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ORIGINAL ARTICLE

LA-ICP-MS and SEM-EDX analyses for spatially resolved element detection in cement clinker phases

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Abstract

This study combines 2D element mappings which allows a more detailed analysis of clinker phase composition by using the advantages of both methods. One mapping is obtained by laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS), providing very good results for minor and trace element concentrations with a low spatial resolution. The other dataset is generated using energy dispersive X-ray spectrometry (EDX) in a scanning electron microscope (SEM) which provides high-resolution element mappings of cement clinker phases, with a low accuracy in chemical composition.
It is revealed that this approach enables to determine the major and trace element concentrations in phases like alite, belite and the interstitial phase (C_3A, C_4AF) of real Portland cement clinker. A protocol is shown how to record and subsequently register both datasets as such, that the combined analysis significantly broadens the output of the individual measurements. The low detection limits of LA-ICP-MS delivers trace element concentrations and the high spatial resolution and analytical accuracy of SEM-EDX identifies the clinker phases. Results show that Ba, K, V, and Rb are preferentially incorporated into belite, while Na, Ti, and Mn is enriched in the interstitial phase. This allows to study the influence of minor and trace elements on the stabilization and reactivity of clinker phases.

Keywords

portland cement clinker, energy dispersive X-ray spectrometry, laser ablation with inductively coupled plasma, mass spectrometry, trace element analyses

1 Introduction

The work presented here has already been discussed in more detail in another peer-reviewed paper [1].

2 Materials and Methods

A 10 mm Ordinary Portland cement clinker grain (type CEM I according to DIN/EN 197-1) obtained from an industrial process has been used for this investigation. It was cut, embedded in epoxy resin and successive mechanically polished using diamond oil pastes with grain sizes of 15, 9, 3, 1 down to 0.25 µm. The specimen was coated with approximately 8-10 nm carbon for the SEM-imaging to avoid charging artifacts. The coating was removed using argon broad ion beam polishing before the laser ablation.

The SEM investigations were done using a Helios G4 UX (ThermoFischer Scientific), equipped with a silicon drift EDX detector (XMAX 80, Oxford Instruments, UK). The EDX-mappings were recorded at 12 kV, 0.8 nA with a dwell time of 0.3 msec and 60 frames were summed up. Aztec 4.3 (Oxford Instruments, UK) has been used for recording EDX maps and to generate phase maps from elemental distribution maps.

The laser ablation (LA) was done using a ns-Nd:YAG-laser at the quintupled wavelength of 213 nm (ESI NWR 213). Helium was used as carrier gas. The gas was analysed using a quadrupole inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer NexION 300D).

In total 3 areas (0.09, 0,12, 0,08 mm²) were mapped.

3 Conclusion

This research presents a way on how to combine LA-ICP-MS and SEM-EDX analysis to characterize cement clinker phases. The combination of both methods allows a more detailed analysis of clinker phase composition by using the advantages of both methods as illustrated in Figure 1.

It is required, that the clinker analysis is performed on the same areas of the clinker. LA-ICP-MS as a destructive

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method must follow the SEM-EDX analysis. It was demonstrated that it is possible to relocate the areas analysed by SEM-EDX for LA-ICP-MS. However, large area BSE images and efficient marking of the polished clinker surface are necessary to simplify this process.

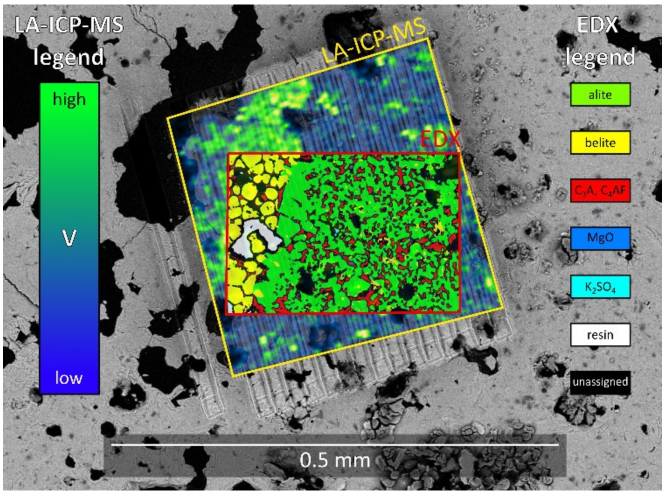

Figure 1 Illustration of the main concept. A SEM-BSE image is combined with a SED-EDX-phase mapping and the respective LA-ICP-MS dataset to allocate minor and trace elements to identified phases.

Generally, SEM-EDX should deliver high-resolution element distribution maps and should allow quantification of spectra. It was shown, that by using 12 kV acceleration voltage a good compromise between high resolution mappings and quantification of spectra was found. A prerequisite for LA-ICP-MS analysis is that EDX phase mappings clearly distinguish clinker phases. LA-ICP-MS spot size should be as small as possible while enabling a valid limit of determination of the elements of interest.

The LA-ICP-MS analysis should be followed up by SEM imaging in secondary electron (SE) or backscattered electron (BSE) mode. This allows to characterize the size of the craters and trenches caused by laser ablation. Knowing the spot size and the exact position of the laser ablation is shown to be essential for data evaluation and interpretation. It was revealed that the sizes of the ablation craters are similar for all clinker phases, while the resin used for embedding is ablated in a more intense way. Nevertheless, one typical source of error in LA-ICP-MS analysis of inhomogeneous materials like clinker is the variation in the material composition in the z-direction. This z-effect is of minor importance in EDX analysis (1.6 - 2.0 µm) while it is more pronounced for LA-ICP-MS (7 µm).

The registration of the datasets was not done fully automatically. Since the datasets differ a lot, four or more points of interest were identified in the datasets and a homography matrix was calculated and transomed using the RANSAC algorithm [2]. After the registration of the datasets, the higher spatial resolution of the Ca, Si, Fe, Al, S and Mg element distribution maps provided by EDX allows to construct a phase map that is applied to the LA-ICP-MS data. This allows us to segment the LA-ICP-MS dataset using the resolution of the EDX data to provide insight into the minor and trace element distribution among clinker phases. Due to a spot size of 6 x 6 µm of the laser and the small size of the interstitial phases, e.g. C_3A, C_4AF and MgO, a relatively large deviation in LA-ICP-MS concentrations is caused by ablating the neighbouring phases such as alite and belite. This deviation can also be found for alite but to a lesser extent. This causes an increased standard deviation for the LA-ICP-MS analysis for these small phases.

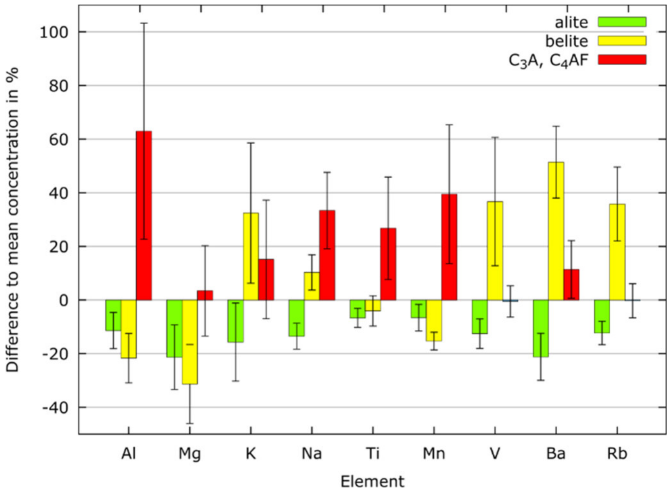

Figure 2 Difference to the mean element concentration for each phase. Concentration data originate from three experiments on the same sample. Segmentation was done using the respective EDX datasets. Only the segmented areas of alite, belite and C_3A/C_4AF were considered for the mean value. The error bars represent the standard deviation of an element concentration within a phase.

The results indicate that alite contains lower amounts of K, Ba, V, and Rb compared to belite, as shown in Figure 2. Previous literature has reported higher levels of Ba, while the accumulation of V aligns with belite's tendency to incorporate larger ions [3]. The formation of the lamella twin structure in belite is a result of the alpha to beta polymorph transformation during clinker cooling [3]. Submicron scale exsolution structures along belite twin lamellas are known to contain alkali sulphate or aluminate phases [3]. However, these submicron phases cannot be distinguished using the current approach.

Na, Ti and Mn is enriched in the interstitial phase. It is already well known from previous studies that Mn can completely replace Fe in the C_3A-C_4AF series and up to 60 atomic percent of the Al [4].

For this study, tools were developed which enable to measure and locate the major, minor and trace elements in cement clinker phases. This includes a python-based script to analyse LA data, allows rapid data processing, and helps visualizing the obtained data. [5]

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