TURNING CEMENT GREEN WITH XRD

Matteo Pernechele & Murielle Goubard, Malvern Panalytical, explain the pivotal role X-ray diffraction technology has to play in making green cement a reality.

Sustainability is an increasingly important priority in the cement sector. Despite challenges such as higher fuel prices, the scarcity of supplementary cementitious materials (SCMs), and water and electricity regulations, there are encouraging opportunities. The European Union's Emissions Trading System is helping to alleviate the shortage of resources and reduce carbon emissions. Moreover, an improved understanding of the impact and performance of alternative fuels and alternative raw materials has opened doors for new processes and materials. Indeed, the solutions for producing green cements and decarbonising the cement industry in the short and medium term are co-processing alternative fuels and reducing the clinker in cement using new SCMs. For that to happen, mineralogical analysis with X-ray diffraction is essential for selecting the proper raw materials and SCMs, optimising pyroprocessing and its intermediate products, controlling blending, and maximising SCMs in the final green cements.

Cement manufacturing is a complex process. The manufacture of ordinary Portland cement starts by mining and then grinding raw materials that include limestone and clay into a fine powder called raw meal. It is then heated to a sintering temperature as high as 1450 C in a cement kiln. The resulting clinker is ground to a fine powder in a cement mill and mixed with gypsum to create cement. The powdered cement is then mixed with water and aggregates to form the concrete that is used in construction.

Cement manufacture is an energy and resource-intensive process. If it were up to the quality managers, only raw meal made from the best part of the limestone quarry would enter the kiln, and only fossil fuels would be used. However, in recent years, sustainability has become an increasingly important priority in the cement sector. New SCMs are being used, such as calcined clays, as well as new alternative fuels (AFs) such as biomass, refuse-derived fuel, municipal solid waste, tyres, sawdust, and many other types of wastes and byproducts.

Mineralogical analysis is currently helping the cement industry to transition to a low-carbon and more circular economy. It is providing the sharp eyed analysis in order to identify solutions for producing greener cements. Fast and automatic full mineralogical analysis using X-ray diffraction (XRD) makes it easier to select the right raw materials for blending. It helps to optimise and control the calcination and clinkerisation processes. It is the only reliable and proven industrial technology capable of quantifying the amorphous content of SCMs and verifying that composition of complex cement meets the required standards.

X-ray diffraction heightens mineralogical awareness

XRD has been around since the 1970s. Today, it is the go-to technique for identifying and quantifying minerals and crystalline phases in a completely automated fashion. In fact, it is the only industrial technique available for quantifying amorphous materials (including some SCMs), which are solids that do not possess order beyond a few nanometres. The lack of order makes these materials extremely reactive and therefore a good SCM that can reduce clinker in cement.

Modern industrial diffractometers tap into the full potential of XRD. Instead of focusing on a specific mineral, they can identify the full mineralogical composition of materials in just a few minutes. This heightened mineralogical awareness can be used to further improve clinker quality, produce new green cements and increase the know-how of entire processing plants. The current use of XRD systems in cement plants focuses on maintaining product quality and ensuring smooth operations while reducing the carbon footprint and overall environmental impact of cement production.

Alternative fuels

A clinker kiln is a particularly attractive destination for alternative fuels for several reasons. The emissions generated by the combustion of AFs are considered neutral and can help the industry to achieve carbon neutrality, while helping to remove municipal wastes and industrial byproducts. Inorganic ashes from the combustion of AFs are incorporated into the clinker, and small amounts of other solid waste such as cement kiln dust can be added to the cement.

AFs can be highly variable, however, and can have a negative impact on the preheater operation, the kiln operation, and clinker quality. AFs high in sulfur and chlorides can generate coatings in the cyclone preheater which can lead to a complete blockage. XRD systems can help detect

Schematic representation of a X-ray diffractometer for cement analysis. From left to right: X-ray source, optical components, sample, optical components and X-ray linear detector.

the onset of these coatings by analysing the mineralogical composition of the hotmeal.

The use of AFs can modify the temperature gradient of the kiln and affect clinker quality. High temperatures are essential to guarantee the reaction between belite and lime to produce alite. XRD systems can easily monitor the yield of this reaction and accurately measure the free lime with a repeatability of 0.1 Wt%. The amount of lime and periclase needs to be kept below certain limits, 2 Wt% and 5 Wt% respectively. The hydration of those minerals is associated with volume expansion that can compromise the dimensional stability of the cement.

The belite and alite in industrial clinker are not pure phases but contain impurities that – together with the proper quenching of the clinker – stabilise high temperature phases with superior hydration kinetics. For instance, improper quenching of the clinker can induce a phase transformation from belite beta to belite gamma, the latter having no cementitious properties. Alite can occur in industrial clinker in two different monoclinic forms or polytypes: alite M1 and alite M3. Most clinkers contain both forms, but it is possible to favour the alite M1 by increasing the sulfur trioxide/magnesium oxide ratio. The alite M1 displays higher compressive strength, and XRD systems can distinguish it from the alite M3.

Using XRD in grinding plants

As the amount of clinker produced in integrated plants increases, so does the number of grinding plants importing clinker. A full mineralogical analysis of the imported clinker is essential to guarantee its quality and avoid potential performance issues in the cement. Also, XRD is widely used to assess the quality and proper dosage of cement additives.

The Aeris black-box solution is based on robust industrial X-ray diffraction (XRD), proven algorithms to quantify the mineralogy of complex materials and seamless integration with the local LIMS systems and fully automated laboratories.

The mineralogy and amount of calcium sulfates must be adjusted in relation to the aluminates content and type to optimise the setting time, strength development, and dimensional stability. The XRD analysis results can be aligned with the sulfur trioxide content measured with X-ray fluorescence (XRF), with the added value of differentiating sulfates in gypsum, basanite, and anhydrite.

The most promising approach to lowering the carbon emissions of cement is to reduce the clinker factor: for instance, by replacing the clinker in cement with natural or synthetic pozzolana. What makes a material pozzolanic is its ability to react with portlandite generated by hydrating cement, increasing its strength and durability. The quality of pozzolanas is defined by their mineralogy as some phases are highly reactive, while others are detrimental or inert.

Volcanic materials rich in quartz, felspars, pyroxenes and magnetite are not a good natural pozzolan. Pozzolanas rich in smectite and kaolinite need to be thermally activated before being used as SCMs. Zeolitic minerals such as analcime, leucite, chabazite, phillipsite, and clinoptilolite have suitable pozzolanic properties.

The quality of ground granulated blast furnace slag (GGBS) and fly ash also strongly depends on their mineralogy and on their amorphous content, which have distinct and quantifiable XRD signals. Slag which has not been properly quenched can contain significant amounts of crystalline melilite and merwinite and therefore has lower reactivity. Fly ash generated at a high temperature can contain large amounts of mullite, a phase without pozzolanic properties. Amorphous determination of SCMs through XRD analysis provides a much faster indication of the suitability of the SCMs compared with other methods. In addition, it is also fully automatable.

The amount of clinker which can be replaced by SCMs is strictly regulated by standards. For instance, standard EN-197-1 describes the 27 types of cement, each with well-defined ranges of clinker, limestone, slag, fly ash, pozzolana, burnt shale, silica fume and other additives. The most recent version of standard EN-197-5 is an update that now includes Portland-composite cement CEM II/C-M and a different type of composite cement CEM VI, neither of which are covered by EN 197-1, whose intended use is the preparation of concrete, mortar and grout in a more sustainable way.

XRD is widely used to verify the proper blending and homogeneity of the product. It is in the interest of grinding plants to stay as close as possible to the allowed upper limit of SCMs, therefore minimising the amount of clinker and the overall production cost of the cement. An imprecise SCMs quantification obliges the quality manager to take larger safety margins at the expenses of the product profitability. XRD systems can provide a precise quantification of the SCMs, and as a result, the return on investment for grinding plants producing blended cement is extremely attractive.

Calcined clay and new cements

The recently discovered synergy between calcined clay and limestone in cement has aroused the interest of regulators and cement producers. In Europe, the new EN 197-5 standard has increased the maximum clinker substitution from 35% in CEM II/B-M(Q-LL) to 50% in CEM II/C-M(Q-LL). These new cements, such as LC3, can potentially reduce carbon emissions by up to 40% without affecting the strength of the cement. Accurate mineralogical analysis is critical for identifying and exploiting suitable clay deposits, calcinating the raw clay, and ensuring the proper blending with clinker and other additives.

Aeris benchtop instrument with XRD technology (Malvern Panalytical).

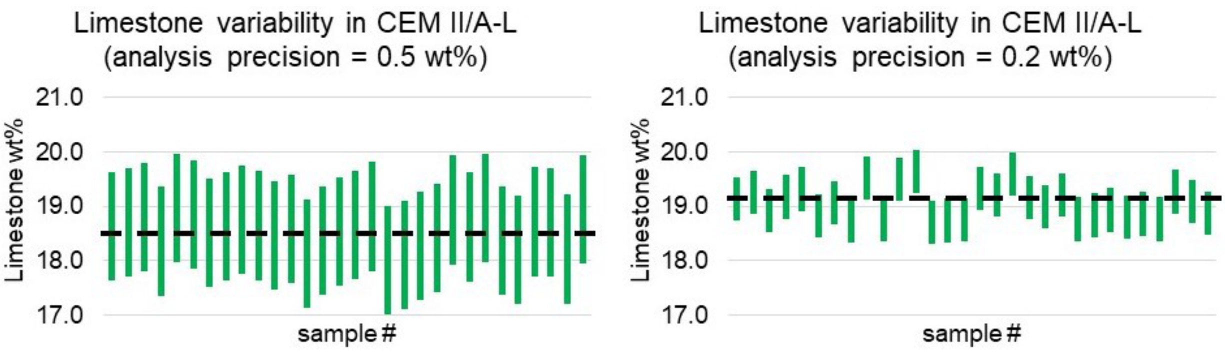
Using the wrong clay can severely compromise the performance of the cement. Kaolinite and smectite are the only common clay minerals displaying pozzolanic properties upon calcination. Their concentration should be above 30 – 40 Wt% for the clay to be suitable for calcination and blending with clinker. Other minerals, such as quartz, hematite, calcite, feldspar, and other clays such as micas and illites, act as filler.

XRD analysis has determined that the dehydroxilation reaction occurring during calcination can cause the collapse of the clay's crystal structure and a loss of crystallinity. These changes are necessary to give the material pozzolanic properties. Low temperatures or short residence times result in residual kaolinite or smectite that do not contribute to the cement's strength and affect workability. The onset temperature of the dehydroxilation reactions is approximately 550 C for kaolinite, and 700 C for smectite.

Therefore, the optimum calcination conditions strongly depend on the clay's mineralogy. High temperatures or long residence times can lead to the crystallisation of refractory phases, such as mullite, cristobalite, anorthite, wollastonite, diopside, and gehlenite. The optimum window is quite narrow, and XRD can provide the necessary data to produce calcined clay in the right way.

The absence or low concentration of calcite combined with the lower kiln temperature dramatically reduce carbon emissions compared to the production of clinker. The resulting calcined clays are then blended with clinker, gypsum, and limestone in the appropriate proportions. These proportions can be accurately quantified with XRD to comply with local standards.

The production of many other types of clinker and cement can benefit from XRD analysis. The list includes, but is



More precise mineralogical quantification (95% confidence intervals in green) enables smaller safety margins. The maximum level of allowed limestone in CEM II/A-L is 20 Wt%. By improving the analysis precision from 0.5 Wt% to 0.2 Wt%, the plant can respectively increase limestone and decrease clinker by approximately 0.6 Wt%.

not restricted to: geopolymers, calcium aluminate cements or ciment fondu, calcium sulfoaluminate cements, belite-ye'elimite-ferrite cements, carbonatable calcium silicate clinkers based on wollastonite, alkali-activated materials, supersulfated cements based on slag and gypsum, magnesia-based cement, and phosphate cements. The application of these cements varies from low-carbon cement, fast-setting cement, refractory cement, and cement for the encapsulation of radioactive and toxic materials.

XRD for a sustainable future

X-ray diffraction has become a key analytical method for controlling the quality of clinker and cements. It is especially important now, given the urgent need to align with net zero targets. This has led to the manufacture of new green cements, based on the use of various alternative fuels, SCMs, and by adopting a circular approach when possible. XRD is the only technique that allows rapid, accurate, and automatic quantification of the mineralogy of all these different compounds, so manufacturers can retain full control over the cement process and make it as green and profitable as possible. Most importantly, it offers a way of making quality, sustainability, and profit compatible as the cement industry searches for new ways of manufacturing green cement. ■

About the authors

Dr Matteo Pernechele holds a PhD in Materials Engineering from the University of British Columbia, Canada and a Master's degree in Materials Science from the University of Padua, Italy. His work spans from scientific research in the general field of solid-state chemistry to industrial projects, especially in the construction and mining sectors.

Matteo has 14 years of experience in X-ray diffraction and Rietveld refinement. He has been with Malvern Panalytical since 2018 as an XRD application specialist at the Application Competence Center in Almelo, The Netherlands.

Dr Murielle Goubard is the Global Segment Manager – Building Materials for Malvern Panalytical. She has extensive experience in materials chemistry and worked 15 years at Solvay Research Center. She has a deep interest in the cement making process and has been involved in developing applications and solutions for French plants and key European cement companies, while looking to improve efficiency and product quality. With 15 years working at Malvern Panalytical, she is now an expert in building materials and is very involved in solutions for green cement plants, circularity, and net zero.