Cement Laboratories: State-of-the-Art

Clockwise from top left: Michael Morrison, Linda M. Hills, Donald J. Broton, Luis Graf, Ella Shkolnik.

Materials Technology Group, Construction Technology Laboratories, Inc., USA, looks at a number of the newest tools being used in today's most advanced cement laboratories and how the industry can benefit from their use.

Introduction

Over the past 75 years, scientists and manufacturers have learned much about cement and concrete through laboratory exploration and analysis. And although people might not expect a typical cement laboratory to be high-tech, advances in computer-controlled equipment, robotics, sophisticated software, electronics, and optics are all changing the way work is carried out in cement laboratories. These advances reduce analysis time, increase the accuracy and precision of results, and enhance our knowledge of cement properties. This article discusses some of the newest tools being used in today's most advanced cement laboratories and how the industry can benefit from their use.

Physical testing

Michael Morrison, Senior Materials Technologist

Physical testing of cement has traditionally been very operator-dependent. It is labour-intensive, time-consuming work, and the volume produced is limited by the speed and capabilities of the tester. Properly training a tester is costly and can take months. But employing a capable physical tester can be key to a cement company's success, because accurate, acceptable test results are required to market the product. All customers want to see the mill certification to evaluate product quality, and a change in operators or a mistake in a test method can cause long-term harm to customer relationships.

For the last 10 years, the cement industry has begun to embrace automation for physical testing. While methodologies on physical testing of cement vary throughout the world (ASTM, EN, DIN, BS) the resultant material properties remain similar. Setting time, strength, fineness, soundness, and air content are the commonly required tests. Today's technology offers preprogrammed automatic paste and mortar mixers, automatic time-of-setting machines, automatic fineness machines, preprogrammed jolting and vibration tables to fabricate flexural and compressive strength specimens, and automatic tamping machines to fabricate strength specimens. A number of these machines are accepted by standards organisations worldwide, while some are still in various stages of consideration.

A number of machines are more widely used in Europe, the Middle East, Asia, and South America, but acceptance has also begun to grow in North America. Automation in physical testing offers many benefits. It improves reproducibility while reducing variability (Figure 1). It can increase laboratory efficiency, increase workflow, and reduce turnaround time (Figure 2). Most importantly, it can reduce training costs and practically eliminate the dependency of a lab on a particular tester or operator to function.

The last decade has offered the cement industry new testing options, helping us move into the next century. The next decade is likely to see the introduction of more new technology, such as automatic false-set testers, automatic normal-consistency kits, and laser-based length-change comparators.

Microscopy

Linda M. Hills, Senior Materials Scientist

Today's well-equipped cement laboratory should have an optical microscope with which to view the clinker microstructure (Figure 3). The clinker's crystal microstructure results from the kiln feed's mineralogy and fineness and from the pyroprocessing conditions. Therefore, a microscopical examination that shows the phase size, amount, distribution, and other characteristics can reveal valuable information about the clinker history and the kiln temperature profile. These results can provide clues to optimise raw feed burnability, improve clinker grindability, troubleshoot production problems, and increase 28 day strength. Analysis is also important to monitor the effects of process changes, such as the use of alternative raw materials or a change in burner pipe position.

In addition to clinker analysis, microscopy of the raw feed helps to optimise production, because the fineness and mineralogy of the kiln feed affect the ease with which it burns. The microscope can also be used to identify cement contaminants, and assist in discovering the causes of buildups.

For most purposes, the optical microscope is sufficient for microstructural analysis. A number of instances, however, require more information, and the scanning electron microscope (SEM) offers the next step up. The scanning electron microscope with energy dispersive X-ray spectroscopy (SEM/EDS) (Figure 4) allows for examination and analysis of microstructural and microchemical characteristics. This tool offers several advantages, including: higher magnifications, with greater depth of field and resolution than are possible with conventional optical microscopy; elemental composition analysis of particles or regions of a sample; and 'mapping' of elemental composition to demonstrate distribution.

Although it may not yet be practical for an individual cement plant laboratory to own and operate an SEM/EDS, cement manufacturers should at least be aware of the available technology. For example, a cement manufacturer might seek out an SEM/EDS in order to determine the chemical analysis of individual clinker phases. Because a number of trace elements affect reactivity, the presence of these elements in specific clinker phases can help explain cement behaviour.

Figure 1. Automated equipment such as this mixer reduces variability and increases reproducibility of physical test results.

X-ray fluorescence analysis

Donald J. Broton, Senior Materials Scientist

X-ray fluorescence (XRF) analysis has taken centre stage in the analysis not only of cement but of many other materials. The operating software of XRF instruments can store different analytical programs to analyse various material types. This software is user-friendly, yet sophisticated enough to select appropriate element lines, advise on line overlaps, and flag potential problems encountered in a particular matrix. As computer technology has improved, the memory needed to run complicated algorithms is no longer an issue. Newer developments such as multi-position sample changers and unattended analysis capability have helped make the XRF instrument the workhorse of the cement lab. A number of XRF spectrometer manufacturers now include both XRF and X-ray diffraction (XRD) in one instrument, to allow cement plants to determine free lime and other crystalline phases as well.

X-ray spectrometers are being used more with the application of standardless automated analysis programs. Cement labs can use these programs to help production staff make decisions on the substitution of alternate raw materials for conventional ingredients in raw mixes. The equipment can also be used for the elemental analysis of materials for which no reference materials exist. Fabrication of pure compound standards (substituting for reference materials) for calibration is costly both in analyst time and in materials.

Even simple, wide range element scans can be interpreted easily using today's software programs. Simple point-and-click or auto-identification of unknown elements can be carried out quickly and reliably. XRF allows both quantitative and qualitative elemental analysis of specimens in powder form, without further preparation. This capability practically eliminates the

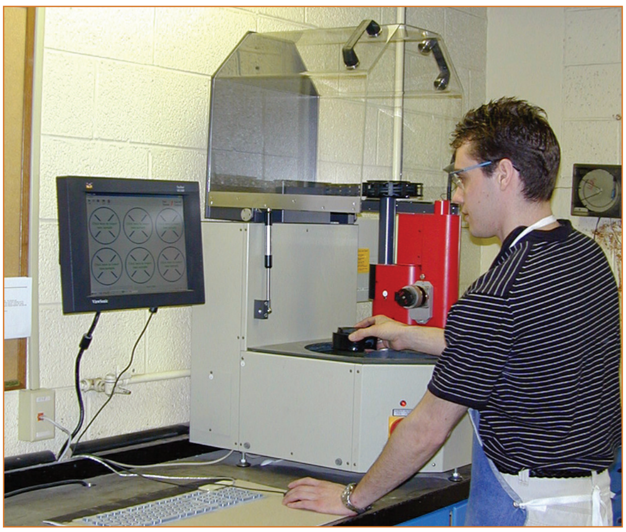


Figure 2. Automatic Vicat time-of-set machine allows simultaneous testing of multiple specimens, increasing lab efficiency and workflow.

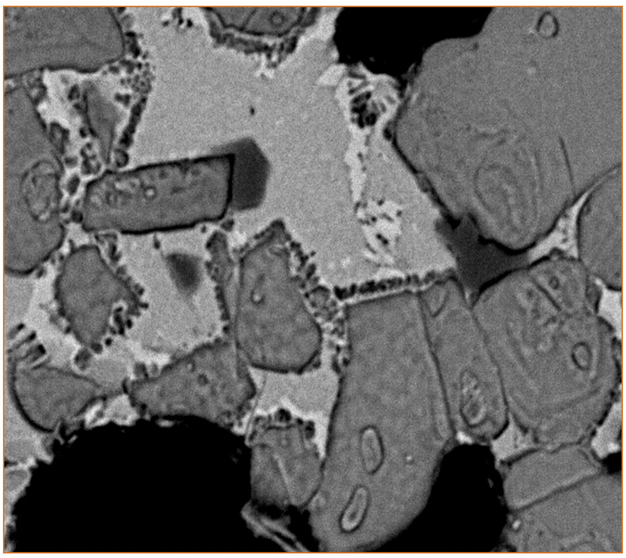


Figure 3. Clinker microstructure at 2000X magnification using the scanning electron microscope.

"In addition to clinker analysis, microscopy of the raw feed helps to optimise production, because the fineness and mineralogy of the kiln feed affect the ease with which it burns."

potential for contamination by specimen preparation equipment or reagents.

Two types of specimen preparation now predominate at cement plants. Pressed powders require fine grinding and pressing into a briquette for analysis. With any of the commercially available automated equipment, fusion allows the fabrication of one to six specimens at a time. New fusion equipment can monitor temperature and run an automated program to melt the flux, dissolve the sample, cast the specimen, and quickly cool the glass disk with fans to produce specimens in just a few minutes. Automated fusion equipment makes specimen preparation easy and reproducible, thus increasing the precision of the analysis.

XRF has become a valuable tool for the analysis of failed concrete and mortar. With today's concrete mix designs incorporating various mineral admixtures, standard test procedures cannot determine effectively whether the specified proportions were used during batching. By using XRF to analyse each ingredient and the concrete for more than 14 chemical elements, traditional elemental mass balance can be employed to determine the amounts of cement, mineral admixtures, and coarse and fine aggregates in the mixture. An investigator no longer needs to guess the amount of acid-soluble material other than cement in the concrete, and therefore can better determine the cement content and water to cement ratio. Problems related to compressive strength, set time, colour, and other factors caused by improper batching of ingredients can now be solved easily.

X-ray diffraction Rietveld analysis

Luis Graf, Engineer III

In 1969, H.M. Rietveld proposed the mathematical calculation of X-ray diffraction (XRD) patterns based on crystal structure parameters. The comparison of these patterns to those observed in a variety of material samples has given rise to the use of the Rietveld method to quantify crystalline phases. The cement industry is one of many that now have modern equipment that uses the Rietveld method (Figure 5) in routine XRD testing.

Several methods have long been used for cement phase quantitative analysis, including phase estimation by clinker microscopy, Bogue calculation based on oxide chemical composition, and XRD analysis using internal standards or standard additions (the 'spiking' method). The complications arising from each of these methods, as well as the nature and origin of Portland cement clinker phases, challenge the accuracy and usefulness of these quantitative determinations. Though the Bogue calculation for potential compound composition has been the most commonly applied method by far, Bogue calculations rely on basic theoretical assumptions that often fail to represent the true phase composition. Microscopy, although a powerful tool for process optimisation and troubleshooting, usually is not practical for routine analysis in the plant, where the determination of phase amount in several samples is required for each hour of production. The use of internal standard and standard additions techniques for XRD analysis requires preparation and data acquisi-

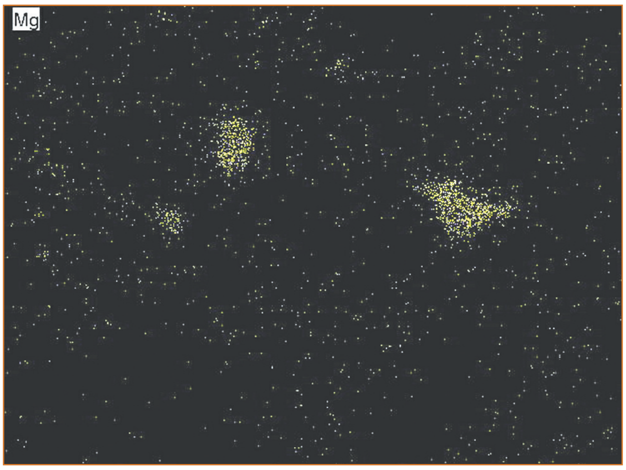


Figure 4. Energy-dispersive X-ray spectroscopy (EDS) feature produced this MgO dot map for the area shown in Figure 3, which demonstrates the location of MgO, or periclase, within the clinker microstructure.

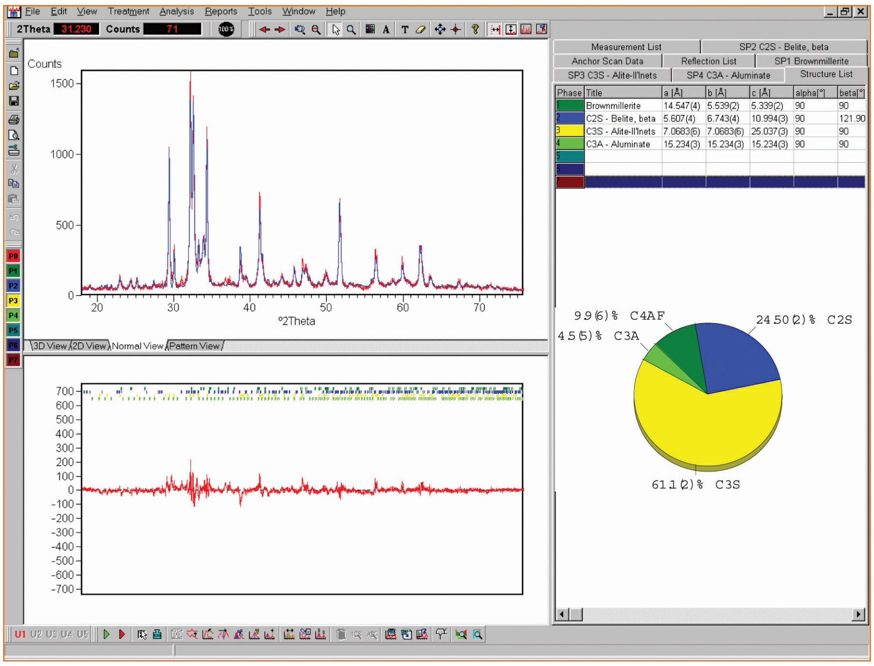


Figure 5. Application screen for Rietveld XRD analysis. The top-left window displays calculated and observed XRD patterns of a clinker sample. The bottom-left window displays the fit, and the program allows changing crystal structure parameters of each clinker phase, as shown in the top-right window. The final output is percentages of each phase, in this example represented as a pie chart.

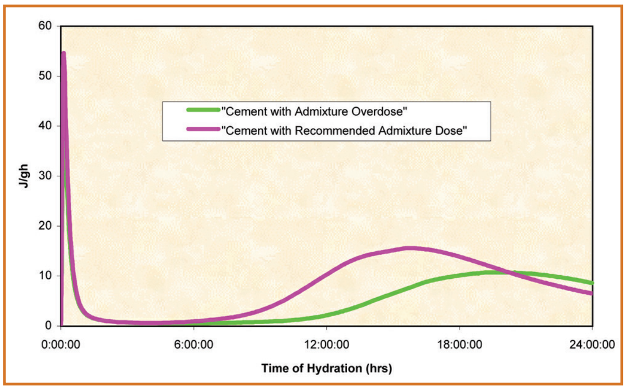


Figure 6. Hydration profiles of various samples.

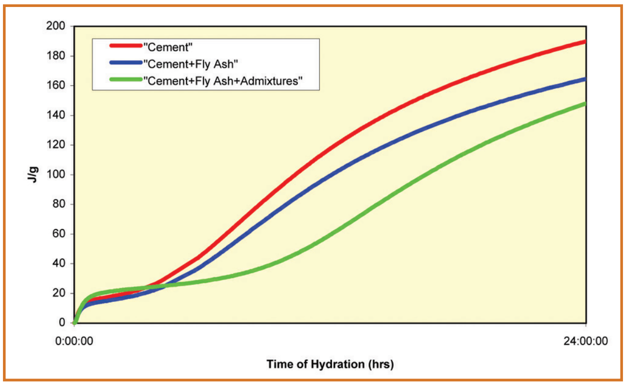


Figure 8. Generated cumulative heat.

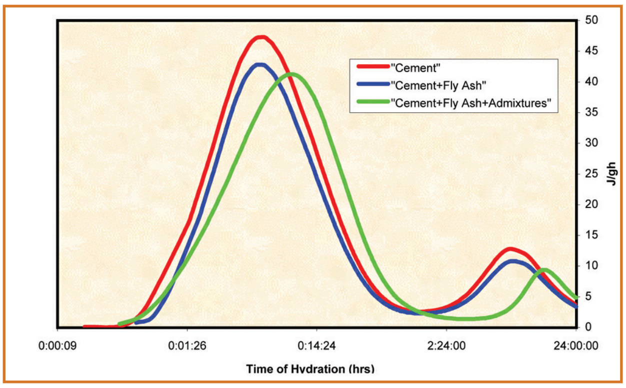


Figure 7. Hydration profile: early hydration.

tion for several samples, also limiting the application of these options in the cement manufacturing process.

XRD equipment manufacturers and other organisations have developed computer software for the implementation of Rietveld analysis. Both the geometric configuration and significant advances in modern X-ray detection technology now allow this method to be used more effectively in the cement industry. Older configurations using gas-proportional counting detectors, scintillation detectors, and even solid-state detectors, are now being replaced by parallel detection systems, such as position sensitive detectors. Data acquisition now is approximately 100 times faster, with no loss of data quality, which makes the Rietveld method of quantitative XRD analysis a very attractive alternative to the methods normally employed. With increased speed of analysis and results of comparable accuracy to other methods, XRD is now able to meet many needs in the cement manufacturing industry.

Conduction calorimetry

Ella Shkolnik, Senior Materials Technologist

In today's cement laboratory, conduction calorimetry helps diagnose and solve problems in cement and concrete production. Designed to measure the total heat and rate of heat evolution, the conduction calorimeter provides detailed information on the cement hydration process and on different factors that influence it. While ASTM test procedures such as C186 (heat of hydration) or C191 (time of set) provide some information on the hydration process, they offer little help in solving challenging problems.

Conduction calorimetry helps to investigate problems related to strength development, setting time and premature stiffening. The rate of hydration reaction of cements is influenced by chemical admixtures added to concrete; conduction calorimetry testing can successfully show the effects of admixtures on concrete properties. Figure 6 shows how the hydration process became retarded due to an overdose of a water-reducing admixture.

Conduction calorimetry also can be used to evaluate the potential effect of supplementary cementitious materials on the hydraulic properties of cement blends. The technology is very useful for studying the interaction of different components of concrete mixes, and thus helping to anticipate and prevent problems from occurring in the field. Figures 7 and 8 represent a calorimetry study of cement, fly ash, and admixtures proposed for use at a job site. In this case, the heat curve for cement paste (red line) was considered normal. The heat curve for the cement fly ash blend (blue line) showed that fly ash might have some deleterious effect on cement hydration. However, results for the mixture of cement, fly ash, and admixtures (green line) showed that the combination would considerably retard cement hydration and create setting problems at the job site.

A new and useful tool for research and quality control, conduction calorimetry also can be used to study cement and concrete behaviour under different weather conditions, the effect of contaminants on the hydration process, as well as other parameters not routinely evaluated in a laboratory setting.

Particle size distribution

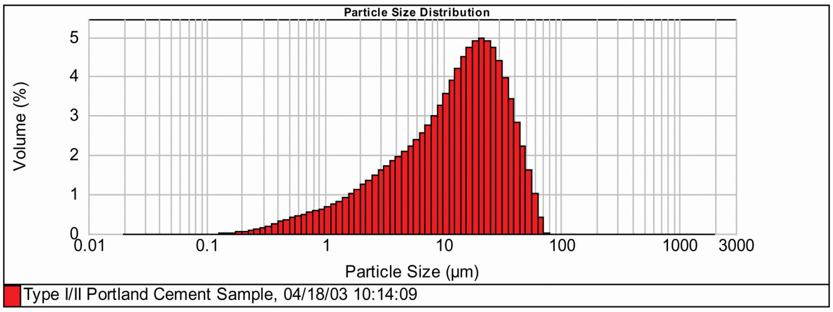
Ella Shkolnik, Senior Materials Technologist

Particle size distribution (PSD) of ground clinker or cement is one of the properties that most affects cement performance. PSD influences cement fineness and specific surface area, which in turn affect early compressive strength and curing qualities.

Sieve analysis and sedimentation using X-ray are commonly used to determine particle size distribution. Sieve analysis can produce satisfactory results for particles larger than 35 mm, but it offers poor reproducibility and is highly operator-dependent. The sedimentation method of PSD analysis, although widely used, has inherent disadvantages: it requires density determination, prolonged measuring time, and accurate temperature control; it is accurate only within a limited particle size range; and it cannot be used to analyse mixtures of different densities.

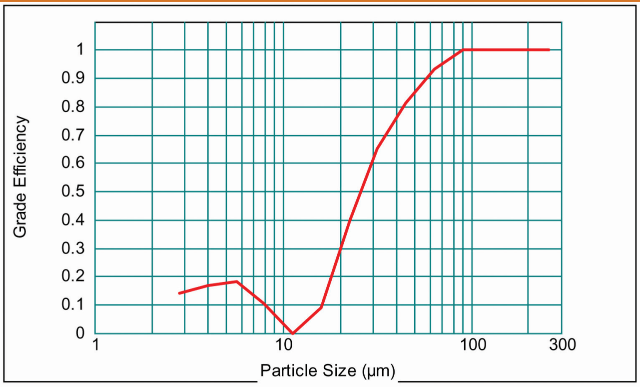
Once introduced to the market, laser diffraction quickly succeeded these as the preferred method for particle characterisation and quality analysis. This method relies on the fact that the laser diffraction angle is inversely proportional to particle size. Laser diffraction provides a fast way to measure particle size distribution, including mean and median particle diameters as well as surface area. The advantages of using this method include its wide particle size range (0.1 - 2000 mm), its ability to analyse dry or wet samples, and the variety of its sample dispersion methods. The method is fast, fully automated, and generates highly reproducible results (Figure 9).

The modern laser diffraction instrument can produce conventional particle size distribution graphs, as well as graphs and tables specific to cement industry such as Tromp or Grade Efficiency curve (Figure 10). In addition, the specific surface area calculated from the PSD curve agrees well with Blaine values, so the method can be used to determine the specific surface area of fine powders.



Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
1.000	4.75	3.000	15.06	7.000	30.34	10.000	39.62	30.000	82.39	45.000	94.80

Figure 9. Laser diffraction quickly measures particle size distribution, including mean and median particle diameters as well as surface area.



Size (µm)	Efficiency	Size (µm)	Efficiency	Size (µm)	Efficiency	Size (µm)	Efficiency	Size (µm)	Efficiency
2.340	0.14	6.630	0.10	18.750	0.40	53.030	0.93	150.000	1.00
3.310	0.17	9.380	0.00	26.320	0.65	75.000	1.00	212.130	1.00
4.690	0.18	13.260	0.09	37.500	0.81	106.070	1.00	300.000	
6.630		18.750		53.030		150.000			

Figure 10. The laser diffraction instrument can produce conventional PSD graphs, as well as graphs and tables specific to cement industry such as the Tromp or Grade Efficiency curve.

Thermal analysis

Ella Shkolnik, Senior Materials Technologist

Thermal analysis (TA) is becoming a more important tool in the cement laboratory. The thermal analytical methods used most in this field include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTA). These thermoanalytical techniques provide information valuable for materials evaluation, new material development, the prediction of product performance, the optimisation of processing conditions, and quality improvements.

Thermal analysis has been successfully applied to identify and characterise raw materials being considered for use in cement manufacturing, as to their potential to contribute to total hydrocarbon (THC) or carbon monoxide emissions. DSC is particularly useful in finding ways to control VOC emissions, or in evaluating the ability of alternate materials to meet environmental standards. Thermoanalytical techniques are widely used in assessing cement performance: for example, to analyse for cement sulfate form and content, and to assess their influence on setting time; or to identify problems related to lump formation, 'pack' and 'silo' sets, or flowability. Results obtained through TA can be correlated to strength development and durability of cement and concrete.

Many problems are solved through a combination of different TA techniques: for example, a combination of DSC and TGA analyses helps in evaluating cement hydration products and estimating the degree of prehydration in 'weathered' clinker. TGA can be used to provide proximate analysis of coal, and DSC is a better way to determine coal's calorific content than traditional methods of coal analysis. Both TGA and DSC are used to study the utilisation of the inherent fuel values of fly ash in cement production.

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Conclusion

Rapid advances in technology are affecting all industries, and this specifically includes the quality assurance, quality control and research labs in the cement industry. The cement laboratory of the future is likely to more closely resemble an air traffic control centre than a high school chemistry laboratory. Understanding and applying advances in technology will be one of the keys to the future success in any cement laboratory.

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