FROM QUARRY TO STRENGTHS: HOW COMPOSITION OF RAW MEAL AFFECTS CLINKER QUALITY AND CEMENT ADDITIVES FORMULATION

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ABSTRACT

The effect of chemical and mineralogical composition of raw materials, including the influence of minor elements, on clinker and cement quality has already been widely discussed in literature since the discovery of Portland cement. From the beginning of the raw meal preparation to the choice of the right chemical additive, modern cements require a global approach to optimization, in which microscopy techniques always play a key role. In this paper we present a detailed study of cement performances, taking into account several clinkers and related raw meals, kiln feeds and quarry materials. In each case, the most suitable cement additive formulation will be discussed, with the target to improve overall performances during cement manufacturing and use.

INTRODUCTION

Manufacturing process of Portland cement is standardised and widely described in several publications [1]. Raw materials (usually limestone and clays) are quarried, then properly blended and ground in order to prepare the so-called raw meal. This is used as feed for the pre-heater tower and kiln, where silica and lime (with alumina/iron oxides used as flux) react in a high temperature process to form the calcium silicates that compose the Portland clinker.
Clinker is then finely ground together with gypsum and secondary mineral additions (such as limestone, fly ash, granulated blast furnace slag, natural or artificial pozzolans) in order to obtain the well known grey powder usually referred to as Portland cement, used by millions of construction workers as hydraulic binder in concrete, mortars, screeds, grouts and many other masonry applications.
Although the basics of Portland cement manufacturing, as described above, have remained more or less similar, huge efforts have been made in optimisation and quality improvement in the latest decades. More specifically, high performance cements for high quality concrete applications, the introduction of supplementary cementitious materials and, recently, the stringent requirements in greenhouse gases reduction have presented the need of better clinker quality. A "good" clinker, meaning a clinker that allows the production of cements with the required hydration rate and strength development, is the starting point for high quality applications.
The use of analytical techniques based on microscopy dates back to the end of nineteenth century, with the work of Le Chatelier (a good summary of the history of clinker and cement microscopy can be found elsewhere [2]). Nonetheless, the images of clinker, cement, raw meal and hydrated cement paste can still be irreplaceable in giving complementary information that can hardly be obtained with other analytical methods.
In this paper we present a study on the relations between raw meal characteristics and clinker quality, with the aim to highlight the fundamental contribution of Scanning Electronic Microscope with Energy Dispersed X-rays (SEM/EDX) systems.

DESCRIPTION OF THE STUDY

Samples of clinkers and corresponding raw meals were received from a cement plant. Quality of each clinker was reported to be very different, in terms of strengths development. Target of the investigation was the correlation of characteristics of kiln feed with clinker quality, with the aim to propose suitable solutions for the improvement of cement strengths.
It is well known that at clinkering temperature (around 1400°C), the main phases present at equilibrium are alite, belite and liquid, while below about 1200°C reactions occurs largely in the solid state [3]. In all phases, clinkerisation process is related to thermodynamic and kinetic considerations. In addition to chemical composition, diffusion of reagents from solid to liquid phase plays a key role. Considering that solid-liquid diffusion is controlled by particle dimensions, the chemical composition should not be set apart from physical considerations: is the chemical composition very different, passing from fines to coarse particles?
Theoretically, it would be possible to separate raw meal in several fractions that are individually analysed. On the other hand, from a practical point of view the collection of fractions below 40 µm is indeed quite difficult and not representative.
The approach based on microscopy, with particular reference to advanced SEM/EDX techniques, allows a deeper insight into the correlation between composition/fineness of raw

meal. Hence, in addition to standard approach consisting in mineralogical and chemical analysis of clinkers and raw meals, the following protocol was followed:

- Kiln feed samples were sieved in order to measure the particle size distribution and to separate two main fractions: 40-90 µm and 90-200 µm.

- Chemical composition of bulk kiln feed and of selected fractions was tested.

- Kiln feed was analysed in terms of morphology and chemical composition using SEM/EDX.

The samples received were clinker (3 samples, labeled 22, 24 and 26) and kiln feed (3 samples, labeled correspondingly 22, 24 and 26).

EXPERIMENTAL

Samples preparation

Particle size distribution of kiln feed samples was tested with air jet sieving (Hosokawa Alpine LS200 N, sieving time: 6 minutes, pressure drop: 4750±250 Pa, reproducibility: ±0.50%). Air jet sieve was used in order to separate raw meals in two fractions: 40-90 µm and 90-200 µm.

For the assessment of chemical composition of raw meals/clinkers and for mineralogical composition of clinkers, respectively X-Ray fluorescence (Bruker AXS S8 Tiger) and quantitative X-Ray diffraction (QXRD) with Rietveld method were used. Powder diffraction data were collected with a PANalytical X'pertPro MPD diffractometer with theta–theta geometry equipped with an X'Celerator detector working with the CuKα radiation (1.54184 Å) in the 2theta range 5–80, a step size of 0.017° 2 theta and a scan step time (s) of 102,1. All data collections were performed at room temperature with back-loading sample holders to avoid preferred orientation of crystallites. Data was analysed by the Rietveld method (Rietveld, 1969) using the Bruker AXS software package TOPAS 4.2 operated in the fundamental parameters mode (Cheary et al, 1992, Coelho, 2000, BRUKER AXS, 2003). Clinker samples were previously ground with vibration jar-ring mill (Herzog HSM100).

Microscopic examination of kiln feed was performed with FEI QuantaFEG-250 (Environmental Scanning Electron Microscope, equipped with a Field Emission Gun). The field emission gun allows to obtain a much higher brilliance of the electronic source than the ordinary tungsten gun. EDX spectra were collected through an EDAX SSD system.

Samples were prepared by simply dipping a conductive adhesive sample holder in cement and eliminating excess material by blowing air. Images were collected working in low vacuum mode using a back scattered detector.

RESULTS AND DISCUSSION

In the first part of the investigation, sieving of the kiln feed samples and of the raw meal samples was carried out. Results are reported in the following table (Table 1).

Sample	Residue @40µm, %	Residue @90µm, %	Residue @200µm, %
Kiln feed 22	40.0	12.8	0.50
Kiln feed 24	38.0	13.1	0.35
Kiln feed 26	37.7	13.4	0.70

Table 1*: results of sieve analysis of kiln feeds*

Although differences are not so huge, for kiln feed samples it is apparent that 200 µm residues are different in the scale

KF26 > KF22 > KF24

Opposite trend is shown for 40 µm residues, meaning that particle size distribution is wider for KF26, intermediate for KF22, and narrower for KF24. In other words, KF24 is more homogeneous and less rich in coarse particles, KF22 is intermediate, and KF26 is less homogeneous and richer in coarse particles.

Chemical analysis

In the second part of the investigation, XRF analysis was performed on all the kiln feed samples, so to assess if any compositional differences could be detected, and on selected samples of sieved samples. In the latter case, the objective was to look for differences in composition between the coarser and the finer fractions. In particular, fractions above 90 µm and between 40-90 µm were analysed. In addition to XRF analysis, TGA (thermogravimetric analysis) was also carried out, so to be able to calculate the amount of calcium carbonate. Combined results of the analysis are reported in the following table (Table 2 - values are expressed in mass %).

Sample	Kiln feed 22	Kiln feed 24	Kiln feed 26	Kiln feed 24 R90µm	Kiln feed 24 R40µm	Kiln feed 22 R90µm	Kiln feed 22 R40µm	Kiln feed 26 R90µm	Kiln feed 26 R40 µm
MgO	0.82	0.85	0.83	1.05	0.77	1.18	0.72	1.03	0.70
K_2O	0.35	0.37	0.34	0.46	0.26	0.53	0.29	0.51	0.29
Al_2O_3	3.75	3.79	3.70	2.64	3.11	2.49	2.93	2.56	3.05
SiO_2	13.32	13.88	13.84	30.44	12.38	36.19	13.03	34,61	13,05
$CaCO_3$	77.77	76.67	76.32	59.41	78.73	53.95	78.89	51,22	75,12
CaO	0.37	0.00	0.00	0.02	0.00	0.85	0.06	0.02	0.00
SO_3	0.04	0.12	0.12	0.27	0.22	0.36	0.27	0.39	0.25
Fe_2O_3	2.42	2.51	2.53	3.69	2.79	2.86	2.42	3.65	2.82

Table 2*: chemical analysis of kiln feeds, bulk composition and analysis of fractions above 90 µm and between 40-90 µm*

The results show that overall composition of all the kiln feed samples is quite similar. On the other hand, huge differences are apparent in different granulometric fractions of raw meal samples. Coarser fractions are much richer in silica and less rich in calcium carbonate, most probably because of the different hardness of the main materials contributing to the composition of these two minerals. During grinding of raw meal and kiln feed preparation, soft materials such as limestone tend to accumulate in the finest fractions. On the other hand harder materials, such as quartz, have the tendency to remain in the coarser fractions.

Of course, this means that fineness plays a crucial role in the availability of a good combinability of Si and Ca: if more coarse particles (rich in SiO_2) are present, less silica will be readily available to react with calcium in the kiln. This is the case with Kiln feed 26 sample, and to a lesser extent with Kiln feed 22. The difference in the amount of smaller particles is less important compared to the difference in the percentage of the coarser fractions, since smaller particles react more easily (quickly) anyway.

Based on the analysis of the results described so far, we should expect that clinker samples 22, 24 and 26 should reflect these differences by showing a similar XRF pattern, but a not-so-

similar XRD-Rietveld phase composition. This is exactly what we found. The following table (Table 3) reports XRF data of the clinker samples (results in %).

Sample	Clinker 22	Clinker 24	Clinker 26
MgO	1.28	1.29	1.32
K_2O	0.59	0.62	0.70
Al_2O_3	5.58	5.52	6.36
SiO_2	20.63	21.64	22.60
CaO	66.10	66.51	64.23
SO_3	0.13	0.22	0.50
Fe_2O_3	3.77	3.64	3.86
LOI and minor elements	1.94	1.56	0,43

***Table 3**: chemical analysis of clinker samples*

Chemical compositions are indeed similar: it is however to be noted that clinker 26 shows a slightly higher Ca/Si ratio, and a higher sulfate content, possibly related to fuel effect (use of pet coke).
Mineralogical composition according to XRD-Rietveld data are shown in the following table (Table 4 - results in mass %).

Mineralogical phase	Clinker 22	Clinker 24	Clinker 26
C_3S M3	42.9	52.9	30.8
C_3S M1	17.5	16.5	16.8
C_2S	15.4	9.6	28.4
C_3A, cubic	2.3	2.8	6.2
C_3A, orthorombic	4.7	3.9	1.4
C_4AF	12.6	11.2	12.6
CaO	3.4	1.4	1.7
MgO	0.1	0.2	0.0
Arcanite	0.4	0.6	0.8
Calcite	0.8	0.7	0.9
Aphtitalite	0.1	0.1	0.2

Based on the mineralogy, overall quality of the clinker is in the scale

clinker 24 > clinker 22 > clinker 26

in terms of total C_3S content. Clinker 24 has the potential for the higher strengths, with clinker 26 giving potentially much lower strengths and being the harder to grind due to the high content of belite.
Soluble alkali sulphates (namely arcanite, K_2SO_4) are higher in clinker 26, as expected based on the higher sulphate content showed by the XRF analysis. This is coherent with orthorombic C3A, that in clinker 26 is lower: it is known that formation of orthorombic C3A is promoted by alkalies not bound in soluble suphates.

SEM/EDX analysis

The first set of micrographs shows the overall picture of Kiln feed 26, 22 and 24 respectively (figure 1). From the pictures, it can be seen the relative abundance of bigger particles in the same scale seen through sieve analysis.

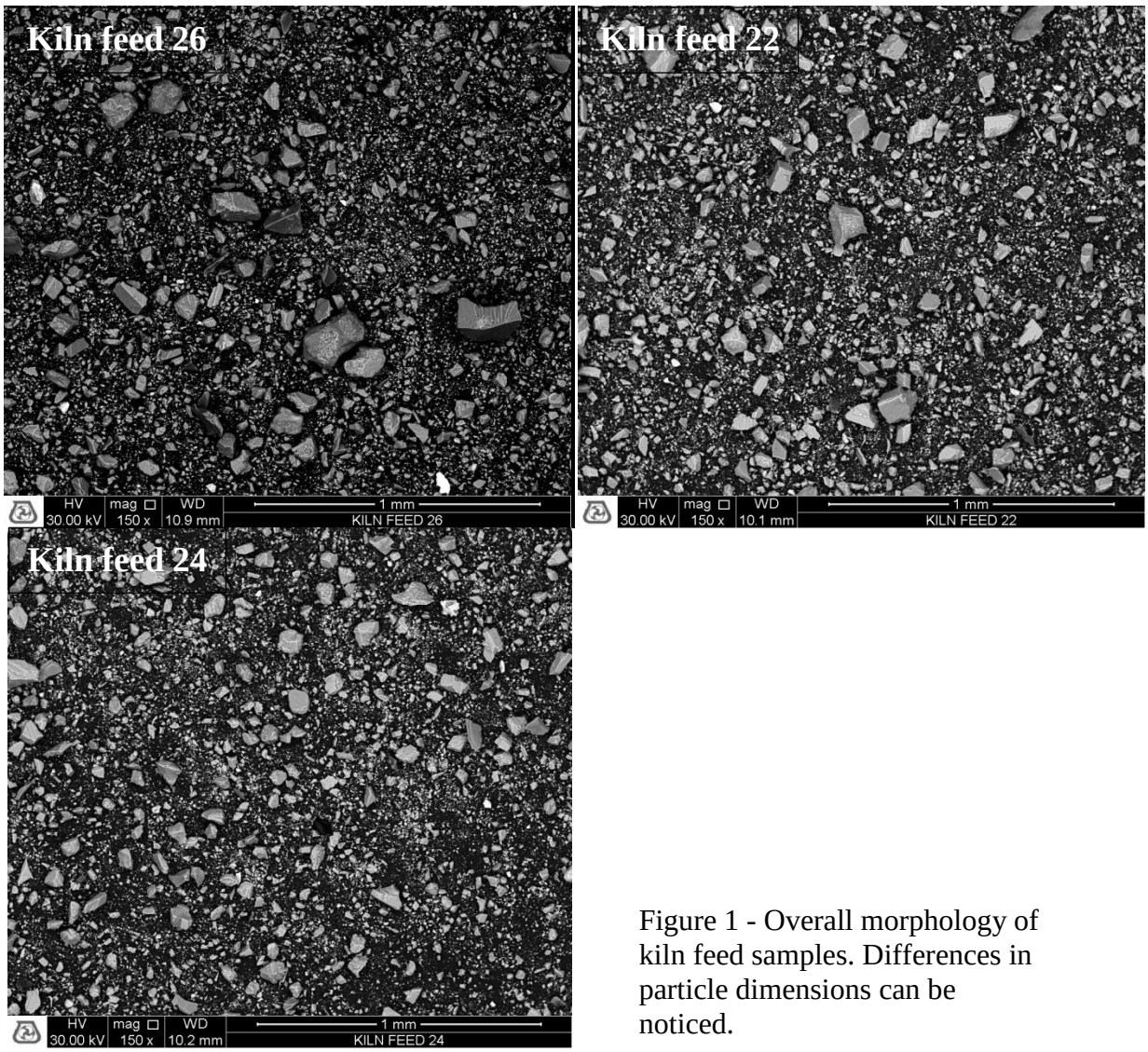
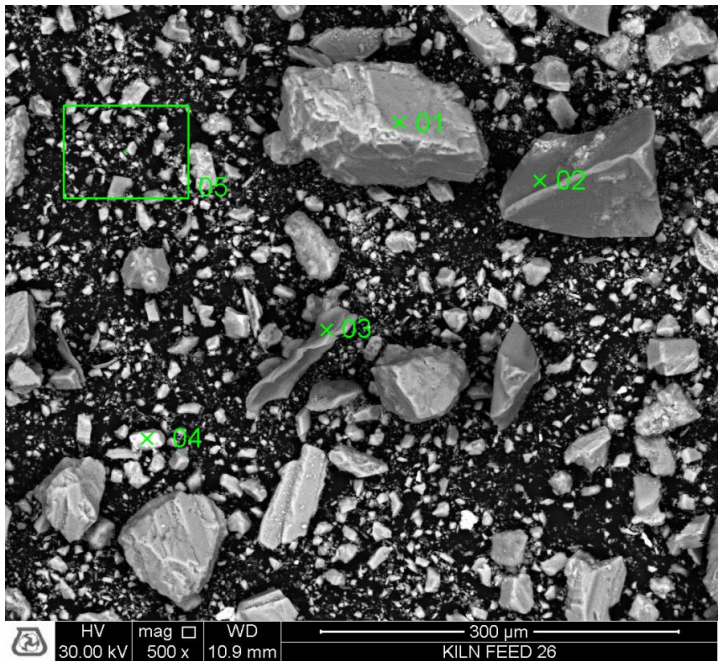
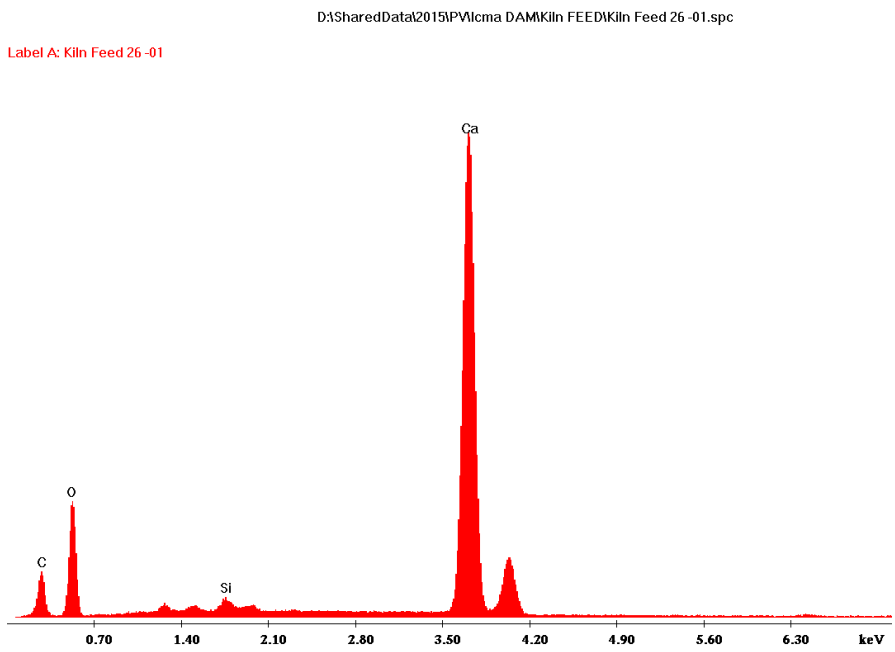


Figure 1 - Overall morphology of kiln feed samples. Differences in particle dimensions can be noticed.

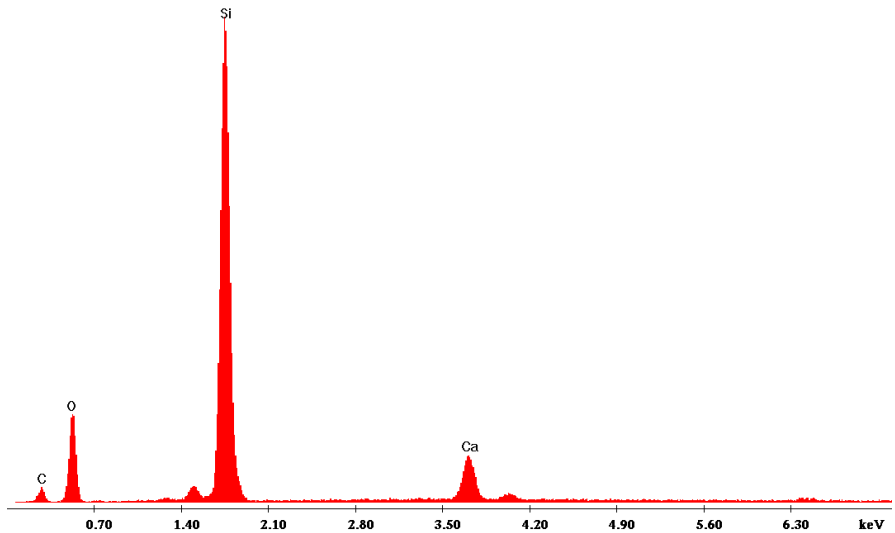
To try and confirm XRF data about the composition of the different size fractions, EDX analysis was applied. Kiln feed 26 sample was analyzed as shown in the following picture (figure 2).
We selected significant points: main crystals (labeled as 01, 02, 03 and 04) and an average area composed mainly of smaller dimension particles. The precise spot for EDX spectra are shown with an X sign or with a rectangular shape in the picture, and spectra are reported as follows. According to chemical analysis, crystal 01 was found to be a calcium carbonate sample; crystal 02 silica; crystal 03 a lamellar aluminosilicate; crystal 04 iron; the area 05 is almost completely composed of calcium carbonate (low silica content).





D:\SharedData\2015\PV\Icma DAM\Kiln FEED\Kiln Feed 26 -02.spc

Label A: Kiln Feed 26 -02



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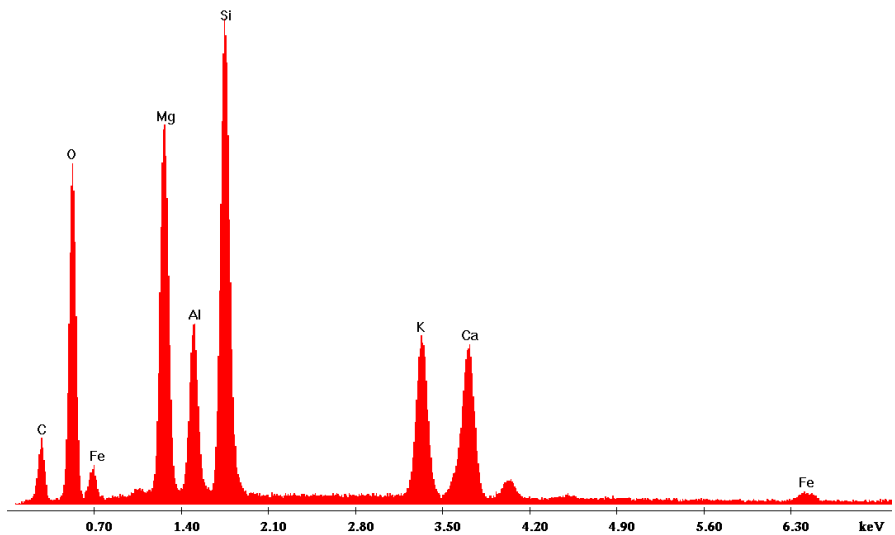


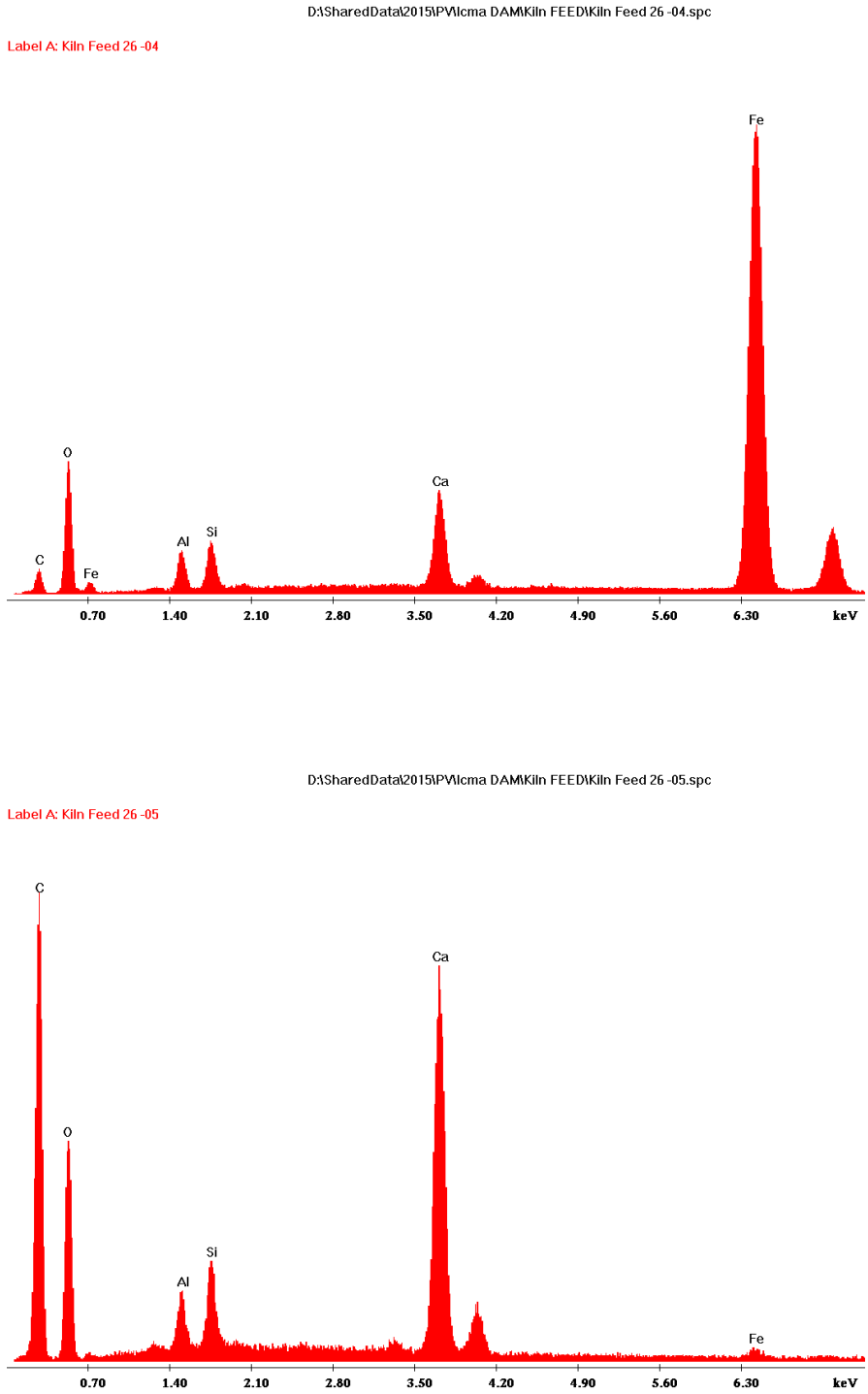
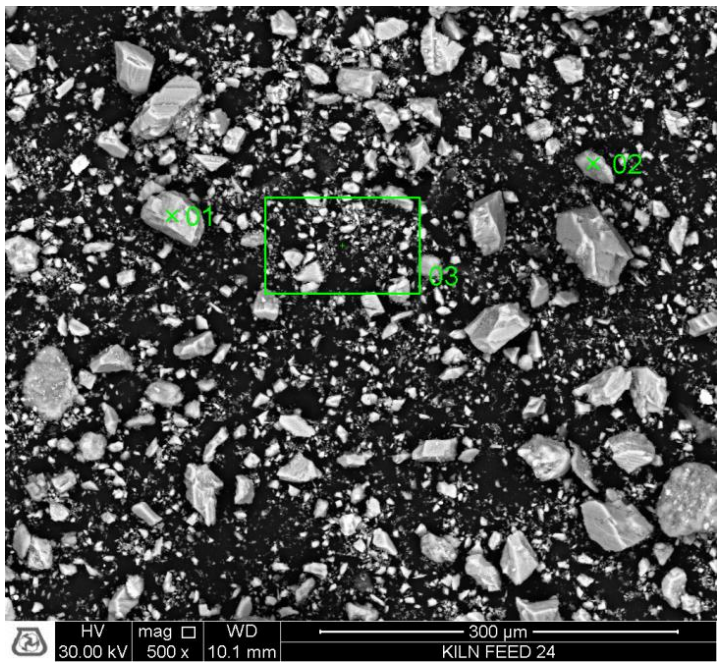
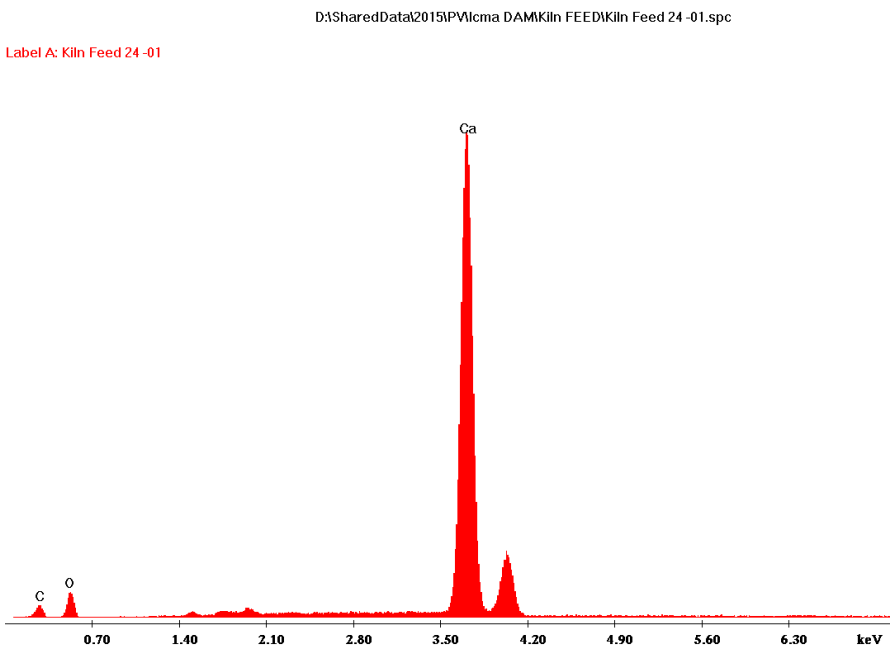


Fig. 2 - EDX analysis of kiln feed 26. Analysis of selected crystals/area with small particles are reported in the graphs.

The same procedure was applied to Kiln feed sample 24 (figure 3). Crystal 01 is calcium carbonate; crystal 02 silica; area 03 is mainly $CaCO_3$, but with higher Si content compared to the fine area analysed for Kiln feed 26. EDX spectra are reported as follows.





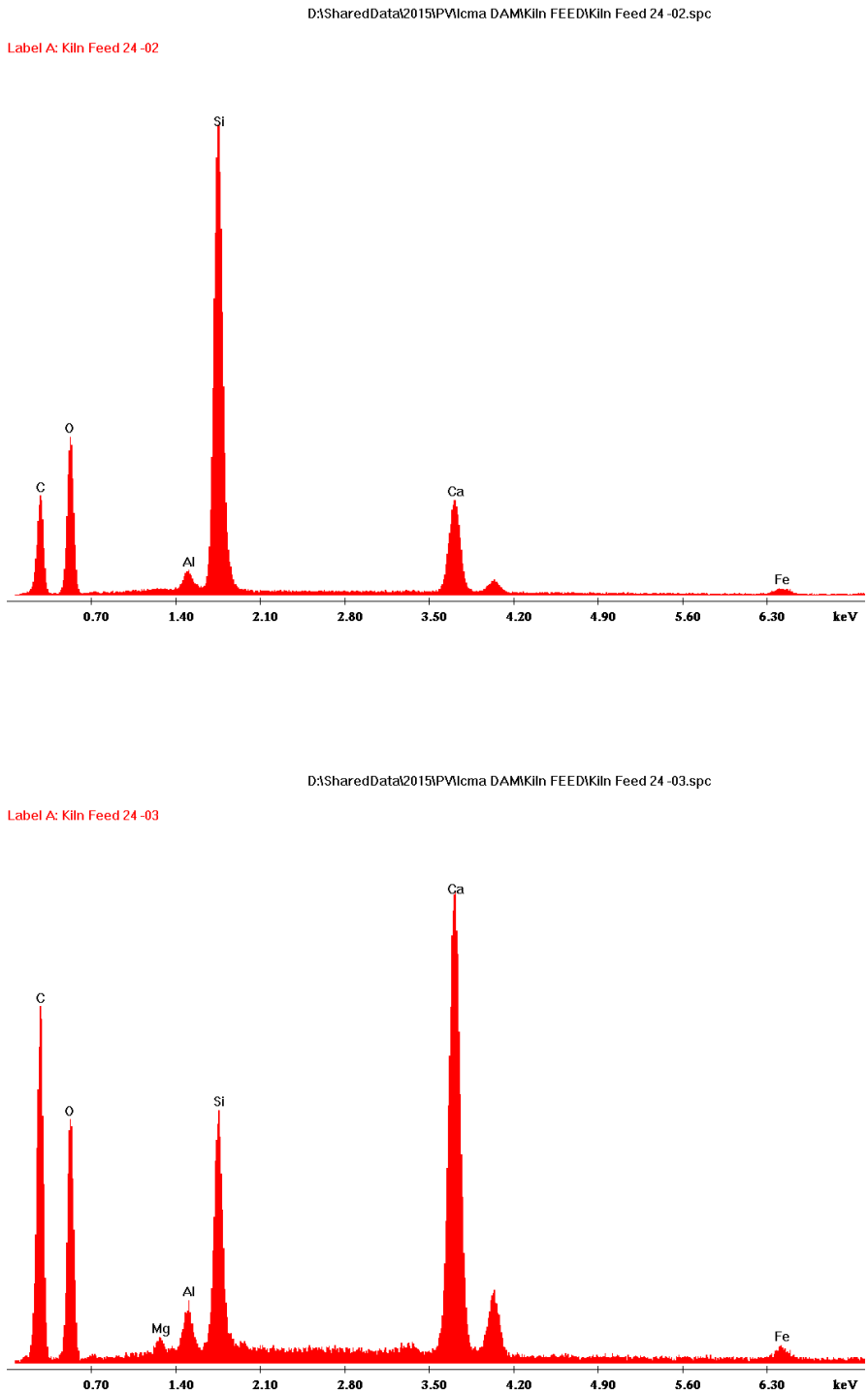


Figure 3 - EDX analysis of kiln feed 24. Analysis of selected crystals/area with small particles are reported in the graphs.

EDX data allow a deeper understanding of the chemical composition of Kiln feed. In addition to confirm XRF data, by showing less homogeneity of Kiln feed 26 sample compared to Kiln feed 24, with the analysis of selected area the limitation of smallest particles sieving and separation can be overcome. SEM/EDX approach allows to ride over the physical limit of

sieving: differences of chemical composition of very fine particles can be determined, leading to a better understanding of solid-liquid diffusion during clinker manufacturing.
Bigger crystals in Kiln feed 26 are mainly composed of silicon-based materials. Hence, the higher C2S content and the lowest conversion to C3S is most probably related to insufficient reaction of silicon. In addition, this should have promoted the presence of big crystals of C2S, with reduced grindability and huge increase in energy requirements for finished cement production.

Influence on the selection of cement additive

In modern cement production the use of suitable cement additive is mandatory. Cement additive (also referred to as grinding aids) are process additive added in the finished cement mill in order to improve grinding (increasing mill output and/or improving particle size distribution) and to enhance performances of cements (mainly in terms of compressive strengths development). A complete approach to cement additive selection and formulation should start with a detailed investigation of clinker characteristics. In the case described in the present paper, it is evident that for cement manufacturing using clinker 26, a process additive should help overcoming the following:

- Global "hardness" of clinker, due to high C2S content.
- Poor strengths development due to low C3S content.

Thus, a formulation with very high grinding properties and a chemical accelerator of hydration mainly focused on early strengths should be used.

CONCLUSIONS

We can conclude that:

- fineness has a much higher importance than chemical composition as a work parameter to produce a better quality clinker.

- Homogeneity of kiln feed in terms both of fineness (narrower particle size distribution) and composition is fundamental in getting a good combinability in the kiln.

- The use of microscopy techniques (with particular reference to SEM with combined EDX analysis) allows a deeper understanding of reasons associated to a reduced quality of clinker.

- All the information obtainable with a high-level approach to clinker analysis can be very useful in the formulation of suitable cement additive, with the final aim to produce a better cement.

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