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OPTICAL MICROSCOPY EVALUATION OF PORTLAND CEMENT CLINKER - ACETIC ACID ETCHING PREPARATION

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ABSTRACT
The microscope has become a more common tool in the cement industry. Evaluation of clinker using microscopy is a powerful technique that can help improve clinker production and cement quality. The key to using the microscopy is understanding the process of clinker production namely how raw materials are transformed into clinker. These transformations involve chemical and physical processes as the material passes through the rotary kiln. Clinker microscopy can provide information about the temperature in the kiln and provide clues to improve clinker grindability, optimize raw feed fineness or increasing 28-day strength. Regarding problems, imagine being able to help identify the causes of poor clinker grindability or low cement mortar strength.

1. INTRODUCTION
Some of essential cement properties as setting time, hardening, heat of hydration, soundness and strength development mostly depend on the composition of clinker phases. The quantitative and qualitative composition of clinker phases depend on the fineness and homogenization of the raw materials, the lime saturation factor (LSF), silica ratio (SR), alumina ratio (AR) as well as MgO, alkali and sulphate and some minor elements (P_2O_5 and F) in raw meal and fuel. It depends also on the burning temperature and residence time and cooling rate of the clinker conditions. The chemical composition of the clinker phases, their crystal size and shape, as well as the structure of the matrix, will control the main properties of the cement and also will directly affect the clinker grindability and electrical energy consumption

Portland cement clinker is produced by sintering limestone, aluminosilicate materials, iron ore and siliceous raw materials at temperature of up to 1450 °C and emerges from a dry process kiln in form of rounded granules and from wet process kiln as irregularly shaped lumps, typically 3-20 mm dimensions. Generally, four main clinker phases are produces corresponding to about 95% of the Portland cement. They emerge from the kiln not as pure phases, but rather as impure crystals which correspond to the next phases [1]:

- alite (tri-calcium silicate, C_3S),
- belite, (di-calcium silicate, C_2S),
- aluminate (tri-calcium aluminate, C_3A),
- ferrite (tetra-calcium aluminoferite, C_4AF, also called brownmillerite)

The important properties of clinkers phases to evaluate include size, morphology, distribution and reactivity to etching [2].

2. SAMPLE PREPARATION

The clinker for microscopy is preparing by crushing and then this amount of clinker sample is screening between sieves 2.0 and 4.0 mm (Figure 1). Such clinker grain size is a representative sample for microscopy. The clinker is then mixed with powder and curing agent, then it brushes on by certain abrasive papers (60, 150, 220 and 400 microns) and polished at the very fine canvas containing only aluminum pastes to get the cleanest cross section polished sample (Figure 2). After preparing a polished section of clinker (Figure 3), next step is etching with acetic acid (Figure 4). Etching with acetic acid helps to make clinker minerals easier to identify and recognize clinker minerals by theirs shapes. Etching time is from 5 to 15 seconds. It depends on concentrate of acetic. The lower the acetic acid concentration, the longer the acetic time for etching.

Figure 1. Clinker

Figure 2. Brushing device

Figure 3. Polished clinker section

Figure 4. Acetic acid

3. CLINKER MINERALS

3.1. Alite

Alite is the main constituent of clinker. It represents usually 50-70% of the total mass (Figure 5). Because of the inclusion of foreign ions such as Mg, Al, Si or Fe originating from the raw materials and fuels, it is not a pure compound. The inclusion of foreign ions usually has stabilizing effect on the crystal matrix. There are only 3 of 7 various form which occur in technical clinker. These are M3, M1 and T2 form of clinker. Alite indicates the rate of temperature rise of the kiln charge between 1200 °C-1450 °C where C_2S combines with CaO to form C_3S. Rapid heating is desirable, and it is indicated by alite crystal size from 10 to 20 μm while slow heating produces crystal size of 40-60 μm or larger. If the cooling is slower, alite is generating with secondary belite on the edge of alite and and that alite has less reactivity (figure 6.) Alite possesses the most hydraulic properties of all the clinker phases and determines the strength development by creating calcium silica hydrates (C-S-H). Alite can be colored by blue, yellow, brown and green by etching with acetic acid. Concerning shapes of alite, there are idiomorphic, hypidiomorphic and xenomorphic. The xenomorphic shape is the most often in the technical clinker [1].

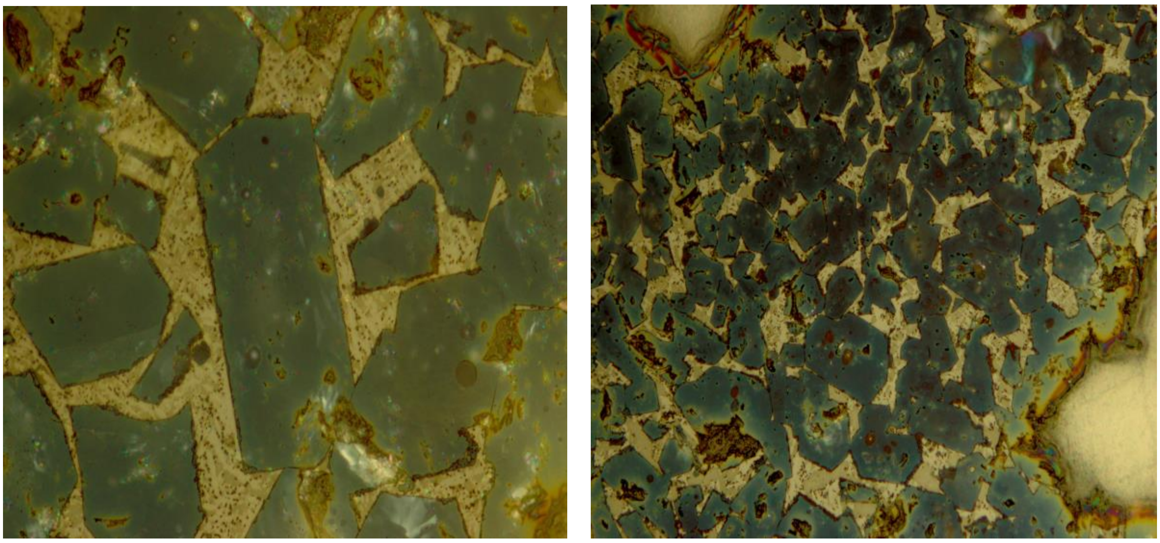

Figure 5. Typical alite crystals

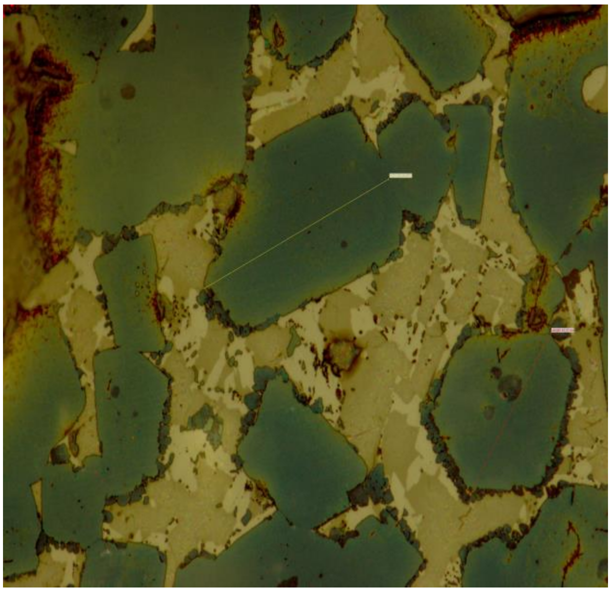

Figure 6. Slow cooling alite crystals with secondary belite on the edge

3.2. Belite

Belite (C_2S) is created in the sintering process and usually comprises from 5% to 30% of the clinker by mass (Figure 7). Up to 6% of the mass of belite is composed of foreign constituents such as alkali metals, iron, sulfur or magnesium. Microscopic structure of belite provides an indication of the conditions under which the clinker was burnt and cooled. The distribution of belite in clinker is often a function of the fineness and homogeneity of the raw meal. Belite occurs ih four forms and they develop one after the other during the cooling process (α, α', β and ɣ). Belite forms round crystal that are usually between 15 and 40 μm in size and which appear under microscope with intersecting lamellae or sometimes parallel lamella, but rarely with no lamellae. These crystal structures reflect the creation of different forms of belite during the sintering and cooling processes. The intersecting lamellae indicate transition caused by cooling from the high-temperature form, α-belite into α'-belite at temperature below approximately 1420 °C. During further cooling below 675 °C β-belite is created and lamella structure remains intact [1].

The crystal size of belite increases with the time spent at sintering temperature. Overburnt clinkers contains belite crystals of a larger size and densely sintered alite. Production clinker primarily contains β-belite and also present α'-belite if cooling is quickly. This type of belite hydrates at a significantly slower than alite, although in the end it can attain similar strength. Finger-shaped belite is caused by further growth of the lamella at slow cooling rates as a consequence of the absorption of Cao and SiO_2 from the melting phase (Figure 8). Lamellae found in belite are an indicate of an upper burn temperature of 1420 °C [1].

Belite can be colored by blue, yellow and brown by etching with acetic.

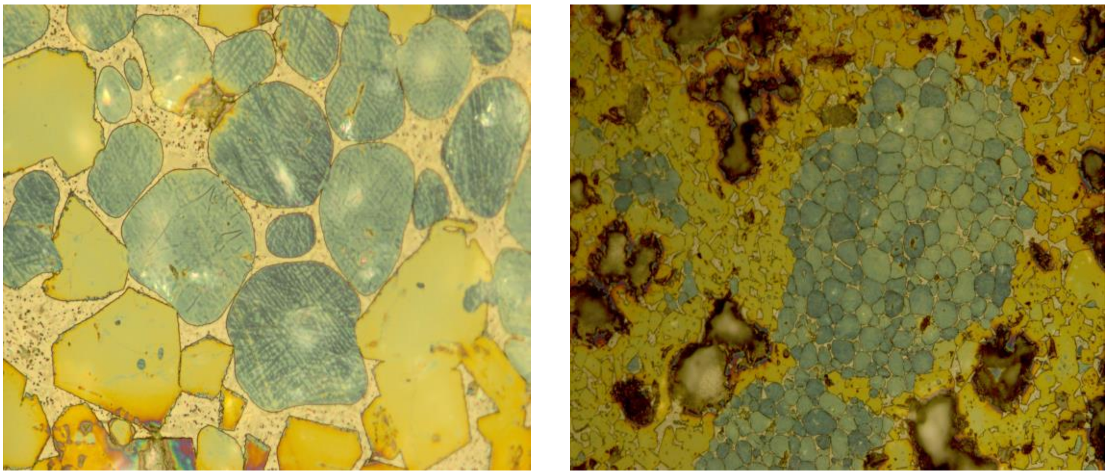

Figure 7. Typical belite crystals (with and without lamellae)

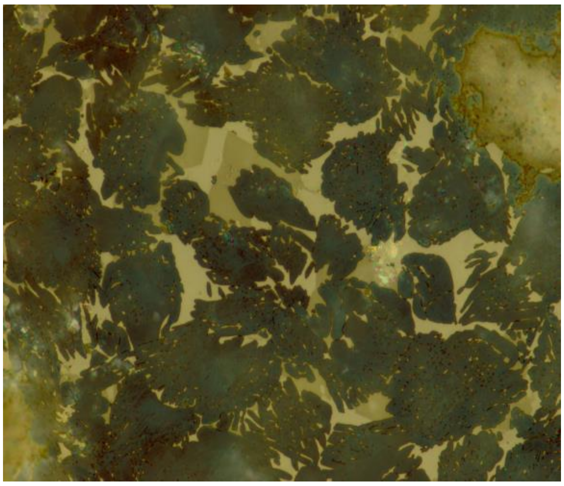

Figure 8. Finger-shaped belite crystals

3.3. Aluminate and ferrite

Other clinker minerals are also important to cement reactivity and performance. Together with alite and belite phases, interstitial phase which is composed of aluminate (C_3A) and ferrite (C_4AF) is also formed upon cooling (Figure 9). The light interstitial mass is ferrite while the brownish mass is aluminate. The faster the cooling occurs, the finer the crystal size. C_3A phase is very reactive and it releases the greatest heat during hydration among the clinker phases.

There is an inverse relationship between these two phases in the base material. When the C_3A content falls the C_4AF content rises and vice versa. Aluminate (C_3A) is present in clinker in cubic and orthorhombic forms. The form of the C_3A modification depends on the amount of alkali input There are next modifications [1]:

1. Cubic (0 – 1% K_2O)
2. Cubic/orthorhombic (1 – 2,4% K_2O)
3. Orthorhombic > 2,4% K_2O

C_4AF is very slow to react and hardly contributes to the strength development and then only at a later age.

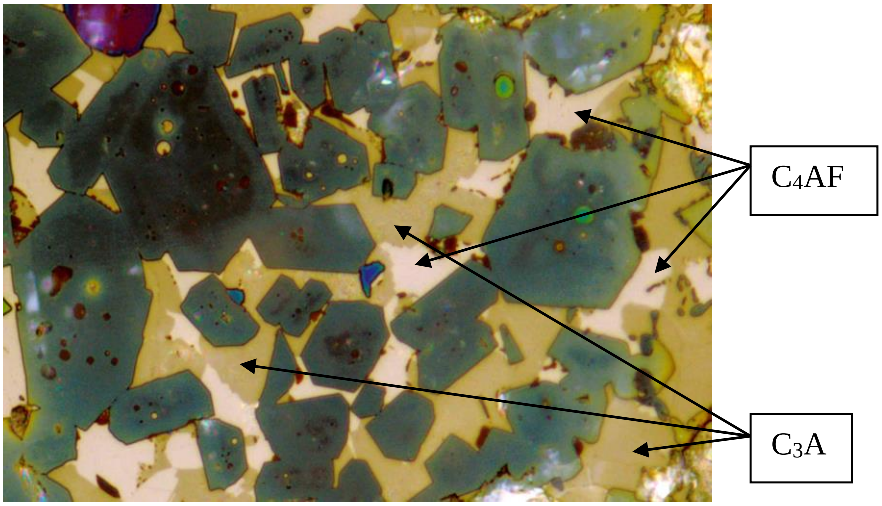

Figure 9. C_3A and C_4AF crystals

3.4 Free lime

Most cement clinkers contain free lime in amounts up to 2% by weight. Free lime occurs in the next cases [1]:

1. Inappropriate preparation of the raw meal (inhomogeneous or too coarse),
2. Inadequate burning (it is not combined by other oxides),
3. Too slow rate of cooling (partial decomposition of C_3S could occur),
4. Too high lime saturation factor (> 100)

The round particles occur in range from a few tenths of a percent to a few percent of total mass and it is a measure of the completeness of burning of raw meal. Free lime is strongly hygroscopic and transforms due to the influence of humidity in air. Free lime causes lime induced deformation by increasing in volume. This can be established by microscopic analysis. If raw meal is not homogenized well, free lime is dispersed (Figure 10) and if there is coarse lime in the raw meal, free lime occurs in clusters (Figure 11).

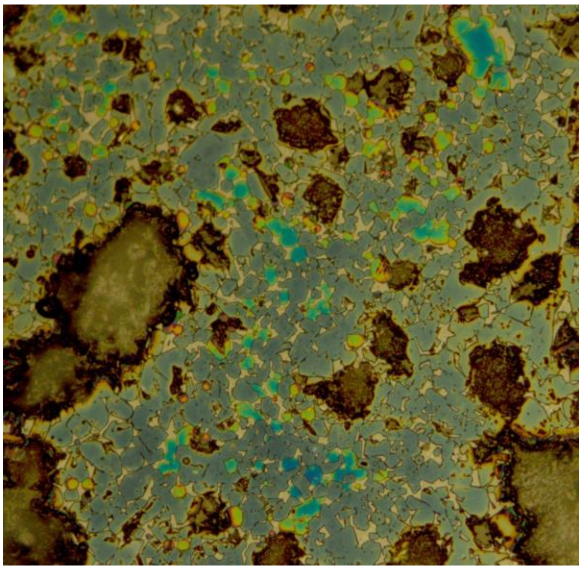

Figure 10. Dispersed free lime

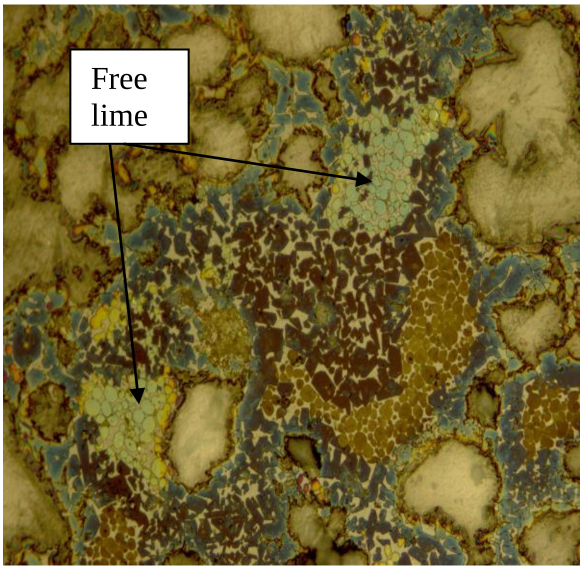

Figure 11. Free lime in clusters

4. CONCLUSION

There is correlation between clinker microstructure, the kiln feed and burning conditions. Besides this, clinker microstructure can reveal important information about cement performance. Clinker microscopy is a valuable tool at the cementplant which can help to produce good quality clinker. If there is a change in the microstructure (crystals are larger and irregular, coarse belite clusters, secondary belite, etc.) operators can very quickly react to modify parameter for clinker production to get better clinker reactivity. Typical physical and chemical testings can provide very good information, but often microscope can help to provide a complete solution.

5. REFERENCE

[1] Heidelberg Technology center, Clinker mineralogy and cement chemistry, 15th edition, Leimen, Germany, September 2012.,
[2] Linda M. Hills: The value of microscope, Construction technology laboratories, USA, April 2004.