

Quantitative determination of sulfur content in concrete with laser-induced breakdown spectroscopy[☆]

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Abstract

Laser-induced breakdown spectroscopy has been employed for the investigation of the sulfur content of concrete. Sulfur compounds are a natural but minor component in building materials. The ingress of sulfates or sulfuric acid constitutes a major risk of chemical aggression for concrete. There is a need for a fast method, which can be used on-site and is able to investigate a wide range of different measuring points, so that damages can be characterized.

For quantitative determination the sulfur spectral line at 921.3 nm is used. The optimum ambient atmosphere has been determined by comparison of measurements accomplished under air, argon and helium atmosphere.

Reference samples have been produced and calibration curves have been determined, the results of LIBS measurements are compared with results from chemical analysis. Defining a limit for the intensity ratio of a calcium and a oxygen spectral line can reduce the influence of the heterogeneity of the material, so that only spectra with a high amount of cementitious material are evaluated. Depth profiles and spatial resolved sulfur distributions are presented measured on concrete cores originating from a highly sulfate contaminated clarifier.

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1. Introduction

1.1. Testing problem

The determination of sulfate content in concrete is carried out for damage assessment before reconstruction and during repair for quality assurance of repair works. Chemical reactions between sulfates or sulfuric acid and the cementi-

tious material lead to destruction of the concrete structure and therefore to a decrease in strength.

So far the standard method of the determination of the sulfate content is chemical analysis, in Germany prescribed in the German norm DIN 4030, part 2 [1].

Concrete cores are taken from the structure and brought to the laboratory. They are cut into slices, grinded and dissolved in hydrochloric acid. The content of the acid soluble sulfates is determined gravimetric by precipitation as BaSO₄. This procedure is time consuming and expensive.

Therefore in most practical applications only few taken concrete cores are investigated and the results are assumed to be representative for the whole structure.

For depth profiles the cores are cut into depth slices with 10–20 mm thickness, i.e. the depth resolution. Smaller slices become difficult to cut depending on the size distribution of the aggregate.

Depth profiles give information about the external ingress of sulfates and the sulfate distribution.

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Investigations of damage mechanisms on a micro-scale are performed by scanning electron microscopy for detailed analysis of the distribution of damaging sulfates.

Therefore investigations are established on a very broad scale (chemical analysis on few cores, coarse depth resolution about 10 mm, extrapolation of few data on large areas) and on micro-scale, which are not suitable for practical applications but for scientific approaches.

A method providing detailed information on the millimeter-scale, i.e. millimeter-scale depth resolution, assess to more measuring points (lower cost, faster measuring, online results) with regard to quality assurance during reconstruction work is missing. The laser-induced breakdown spectroscopy (LIBS) has these features and spatially resolved evaluation allows even conclusions on ingress mechanisms, e.g. along the aggregate–cement interface.

1.2. LIBS in civil engineering

The advantages of LIBS compared with other techniques have been reported to be the use in harsh environments and onsite, no sample preparation and real-time measurements [2–6]. Applications of LIBS in civil engineering are the analysis of cement and concrete, the detection of hydrophobic coatings, the quantitative measurement of the lead content in mortar specimens or the measurement of the salt distribution in different building materials [7–11]. An important task is the determination of chloride contents, as chlorides may cause severe corrosion in reinforced concrete. The measurement of elements like chlorine and sulfur in building materials is a challenging task because of the limited number and relative weakness of the spectral lines of these elements. Due to the natural heterogeneity of building materials a statistical evaluation of the results needs to be carried out.

1.3. Concrete composition

Concrete is a chemically and micro-structurally highly complex composite material [12] consisting of aggregates, cement (as adhesive agent), water and chemical admixtures.

There are many categories of cement, characterized by different percent by weight of the oxides of the elements Ca, Mg, Si, Al and Fe. For each type of cement a certain range of allowed oxide contents is given, e.g. for Portland cement the CaO-content can vary between 61 and 69 wt.% and the SO₃-content has to be in the range of 2.0–3.5 wt.%. (In civil engineering the measured contents are stoichiometrically converted to the percent by weight of the respective oxide, in case of sulfur compounds the value is given as SO₃-content, although most will be sulfates). Composition of cements is regulated in Germany by the norm DIN EN 197 [13].

The concrete can contain different amounts of water, either as water of crystallization (fixed by the cement) or as pore water.

The aggregates are normally varying between fine sands with grain sizes from microliter-scale, up to stones with

some centimeter in diameter. Aggregates consist mostly of SiO₂, but other materials can also be abundant, mainly minerals containing iron or magnesium. As aggregates are natural materials there is always a fluctuation in composition, even for sand originating from the same source. The ratio of aggregate mass to cement mass varies for most concrete between 6:1 to 7:1. Especially the large amount of aggregates has a great impact on the measured spectra and leads to a great fluctuation of the intensity of spectral lines.

Summarizing the cement powder varies in composition, the cementitious material (comprising cement, water and chemical admixtures, e.g. gypsum) can contain different amounts of water, and the aggregates can consist of different minerals, varying in size and percent by weight. Samples taken from the same concrete have an uncertainty in composition, because the fraction of cement and aggregate varies. This is true not only for the evaporated volume in LIBS measurements but also for samples used for chemical analysis. Therefore the uncertainty of the measured result is dominated by the uncertainty in sampling due to the spatial variation of composition.

1.4. Sulfur compounds in concrete

Sulfur compounds are a natural, but minor component in cement. As example gypsum is added in order to decelerate the hardening of concrete (whereas excess gypsum leads to an acceleration). The allowed amounts of additional gypsum or rather the allowed range of the sulfur content in cement is regulated by national norms, e.g. in Germany DIN EN 197 [13]. The four hydrated calcium sulfate compounds of primary interest during sulfate attack in concrete are gypsum (CaSO₄·2H₂O), ettringite ([Ca₃Al(OH)₆·12H₂O]₂(SO₄)·2H₂O), monosulfate ([Ca₂Al(OH)₆]SO₃) and thaumasite ([Ca₃Si(OH)₆·12H₂O](SO₄)(CO₃)) [12].

Chemical reactions of sulfates or sulfuric acid with the cementitious material, e.g. the formation of expansive ettringite, cause structural changes, which could lead to a loss of tensile and compressive strength.

The origin of sulfate may be external from environmental actions like the presence of certain soils, sewage waters, biological decomposition of organic materials, industrial waste (mining or metallurgical industry, combustion processes), atmospheric pollution, or internal from the cement, gypseous aggregates, supplementary materials (e.g. fly ash, slag) or water. Skalny et al. [12] give an overview on the sulfate attack on concrete.

2. Experimental

2.1. Samples

Four series of reference samples are used for calibration, starting with rather homogeneous powder pressings going to more heterogeneous, but realistic samples.

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