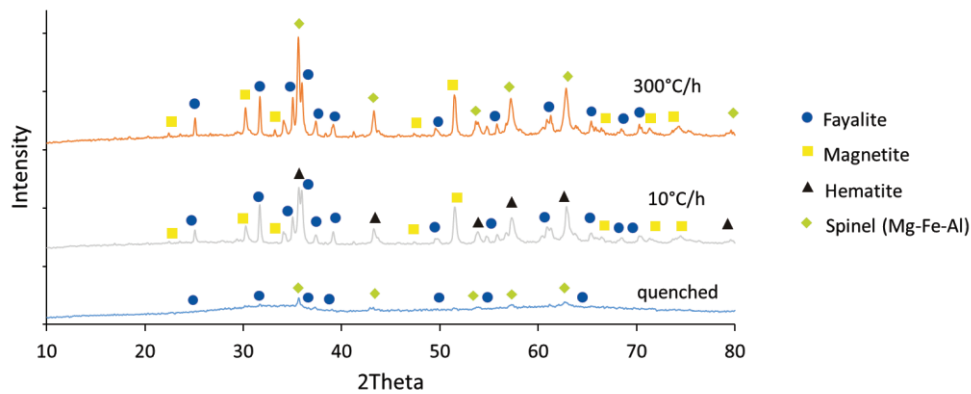
To identify the primary elements present in the amorphous and crystalline phases indicated in Figure 2, EDS-Mapping (shown in Figure 3) was performed on these regions, accompanied by XRD analysis (shown in Figure 4) to validate the identified phases. As depicted in Figure 3 a), the EDS-Mapping of the quenched slag reveals that the amorphous structure is predominantly composed of iron- and silicon oxides. The XRD analysis in Figure 4 corroborates that this material corresponds to fayalitic glass, along with small spinel-type grains. For a cooling rate of 300°C/h, as illustrated in Figure 3 b), both EDS-Mapping and XRD results indicate a reduced presence of fayalitic glass and increased occurrence of crystalline structures. Furthermore, elongated fayalitic needles are observed within magnetite-containing grains, alongside the detection of spinel grains. A comparable result is noticed for a cooling rate of 10°C/h, as shown in Figure 3 c). In contrast to the conditions at 300°C/h, larger fayalitic needles are evident, along with initial formations of hematite grains.



**Figure 3:** EDS-Mapping of: a) quenched slag; b) cooling rate 300°C/h; c) cooling rate 10°C/h

The results indicate that the transformation of fayalite to magnetite and subsequently to hematite occurs at lower cooling rates, as confirmed by EDS data presented in

Figure 3 and XRD analysis presented in Figure 4. This process leads to the formation of a more stable form of iron in terms of material stability. The phase transition from magnetite to haematite necessitates the presence of oxygen. Given that the entire process was conducted under an argon atmosphere, it can be inferred that the required oxygen is derived from the slag system itself, resulting in the reduction of another oxide.



**Figure 4:** XRD Results of: quenched slag; cooling rate 300°C/h; cooling rate 10°C/h

Moreover, with extended cooling times per hour, a metallic copper-magnesium alloy was increasingly detected in the samples through EDX, as illustrated by the areas shaded in pink in Figure 3. This observation was further confirmed by XRD analysis shown in Figure 4. The formation of hematite is advantageous for enhancing properties such as long-term solar absorptance of the oxidic material, which is essential for its application as solar heat absorber and storage medium within CSP technology.<sup>2</sup>

## Conclusion

The engineering of fayalitic slag is accomplished by emphasizing of melting and cooling strategies. Systematic variations of different cooling strategies are conducted through laboratory-scale trials to enhance and maximise crystallisation within the fayalitic system. The findings indicate that lower cooling rates lead to increased crystallinity, thereby facilitating the formation of more stable iron-rich phases, specifically in the transition from fayalite to magnetite and ultimately to haematite. Furthermore, previous studies conducted by Alkan *et al.*<sup>1,2</sup> have demonstrated that the phases characterized by reduced amorphous content and elevated crystallinity are advantageous for application as ceramic particles in solar heat absorbers and storage media. The observed increase correlates with enhanced abrasion resistance of the particles within the CSP plant, highlighting their potential utility in this context.

Future research will concentrate on enhancing the properties essential for CSP applications, including high heat capacity, excellent wear resistance, long-term durability, and effective solar absorptivity<sup>5,6</sup>. The objective is to investigate a broader

spectrum of cooling rates to further develop the fayalitic slag as a foundational material for subsequent modifications<sup>1,7</sup>. In forthcoming studies, targeted control of reactions through the incorporation of nucleating agents during the melting process will be modelled using FactSage<sup>TM</sup> <sup>8</sup> calculations and subsequently tested in laboratory-scale trials. The introduction of oxides as nucleating agents has the potential to refine the crystallisation process and optimize the products of the melting, thereby enhancing the functional properties necessary for application as solar heat absorbers and storage media for CSP technology<sup>1,2</sup>.

## Acknowledgements

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