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Simultaneous assessment of phase chemistry, phase abundance and bulk chemistry with statistical electron probe micro-analyses: Application to cement clinkers

William Wilson, Konrad J. Krakowiak, Franz-Josef Ulm *

Civil and Environmental Engineering Department, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139-4307, USA

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ABSTRACT

According to recent developments in cement clinker engineering, the optimization of chemical substitutions in the main clinker phases offers a promising approach to improve both reactivity and grindability of clinkers. Thus, monitoring the chemistry of the phases may become part of the quality control at the cement plants, along with the usual measurements of the abundance of the mineralogical phases (quantitative X-ray diffraction) and the bulk chemistry (X-ray fluorescence). This paper presents a new method to assess these three complementary quantities with a single experiment. The method is based on electron microprobe spot analyses, performed over a grid located on a representative surface of the sample and interpreted with advanced statistical tools. This paper describes the method and the experimental program performed on industrial clinkers to establish the accuracy in comparison to conventional methods.

1. Introduction

The grindability and reactivity of Portland cement depend, in general, on the chemical composition of the clinker, the level of crystallinity as well as the clinker microtexture [1,2]. Such properties tend to be a complex function of the raw materials and the processing conditions in the kiln. In the quality control of the manufacturing process, the chemical and mineralogical compositions are important indicators, which may be measured on cement clinkers, the intermediate product produced by air quenching of the melt after kiln firing.

Bulk chemistry is usually assessed with X-ray fluorescence (XRF), which is widely used with the Bogue method [3] (or the modified Bogue method [4]) to estimate the relative abundance of the main clinker phases (alite [~C_3S], belite [~C_2S], aluminate [C_3A] and ferrite [~C_4AF]). However, due to the propagation of uncertainties in the Bogue calculations, small errors in chemical analysis lead to large errors in phase abundance [5]. Thus, the cement industry is now in a transition toward an increased use of X-ray powder diffraction (XRD) along with the Rietveld method [6], which allows a better quantification of clinker phases and the distinction between the polymorphs for each phase [5,7,8]. The use of scanning electron microscope (SEM) image analysis was also proposed for quantitative mineralogy by combination of back-scattered electron images and X-ray chemical mappings [9,10].

The chemical composition of each phase may be quantitatively measured with an electron probe micro-analyzer equipped with wavelength dispersive spectrometers (EPMA-WDS) [11,12] or with a SEM equipped with an energy dispersive spectrometer (SEM-EDS) [13]. Although the chemistry of the phases is not yet monitored on a regular basis at the cement plants, the demand for such monitoring is expected to grow in the future. Indeed, recent experimental and simulation works on chemical substitutions in the clinker main phases indicate new possibilities for engineering clinkers with better grindability and reactivity [14,15].

In this context, a method is developed to extract three important quantities from a single experiment: the chemistry of the individual phases, the relative abundance of these phases and the chemistry of the bulk material. The method is based on the combined use of grid EPMA spot analyses performed over a representative sample surface and statistical methods to extract the desired quantities. This paper describes the method and applies it to four industrial clinkers. The accuracy is assessed in comparison to reference techniques (quantitative XRD and XRF) and the results are further explored with the support of SEM image analyses. To optimize the quality of the results, three different sample preparation methods are investigated: bulk samples, coarsely ground samples, and finely ground samples.

2. Material and methods

2.1. Materials

Four industrial cement clinkers are investigated in this work. These were obtained from four distinct cement plants and labeled as C1, C2, C3 and C4. In order to ensure integrity, the samples were stored in doubled plastic bags and placed in an environment with controlled temperature and humidity.

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* Corresponding author.
E-mail address: ulm@mit.edu (F.-J. Ulm).

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2.2. Sample preparation

2.2.1. Powdered samples

A representative sample of 30 g was randomly selected for each clinker after homogenization. The samples were coarsely ground in an agate mortar for 10 min per 5 g, then dried for 12 h at 110 °C, and finally cooled in a desiccator for 30 min. After homogenization, 4 subsamples of 2 g were finely ground for each clinker in the agate mortar for 3 min per 0.4 g. The coarsely ground and finely ground powders were dried, and then stored in hermetic bottles placed in a desiccator.

2.2.2. Epoxy-embedded polished surfaces

One of the requirements for scanning electron microscopy (SEM) and electron probe microanalyses (EPMA) is a flat polish (<1 μm) of the specimen surface [16]. To fulfill this condition and minimize the influence of surface geometry on the measurements, clinker samples were impregnated in epoxy and polished with a semi-automatic procedure optimized for hard and porous clinker samples.

The bulk samples (B series) were prepared with clinker nodules of 20–30 mm in diameter. Slices of 12 mm thickness were cut with a low speed diamond saw and impregnated with epoxy (EpoThin, Buehler, USA) under pressure cycles (1 min under vacuum of 26 ″ Hg and 1 min at atmospheric pressure, as suggested in Buehler [17]).

After hardening, specimens of 4 mm thickness were cut and mounted on standard AFM bases of 15 mm in diameter (Ted Pella, USA). The specimens were automatically leveled and ground with a specially designed jig and post system (described elsewhere [18]) using a hard perforated cloth (TexMetP, Buehler, USA) and 9 μm oil-based diamond suspension (MetaDi, Buehler, USA). Manual dry polishing was then achieved using 3 μm diamond abrasive disks and 1 μm aluminum oxide disks (FibrMet, Buehler, USA). Ultrasonic cleaning of 3 min in n-Decane (TCI, Japan) was performed after each step. The surfaces obtained were characterized by a high mirror-like reflectivity and by rare occurrence of surface irregularities visible under 20× and 50× objectives of the optical microscope. Finally, the specimens were dried in an oven at 40 °C for 12 h, coated with a 25 nm carbon layer and stored in a desiccator.

In addition to the bulk samples (B series), two series of epoxy impregnated samples were prepared with the ground powders: a first series with the coarsely ground clinkers (C series) and a second series with the finely ground clinkers (F series). For each sample, 2 g was compacted with a post in a 12 mm cylindrical mold. Epoxy impregnation and sample polishing were performed with the same procedure used for bulk samples, except for the choice of dry abrasive disks which was, in this case, successively 9, 3 and 1 μm aluminum oxide pads. Indeed, polishing with diamond pads was found to be inadequate, leading to the removal of surface grains along with a diminution of the quality of the surface.

2.3. Electron probe micro-analyses

2.3.1. Experimental protocol

Chemical analyses were performed on the polished samples with a JEOL JXA-8200 Superprobe electron probe microanalyzer coupled with a wavelength dispersive X-ray spectrometer. The accelerating voltage was set to 15 kV and the beam current to 10 nA. The beam diameter was 1 μm and the counting time was 10 s per element. The following elements were measured for each spot analysis on the polished surface, after background correction: Ca, Si, Al, Fe, S, Mg, Na, K, and O. The calibration of the instrument was performed with the following standards: synthetic diopside for Al, Na, Si, Ca and Mg; high purity hematite for Fe and O; nickel sulfide for S; and synthetic orthoclase for K.

The raw data was corrected for matrix effects with the CITZAF package implemented in the probe software [19], using the $\phi(\rho z)$-method: stopping power, back-scatter corrections and $\phi(0)$ from Love and Scott; mean ionization potential from Berger and Seltzer; Heinrich's tabulation of mass absorption coefficients; and Armstrong's modified equations for absorption and fluorescence corrections [16,20]. Preliminary testing revealed significant deviations in the direct measurement of the oxygen content, therefore it was alternatively determined from stoichiometry.

2.3.2. Application to heterogeneous materials

2.3.2.1. Interaction volume. Each EPMA spot analysis is assumed to be representative of an interaction volume, which corresponds to the region inside the bulk of the sample from which the characteristic X-rays are emitted. This interaction volume is a function of the accelerating voltage of the electron beam and the composition and density of the probed material [16]. Monte Carlo simulations were performed with the non-commercial program CASINO [21] to estimate the interaction volume for cement clinker. The radius of the interaction volume, including 90% to 95% of emitted X-rays for all measured elements, was found to range between 0.5 and 0.75 μm when probing a flat clinker surface with a 15 kV electron beam.

2.3.2.2. Statistical grid measurements. In heterogeneous materials such as clinkers, a mixture of phases is measured when the interaction volume is not entirely inscribed in the domain of a single phase. If the scale of the heterogeneities is much larger than that of the interaction volume, imaging can be used to focus spot measurements on a single phase within acceptable error. In the case of similar scaling, an alternative method is the random probing at discrete locations on a grid $l_x \times l_y$ that spans a specific region on a material surface $L_x \times L_y$ (e.g., Fig. 1). This method results in probing both pure phases and mixtures of phases. The estimation of statistically distinct chemical species and their properties can then be performed with advanced statistical tools.

In this work, the total number of grid points, N, was determined according to the following criteria: a) the minimum number of observations on each of the principal clinker phases should be ≥30, thus the normal approximation to the error distribution may be applicable; b) the total number of observations on the clinker material should provide a stable estimate of the volumetric proportions; and c) the measurement over a representative region-of-interest must be done at the prescribed time cost. Based on these criteria, on results of quantitative x-ray diffraction and scanning electron microscopy, as well as on previous investigations on cement pastes [22], a grid of 32-by-32 points was chosen as a compromise for different types of samples. The grid spacing, L, was adjusted to ensure that each grid covers a representative surface

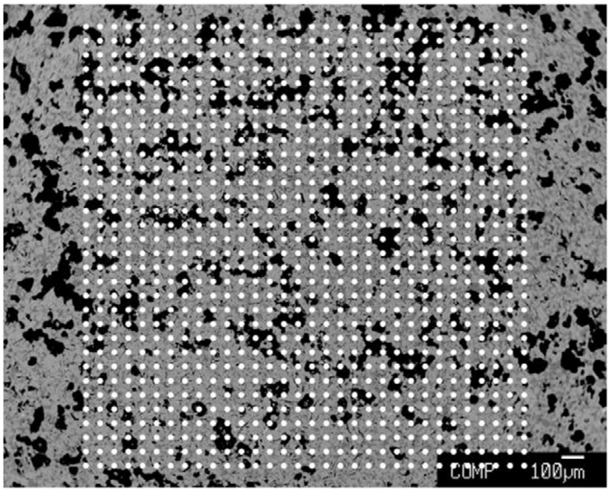

Fig. 1. Schematic of the EPMA grid superposed on a BSE image of bulk sample B-C3. The white dots represent the sampling grid, which covers a clinker surface composed of the clinker matrix in gray and the porosity in black.