Beyond particle size

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The increasing use of cement additives like limestone or fly ash in 'new' blended cements adds complexities to modern cement production. Cement companies also want to market the benefits of these new cements, which combine green credentials with well-defined performance. Therefore, information about the particle size of the chemically different components of the final cement, rather than the product as a whole, is becoming essential for success[1].

Automated imaging offers an analytical approach that has the capability to provide the necessary particle characterisation data. This technique enables analysts to measure particle size and shape of different particulate species within a blend. Relatively recently, automated imaging has been combined with Raman spectroscopy, enabling the determination of correlations between particle size, shape and chemical composition.

For cement manufacturers, these new capabilities make it possible to determine whether the components of a cement blend are represented equally across all size fractions, or are unequally distributed with respect to size. Correlating such information with product performance helps advance understanding of how to engineer high-performance cements, pinpoint a precise specification for the use of cement additives, and establish and control processes for their inclusion.

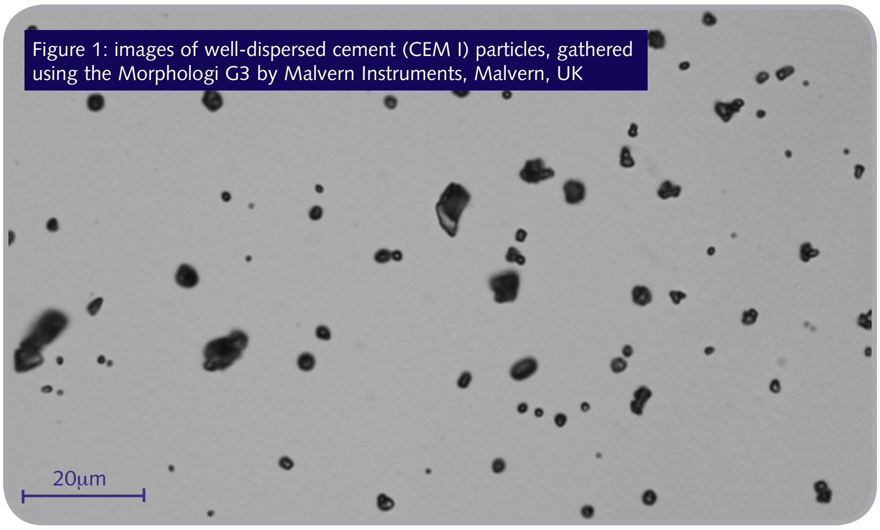


Figure 1: images of well-dispersed cement (CEM I) particles, gathered using the Morphologi G3 by Malvern Instruments, Malvern, UK

The growing use of replacement materials

The aggressive CO_2 capping reduction strategies in place for the global cement industry bring every aspect of production into the spotlight. For many industries CO_2 reduction focusses attention on energy consumption. This is the case in cement production too. However, there is a bigger challenge to address. Around half of the CO_2 emissions associated with cement production come as a byproduct from the calcination of limestone. CO_2 release is therefore inextricably linked with the production of clinker and/or Portland cement, no matter how efficient a plant is.

Cement is an ancient material, though not in its current form. In Roman times pozzolan-lime cements were widely used and evidence from remains around the world bear witness to their durability. Pozzolans – materials that contain silica or alumina – do not perform on their own as cements. Pozzolans will, however, form cement-like compounds when reacting with water in the presence of calcium hydroxide (lime), hence pozzolan-lime cements. These cements develop strength slowly, but ultimately become stronger than Portland cement. [2,3,4]

The strategy of replacing a proportion of fresh Portland cement with pozzolanic materials, such as fly ash and blast furnace slag, to produce a new cement therefore offers multiple rewards:

- reduced CO_2 emissions as a result of producing less clinker
- lower feed costs, as suitable pozzolans are typically from industrial waste streams
- a wider choice of strategies for performance control
- reduction in energy consumption.

However, learning how to successfully incorporate these new materials to make products that meet industry standards is an ongoing process.

Controlling cement performance

Many parameters that affect the quality of cement are controlled as described by EN197-1.[5] Two of these are particle size distribution and composition which affect the rate of hydration of the cement when it is used in the field and, as a result, the properties, most especially the strength, that the cement goes on to develop.
In conventional cement manufacturing processes composition is controlled by the feed to, and the operating conditions of, the kiln that produces clinker. Products of different grades are then made from compositionally-identical clinker, simply by varying milling conditions in the finished grinding circuit.

As the industry has embraced more sophisticated particle sizing techniques (laser diffraction in place of Blaine), the correlations between certain size fractions and cement performance have become better understood for traditional Portland cements.

For instance, it is now widely recognised that because fine particles hydrate more quickly than coarser particles, a cement with a high proportion of fines may dry exothermically and too quickly, making it prone to cracking and reducing the material's overall strength. This controlling impact of the size distribution of cement components remains intact whether using standard materials or newer additives, but the exact correlations are not identical. Effective control of the particle size distribution of each component is thus becoming crucial.

There are two aspects to efficient particle size control for cement containing additives, as there are for conventional cement. The first is to uncover the correlations needed to set a suitable particle size specification. This involves quantifying the impact of the particle size of each component of the cement on its performance and is a more complex task where additives are involved.

The second issue is to design and control a process that enables consistent achievement of the defined specification. Again this is complicated by the inclusion of cement additives. For example, clinker and slag are hard and relatively difficult to grind whereas gypsum and limestone are more brittle and, under the same milling conditions, will produce much finer particles. This means that if materials are blended before grinding, the resulting product will be different from one where materials undergo grinding and then blending. For cement additives, whose processing characteristics are as yet relatively ill-defined, being able to understand the impact of the process on particle size helps indicate how best to incorporate these materials into the final product.

Analysing the size, shape and chemistry of cement particles

Most cement manufacturers now use laser diffraction techniques to measure particle size distribution. Fast and efficient, laser diffraction technology is commercially available in the form of powerful systems for both laboratory and on-plant use. As a result the measurement technique is applied from R&D through to quality control with real-time particle sizing systems in routine use to drive automatic control of the finish grinding circuit.

However, laser diffraction does not measure the size of individual particles but rather provides robust ensemble data for a complete sample, with no differentiation of the components within in it. For conventional Portland cements this is not a significant limitation but for newer cements with a greater number of components, laser diffraction cannot provide all the information required to understand how to make them. Here, more complete analysis comes from the use of complementary techniques, primarily laser diffraction in conjunction with microscopy-based particle imaging techniques.

Automated image analysis allows analysts to accurately measure the size and shape of individual particles within a sample (see Figure 1). The Morphologi G3 by Malvern Instruments for example, is an automated imaging system that measures across the size range 0.5-10000μm and is capable of capturing images of tens of thousands of particles in a single measurement cycle, over a short period.

Relatively recently, this automated imaging has been combined with Raman spectroscopy (in the Morphologi G3-ID) to add compositional analysis to particle size and shape measurement. Such systems deliver morphologically-directed Raman spectroscopy to produce size information for specific, chemically-differentiated populations within the sample. Size and shape information is first obtained using image analysis. The positional information from this analysis is then used to automatically return to the particles of interest from which the Raman spectra are acquired to determine composition.

The following case study illustrates the value of this technology in supporting the incorporation of cement additives.

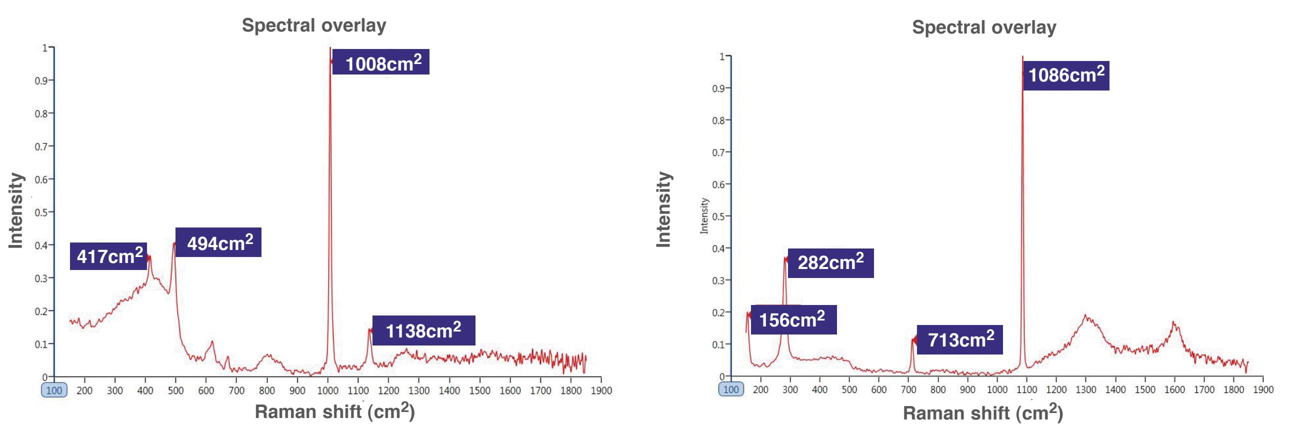
Case study

The Austrian Cement Association (VÖZ) is working on research programmes designed to scope the application of morphologically-directed Raman spectroscopy in cement analysis, using the Morphologi G3-ID. To date this research has centred on establishing best practice for sample dispersion, measuring reference spectra for all relevant components and then using the technique to investigate the properties of cement samples.

The analysis of two cement samples containing different levels of cement additives was carried out using morphologically-directed Raman spectroscopy. Size data and Raman spectra were gathered for 1000 particles and referenced to a database or library of pre-measured spectra developed by the research group for cement materials in VÖZ (see Figure 2).

This study enabled the identification of different particle populations and the

Figure 2: example reference spectra for limestone (right) and gypsum (left) highlight the ability of Raman spectroscopy to differentiate the chemical components of cement



generation of particle size distributions specifically for two individual components within the cement (see Figure 3).

Further research was carried out on another commercially available multi-component cement, CEM II/B-M (S-L), which is made up of clinker, limestone and slag. Figure 4 shows the particle size distribution for each component within the mixture.

The data shown in Figure 4 suggest that these materials may well have been milled together, with their respective differences in grindability giving rise to the observed differences in particle size distributions in the finished product.

Clinker is a much harder material than limestone or slag and if processed under comparable conditions would therefore be expected to exit the mill as a coarser product, as is evidenced in the sample. Such analysis and the insight it provides can be of great help to cement producers when optimising grinding processes to meet quality targets for cements that incorporate cement additives.

Figure 3: component specific data (Morphologi G3-ID, Malvern Instruments) for a CEM II/A LL, 32.5 R sample showing particle size distribution data for clinker (red) and limestone (blue)

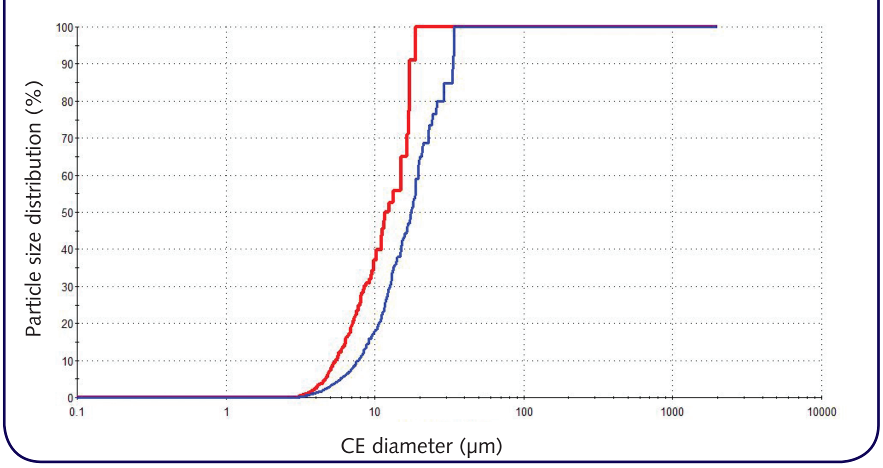
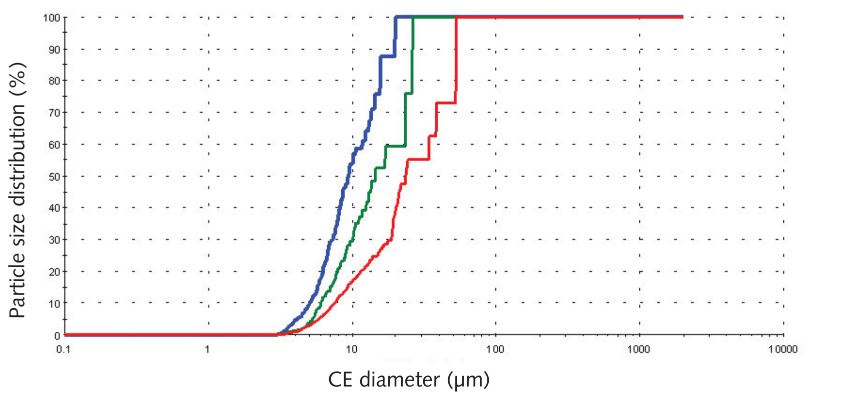


Figure 4: size distribution analysis for a CEM II/B-M (S-L) 42,5 N sample shows that within the sample the limestone (blue) has the finest particle size distribution, followed by the slag (green line), with the clinker (red line) present as the coarsest particles



Conclusion

Particle size data have been instrumental in helping the cement industry to improve product performance and exert efficient process control. However, the use of replacement pozzolan materials to reduce the CO_2 footprint associated with Portland cement production makes the control of particle size a more complex issue.

The use of replacement materials is a strategy that pays multiple dividends in terms of economic and environmental impact, but the successful incorporation of these materials is challenging. Understanding how the particle size of each component influences product performance is critical, but so too is identifying robust process designs that will deliver materials with a defined particle size specification, for each constituent.

Automated imaging, in combination with Raman spectroscopy, delivers the component-specific particle size information needed to advance the successful inclusion of replacement materials. The example data included here show how morphologically-directed Raman spectroscopy can successfully differentiate between clinker in a sample and other components, such as limestone and slag, to generate component-specific size distribution data for each one. This enables the differentiation of samples that have been blended pre- and post-milling, spotlighting the impact of the differing grindability of individual components on the product that emerges from a joint milling process.

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Such data support the development of optimised processes for replacement material inclusion, a vital strategy for reducing the CO_2 emissions associated with cement.

References

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