



ecra

european cement research academy



2 / 2012

NEWSLETTER

Contents

- | | |
|--|-------------|
| How AFR can influence the microstructure and mineralogy of clinker | p. 2 |
| The renaissance of waste heat recovery in clinker manufacturing | p. 3 |

Next ECRA events:

- Influence of Fuel and Raw Material Properties on the Characteristics of Clinker and Cement
26-27 June 2012
- Thermal Energy Efficiency and Waste Heat Recovery
12-13 September 2012

How AFR can influence the microstructure and mineralogy of clinker

Understanding the effects of alternative materials is the key to their optimal use

Each fuel and raw material used in the clinker burning process influences it and thereby the properties of the resulting clinker. Since Portland cement clinker essentially controls the performance of cements, the continuous and detailed monitoring of clinker properties is state-of-the-art in modern cement production. Research findings as well as case studies help to further understand the possible impacts of alternative fuels and raw materials (AFR) on the clinker microstructure and mineralogy.

In a case study the effects of an alternative raw material on the clinker microstructure were investigated. The material was used as a source for CaO, but also had fuel properties due to a certain content of organic compounds.

CaO source with fuel properties

In the clinker sample investigated with an optical microscope, finely intergrown crystals of belite and free lime were observed (Fig. 1). This microstructural feature is a typical sign for reducing burning conditions and results from the decomposition of alite crystals to fine grained belite and free lime. Unusually, it occurred exclusively in the vicinity of free lime clusters in this clinker. Due to their high CaO-content, coarse particles of the alternative raw material had

caused the formation of free lime clusters in the clinker granules. The organic compounds in the material had simultaneously caused reducing burning conditions in the immediate vicinity of such coarse particles. Only the combination of both the raw material and the fuel properties of the alternative calcium source used for the clinker production had led to this quite unusual combination of microstructural features.

The case study also showed the importance of fast cooling for clinker potentially exposed to reducing burning conditions. The clinker sample described above had been cooled slowly in an old cooler system. A second sample from the same plant, taken after the installation of a modern grate cooler system and therefore cooled much faster than the first sample, was produced with the same or even a higher amount of the alternative CaO-source. However, no signs for reducing conditions were found in this sample. The faster cooling prevented the decomposition of alite or other results of reducing burning conditions.

Aluminum-rich ash

In laboratory experiments the inhomogeneous distribution of Al_2O_3 due to coarse Al-rich ash particles and the accumulation of Al-rich ash particles

on the surface of clinker granules were simulated. Such ashes can result from Al-rich refuse-derived fuels (RDF).

To simulate coarse grained Al-rich fuel ashes, microgranules of $Al(OH)_3$ with diameters of 0.125 to 0.5 μm were incorporated into otherwise homogeneous raw meal granules. To simulate the accumulation of Al-rich particles on the surface of clinker granules, a thin layer of $Al(OH)_3$ powder was applied on the surface of homogeneous raw meal granules. A third type of raw meal granules with homogeneous composition was prepared for comparison. The bulk chemistry of all three types of raw meal granules was identical.

The Al-containing clinker phases C_3A and C_4AF were distributed homogeneously in the microstructure of the laboratory clinker granules produced from all three types of raw meal granules. In the clinkers prepared from granules with an $Al(OH)_3$ -rim and with embedded $Al(OH)_3$ -microgranules, a rim of belite crystals (Fig. 2) and clusters of belite crystals (Fig. 3) were observed respectively. The belite clusters mostly enclosed central pores (Fig. 3, Fig. 4) and had diameters coinciding with those of the $Al(OH)_3$ -granules. In the laboratory clinker granules prepared from homogeneous raw meal granules no comparable belite rims or clusters were observed.

The observations led to the following conclusions: During the burning procedure the accumulated Al_2O_3 reacted with CaO from the neighbouring raw meal to form calcium aluminates and ultimately the clinker melt. The melt was distributed homogeneously in the clinker microstructure. This left

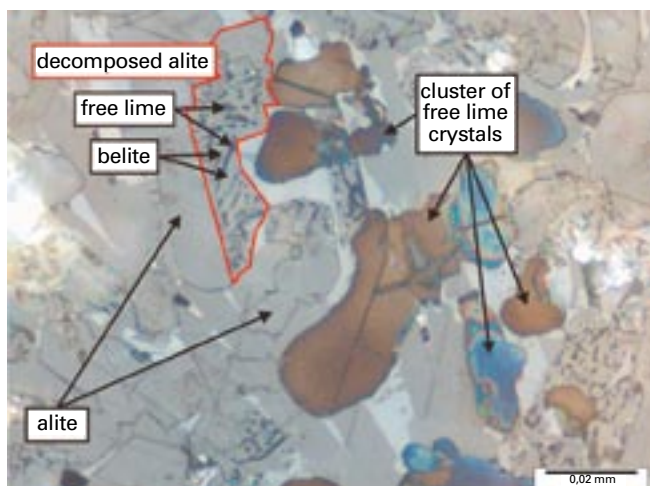


Fig. 1: Alite crystals partly decomposed to belite and free lime in the vicinity of a free lime cluster.

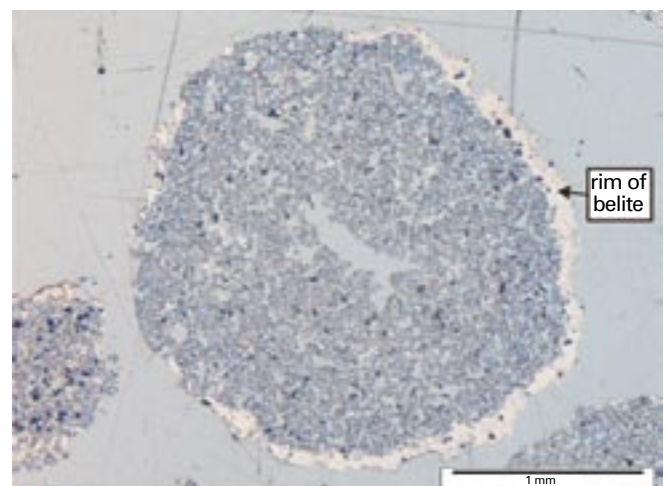


Fig. 2: Laboratory clinker granule with a dense rim of belite, produced from a raw meal granule with a rim of $Al(OH)_3$.

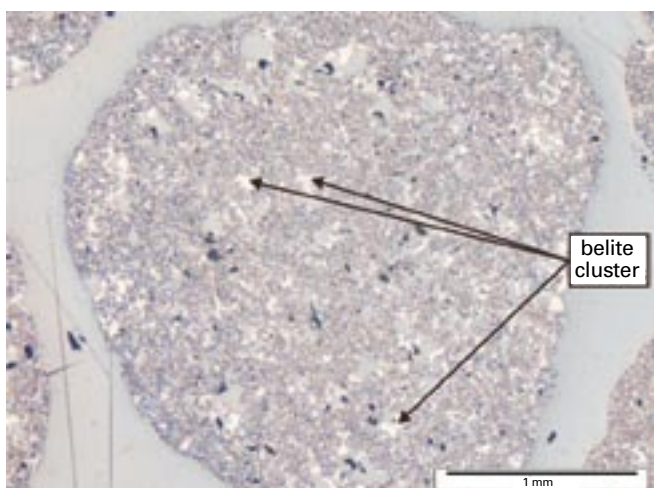


Fig. 3: Laboratory clinker granule produced from a raw meal granule with microgranules of $\text{Al}(\text{OH})_3$, and containing belite clusters with diameters comparable to those of the microgranules.

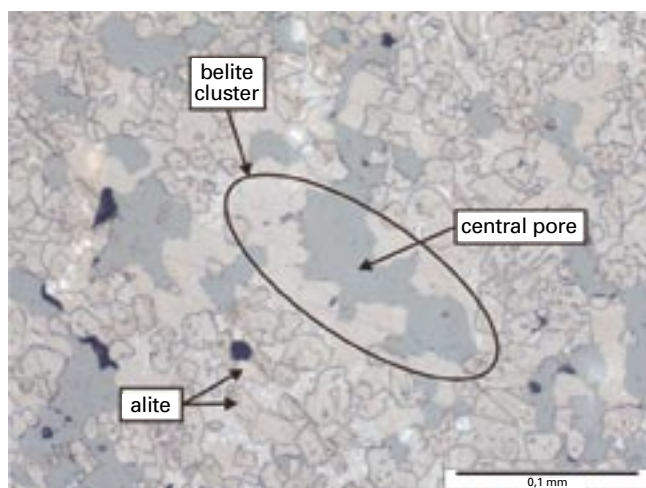


Fig. 4: Belite cluster with central pore, (detail from Fig. 3.).

pores in the sites of former $\text{Al}(\text{OH})_3$ -microgranules. As a component of the clinker melt, CaO was partly removed from the direct vicinity of the former $\text{Al}(\text{OH})_3$ -rims and -microgranules. This led to the local depletion of CaO relative to SiO_2 in these domains, resulting in the locally concentrated formation of belite instead of the alite. To what extent this effect observed in laboratory clinker also occurs in technical clinker has yet to be investigated. However, the results imply that belite clusters in clinker

cannot be attributed in all cases to local enrichments of SiO_2 . Mechanisms leading to local depletions of CaO also have a significant impact on the clinker microstructure.

X-ray diffraction analyses of the described laboratory clinkers did not reveal any changes in the clinker mineralogy due to the inhomogeneous distribution of Al_2O_3 compared to clinker prepared from the homogeneous raw meal granules. This is not surprising, since a constant amount

of calcium aluminates can be expected in the clinker samples when the total amount of Al_2O_3 is not varied.

Practical use

The information gathered from case studies and laboratory experiments helps to interpret the clinker microstructure with regard to the influence of the fineness and composition of raw meal and fuel ashes. This enables an excellent process evaluation which guarantees a high clinker quality even with high amounts of AFR used in the clinker burning process.

The renaissance of waste heat recovery in clinker manufacturing

Waste heat recovery for power co-generation can supply up to a third of power demand

With the introduction of rotary kilns in cement clinker manufacturing at the end of the 19th century, clinker was burned in wet and dry rotary kilns without preheater technologies as we know them today. The kiln exhaust gas left the furnace with temperatures between 600 and 1,000 °C according to the kiln type and kiln length. Lost heat was recovered for the drying of the raw materials as well as for the preheating of the combustion air. Surprisingly, from today's point of view, even steam boilers were used for waste heat utilisation in the early days of cement production.

Fig.1 displays the utilisation of heat in flue gas by a system of heating

tubes as it was done more than a hundred years ago. As lost heat in flue gas exceeded the heat demand for raw material drying and combustion air preheating, lost flue gas heat was already being recovered by steam boilers in the first decades of the last century.

History of waste heat recovery

In the last couple of years, waste heat recovery systems have been experiencing a renaissance. Today, in the Middle and Far East more than 100 applications in the cement industry are known, in the beginning initiated especially in cases with high energy prices or with a low service security of the public electric power grid. State-of-the-art technology for waste

heat recovery systems, the development of energy prices, and the growing need to improve energy efficiency all provide new opportunities for implementing waste heat recovery systems in the already highly efficient kiln systems of the cement industry. To date, three applications are currently in operation in European cement plants while a further two are under construction.

Heat losses in the clinker process

Specific thermal energy consumption in the cement industry has declined significantly over the past 60 years. This is mainly attributable to improvements in plant and process technology. In the pyroprocess of clinker manufacturing, thermal ener-

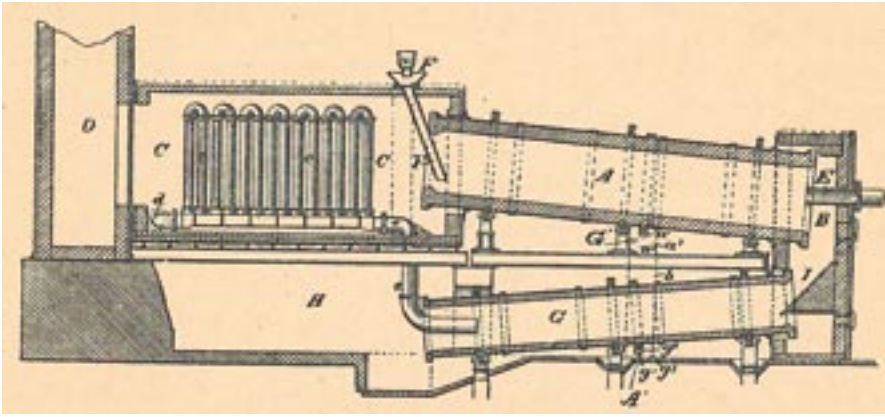


Figure 1: Waste Heat Recovery from kiln exhaust gas for preheating combustion air around 1906. Source: Carl Naske: *Die Portlandzement-Fabrikation*. Leipzig: Verlag für Wissenschaft, Kunst und Volksbildung, 1922.

gy is required for the drying and calcination of the raw material as well as for the clinker burning process. In addition, heat losses increase the energy demand of the kiln line.

Heat losses occur in the flue gas and the bypass gas from the rotary kiln and cooler exhaust air. They also appear as kiln shell heat losses and heat remaining in the clinker granules leaving the cooler. Potential heat sources for recovery are therefore the flue gas, the kiln shell, the freshly-produced still-warm clinker and excess cooler exhaust air. In clinker manufacturing there is no need for an advanced process-integrated use of heat as the process does not require any further heat.

Waste heat for power generation

A maximum possible heat transfer in the cooler from still-hot clinker granules to the combustion air should be envisaged as the combustion process benefits very significantly from the heat recuperation in the cooler. A high secondary air temperature reduces the required fuel energy input into the firing.

Waste heat can be recovered either for other processes requiring thermal energy, heating or drying purposes, or used for electric power co-generation. The subsequent use as heat for thermal processes or heating, which is usually more energy efficient than power generation, requires either a heat consumer on site or close to the cement plant, or a district heating network nearby. This however is usually not the case, particularly since seasonal heat supply and demand differ from each other. If there is no use for the heat as such, generating electricity from waste heat can be an option. Electricity can either partly cover the cement works' energy de-

mand or be given to the public power grid.

Electric power generation requires a heat recovery boiler and a turbine system. Power co-generation can be based on a conventional steam process, the Organic Rankine Cycle (ORC) process or the Kalina process. **Fig. 2** shows a recovery boiler using ORC technology.

Gas impurities and the need to uncouple the clinker manufacturing from the waste heat utilisation unit require a heat exchanger to transfer the captured heat. Such heat exchangers are placed downstream of the preheater or the cooler to capture heat from the preheater exit gas or from the cooler exhaust air. If the raw material moisture is low, the adaptation of cyclone stages can optimise the overall efficiency of the heat economy of the pyroprocess, the drying purposes and the power co-generation. The steam turbine is the technology best known from power plants. If the available temperature level is too low to run a steam cycle with water as a working medium, other mediums like organic fluids (ORC) or ammonia (Kalina cycles) can replace water. Both working fluids are used to drive a steam turbine.

The best economic benefit can be achieved by implementing waste heat recovery applications in a green-field cement plant. On the other hand, existing cement plants can also benefit from power co-generation. However, the subsequent retrofit is challenging with regard to building and construction sites as well as the cross-linking of the thermal and electric energy flows. In any case the economic feasibility depends on the overall situation on site and might in many cases not be given.



Figure 2: ORC waste heat boiler using cooler exhaust air heat at 275 °C. Source: Jan Theulen: *Waste heat power generation at modern cement plants*. Verein Deutscher Zementwerke: *Process Technology of Cement Manufacturing: 6th International VDZ Congress 2009*, Duesseldorf.

Power co-generation

Depending on the waste heat sources used and the applied technology, between 8 and 22 kWh/t clinker of electricity can be achieved by power co-generation without modifying the process and with the same energy input. Values of up to 45 kWh/t clinker have been reported in cases of considerable modification of the kiln line or if additional fuels are co-fired into the boiler.

Despite the progress that has been made in waste heat recovery in the cement industry it is important to keep in mind that the overall efficiency of waste heat recovery and the economic situation is very plant-specific. The experiences of one plant might not be easily transferred to another and a detailed individual analysis is required in each single case.



ecra
european cement research academy

European Cement Research Academy

Tannenstr. 2 · 40476 Duesseldorf
P.O. Box 30 03 32 · 40403 Duesseldorf
Germany

Phone: +49 (0)211 2 39 83 8-0
Fax: +49 (0)211 2 39 83 8-500

info@ecra-online.org
www.ecra-online.org