

Contemporary chemical techniques in concrete analysis

With the frequent revisions in Standards and Codes of Practice, alongside constant development of analytical techniques, it may not always seem straightforward to know where to start with chemical analysis.

DAVID CROFTS, STATS LIMITED

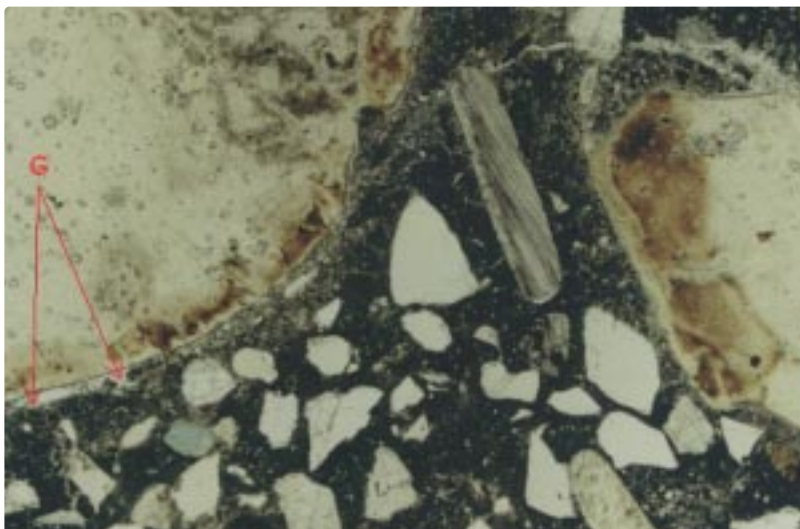
By reviewing and summarising some current methods, the following article is intended to provide assistance in successfully assessing both hardened concrete and conditions.

Traditional 'wet' chemical analysis

Recent high-profile reports regarding the supply of cement with higher than expected alkali content have led to a resurgence of interest in alkali-silica reactivity (ASR) in concrete in the UK. While resulting structural problems may have been overestimated in some cases, the need for reliable and timely analysis of materials and products has been highlighted. The key to identifying potential ASR damage lies in using a combination of petrographical and chemical analysis to characterise the aggregate and the binder; then assessing the potential for ASR to affect the concrete. A vital element of the investigation is sampling. Owing to the uneven distribution of alkalis through the concrete, it is vital that sufficient samples are taken from the right locations to ensure that the test results are representative of the concrete as a whole.

Chemical analysis should include determination of the alkali content of the concrete as sodium oxide (Na_2O) equivalent, as well as a determination of the cement content and aggregate/cement ratio. These tests are carried out in accordance with well-established methods described in BS 1881-124⁽¹⁾. It is important that a concrete specialist analyses the concrete. The test methods are relatively straightforward, but the interpretation of the results is much less so. Consideration must be given to the type of

Figure 1:
Photomicrograph of concrete piling in thin section, showing the presence of alkali-silica gel deposits (G).



aggregate, the age and intended life span of the structure. It is never easy to correlate alkali contents in hardened, aged concrete with those in the raw materials and some aggregates are prone to release alkalis analytically but not necessarily in practice. An experienced concrete scientist will be able to assist in drawing the correct conclusions from the results of an investigation.

A photomicrograph of a concrete core in thin section, recently taken from piling where the presence of ASR was suspected, is shown in Figure 1. Chemical analysis of the concrete indicated that the alkali content was consistent with the materials analysed. A detailed petrographic examination indicated that while there were areas where evidence of some ASR was present, there was no evidence of expansive ASR causing damage to the concrete. The piling contained substantial reinforcing steel, was encased in steel and supported a large building; consequently, expansion of the concrete in the piling was restricted in this case.

High alumina cement (HAC) concrete

Following a small number of roof collapses in the 1970s, notably in schools and swimming pools, the use of HAC concrete was banned in structures for some time. HAC concrete was still used in non-structural applications following the ban and in the 1990s there was a reconsideration of the evidence surrounding HAC concrete (renamed calcium aluminate cement by its manufacturer), possibly to allow its renewed use in construction.

A requirement of the maintenance of an HAC concrete structure is regular assessment to monitor for conversion of the cement, any structural degradation caused by alkaline hydrolysis and/or sulfate attack and the effect on any embedded steel of the 'carbonation' of HAC. The chemical analysis of HAC concrete, using the methods referred to in BRE Special Digest 1⁽²⁾, is a key part of this assessment, together with petrographical examination of suspected weakened concrete. An experienced concrete technologist is vital in interpreting the results to assess the potential for structural damage or weakening. A recent study in the south-west of England found that while there were areas of apparently damaged HAC concrete, and these did have elevated levels of alkalis with respect to alumina, the structure was assessed as being sound for the time being. Regular inspections of such structures to assess the integrity of the HAC concrete are prudent.

Reinforcement corrosion

Corrosion of reinforcement steel in concrete structures has led to widespread damage and, occasionally, to structural failure. Key to this is the integrity of the cover and the chemical environment of the concrete surrounding the steel. Apart from measuring cover depth, the two techniques most commonly used are assessment of the depth of carbonation and the chloride content of the concrete. The sulfate content of the concrete is also an indicator that degradation in the environs of reinforcement is a risk, together with subsequent corrosion of the steel and damage to the structure. Recent developments in titration technology have led to the automation of chloride analysis to varying degrees. The sample preparation and extraction are still in accordance with BS 1881-124⁽¹⁾. Analysis of the extract for chloride content using potentiometric titra-

tion is now routine and automation of this stage in the testing is becoming widespread. This has added value and reliability to the test method.

Aggressive ground

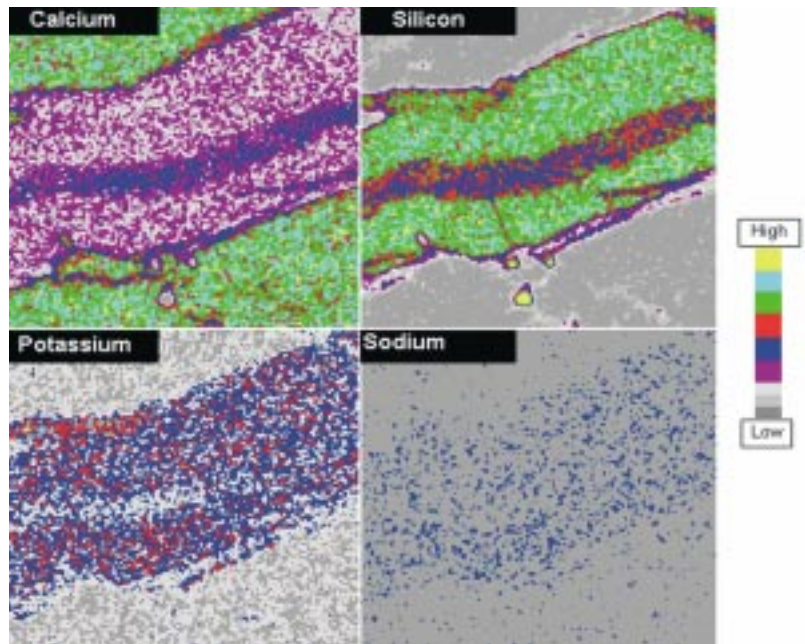
A vital part of any construction project is the assessment of ground conditions prior to installation of foundations and other buried concrete. The chemistry of the soil is key to the performance of the concrete in service and the fundamental tests that must be carried out are the analysis of the ground for pH and for sulfate content. Sulfate attack of concrete in service can lead to severe deterioration in the structure. The gravimetric method in BS 1881-124 remains the standard analysis for sulfate content of concrete. The guidance on the determination of sulfate content of soil and groundwater in the latest version of BRE *Special Digest 1 (SD1)*⁽²⁾ (via TRL Report 447) advises the use of inductively coupled plasma (ICP) – atomic emission spectroscopy (AES), to determine the sulfur content of extracts obtained using the procedure described in BS 1377-3⁽³⁾. BRE SD1 does indicate that traditional, gravimetric methods for sulfate determination can still be used where appropriate. BRE SD1 also contains advice regarding the assessment of ground thought to contain pyrite, following cases in which the sulfate design class of some ground conditions was found to have become more aggressive over time. In investigations of such ground, it is necessary to determine the total sulfate and total sulfur content of the soil, from which the total potential sulfate and oxidisable sulfide content can be calculated. The sulfate class equivalent to the total potential sulfate content can then be determined. This is then compared with the sulfate class determined using the water-soluble sulfate and pH of the soil. The higher of these classes is taken as the design sulfate class. The pH of aqueous extracts is determined using the electrometric method in BS 1377-3. Other potentially harmful species, such as nitrate, chloride and ammonium ions in the ground can be detected using similar techniques and referred to the relevant guidance in BRE SD1⁽²⁾. The aggressive chemical environment for concrete (ACEC) class of the ground is determined using the design sulfate class, water conditions and pH.

Instrumental analytical methods

Atomic spectrophotometry

The use of atomic absorption/emission spectrophotometry (AAS/AES) in concrete analysis has become widespread. Aqueous, acidic extracts of concrete are now generally analysed using these techniques to determine their alkali and aluminium contents. In traditional AAS/AES, the sample in dilute solution is atomised in a flame and either absorbs or emits electromagnetic radiation. This absorption/emission is detected and compared with standards to determine the concentration of the element in analysis. A more recent development is the use of ICP-AES, in which the sample is introduced as a fine droplet aerosol into an argon plasma at about 10,000°C. This leads to emission of radiation at characteristic wavelengths, corresponding to the constituent elements in the sample. The different wavelengths are separated by a grating and detected, thus ICP-AES is a multi-element technique and enables rapid analysis of extracts of concrete samples.

The technique is also very useful in the assessment of contaminated ground. Not only can it be used to determine the sulfate content of soils, it can also simultaneously detect a wide range of potential contaminants, considerably speeding up the time taken to assess the ground before construction.



Fourier transform infrared (FTIR) spectroscopy

A wide range of organic admixtures is now used in the formulation of concretes. It is important to be able to detect and identify these admixtures for a variety of reasons. Infrared spectroscopy is a very useful tool in the detection of organic compounds and can easily be applied to concrete samples. As always, interpretation of the resulting

Figure 2: SEM microanalysis element map of alkali-silica gel deposits filling a parting along the edge of a limestone coarse aggregate particle.

Consultancy and allied technical services

for Construction Materials and Building Technology



- Ceramics and glass
- Cladding and roofing
- Concrete and mortar
- Chemicals and plastics
- Fire and blast damage
- Flooring and paving
- Quarry products
- Render and plaster
- Road and rail structures
- UKAS Laboratories plus Centre for Stone and Slate Technology

Porterswood House
Porters Wood
St Albans AL3 6PQ
Tel: 01727 833261, Fax: 01727 798613

The Enterprise Centre
Puma Way
Coventry CV1 2TX
Tel: 02476 236816, Fax: 02476 236014

Email: info@stats.co.uk
www.stats.co.uk



Engineering, Materials and Environmental Consultants

Reader Enquiry Number 326

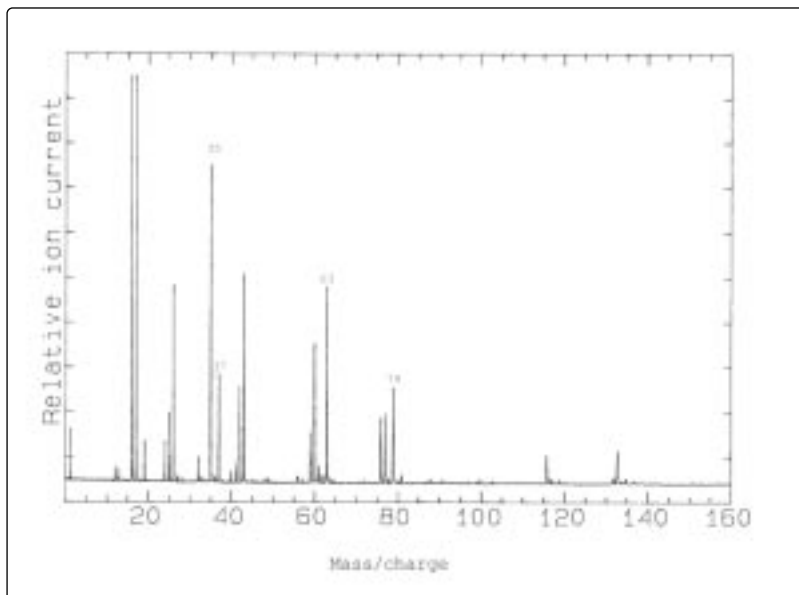


Figure 3: Laser Microprobe Mass Spectrum from a concrete surface, note the peak separation 63-79 indicating loss of a $^{14}\text{NH}_2$ fragment. Note also the characteristic peaks corresponding to ^{35}Cl and ^{37}Cl fragments.

spectra is not always as simple as obtaining them and it is helpful to have access to an experienced concrete scientist to assist in the latter.

It should be noted that, owing to the proprietary nature of most admixtures, it is not always possible to precisely characterise an admixture using FTIR, but a reliable generic identification of an admixture is possible. If a particular admixture has been specified, this method can easily confirm, or otherwise, its presence in the concrete. FTIR spectroscopy is a stronger tool when a comparison material is available or when specific targets are described. The use of most analysis techniques can be time-consuming and expensive when there is no information available regarding the nature of an admixture and/or when quantification is required. Furthermore, organic admixtures generally undergo a chemical change upon incorporation in the concrete, so that special reference mixes are often required.

Scanning electron microscopy (SEM)

Surface and microstructure analysis can be a vital part of the assessment of concrete. Defects on the surface can be a problem for cosmetic reasons but may also be a symptom of a deeper-rooted problem. SEM uses electrons instead of light to scan a surface and can obtain information about the topography, including pore structure and composition. This technique can therefore provide valuable information about the microstructure of the concrete; can chemically map the surface, either generally or in ‘spot’ locations; as well as detecting inorganic contaminants such as salts and metals. From the SEM data, it is possible to assess the condition and composition of the concrete, including studying shrinkage. Figure 2 demonstrates how SEM chemical mapping can provide evidence of ASR.

X-ray fluorescence (XRF)

XRF can provide valuable information about the composition of concrete and uses X-rays to probe the inorganic constituents of the sample. XRF provides elemental analysis, namely raw percentage elemental composition. A key feature of XRF is that the results can be obtained rapidly and, when interpreted by a specialist, should be dependable and can be quantitative when required.

X-ray diffraction (XRD)

XRD is useful for identifying crystalline mineral phases, is an excellent complement to thin-section microscopy and will provide valuable additional constituent information.

‘Modern analytical techniques for the chemical investigation of concrete structures are many and varied.’

XRD is not very widely used for routine concrete analysis, because many of the most important constituents, including hydrated cement, are variously non-crystalline or poorly crystalline. The diffraction of X-rays by a sample is dependent on and provides information concerning the atomic structure of particles in a material. This can be particularly useful, for example, when characterising clay minerals according to the separation between layers and/or the ability of these layers to be expanded by the absorption of water.

Laser microprobe mass spectrometry (LMMS)

LMMS is a technique that uses a laser to ionise a very small volume of a sample. The resulting plasma contains atomic and molecular fragments that are analysed using a time-of-flight (ToF) mass spectrometer. This can produce a rapid analysis of the constituent elements at the surface of the sample. LMMS is a particularly useful tool as it can detect both organic and inorganic species. This can allow the study of, for example, stains on a concrete surface, with respect to the constituents of the staining. Figure 3 shows a typical mass spectrum obtained using this technique, which indicated the potential presence of organic, nitrogen-containing compounds on the surface, which may have been responsible for staining the concrete. The peaks can be assigned and compared with reference materials to pinpoint the cause of the surface defect in question.

Concluding remarks

Modern analytical techniques for the chemical investigation of concrete structures are many and varied. This article has briefly summarised a few of the more common approaches with regard to the type of investigation that might be undertaken using each. Some of the traditional techniques are still very powerful for assessing a concrete sample, subject to appropriate sampling and expert interpretation. Meanwhile, technological developments have led to a range of modern, instrumental analytical techniques that have added value and depth to concrete analysis.

Many of the techniques are easily accessed through a variety of sources. However, the resulting data require experienced processing and interpretation and this must be dealt with by a concrete technologist who is capable of drawing together chemical information and assessing it alongside petrographical and other information to reach reliable conclusions regarding the concrete. ■

References:

1. BRITISH STANDARDS INSTITUTION. BS 1881: 124. *Testing concrete. Methods for analysis of hardened concrete.* 1988.
2. BUILDING RESEARCH ESTABLISHMENT. *Special Digest 1: Third Edition. Concrete in aggressive ground.* 2005.
3. BRITISH STANDARDS INSTITUTION. BS 1377: 3. *Methods of test for soils for civil engineering purposes. Chemical and electro-chemical tests.* 1990.