SCCT Annual Concrete Seminar 2017

Durable Concrete and Innovations

26 April 2017

Measurement of Concrete Durability Using Laser-induced Breakdown Spectroscopy

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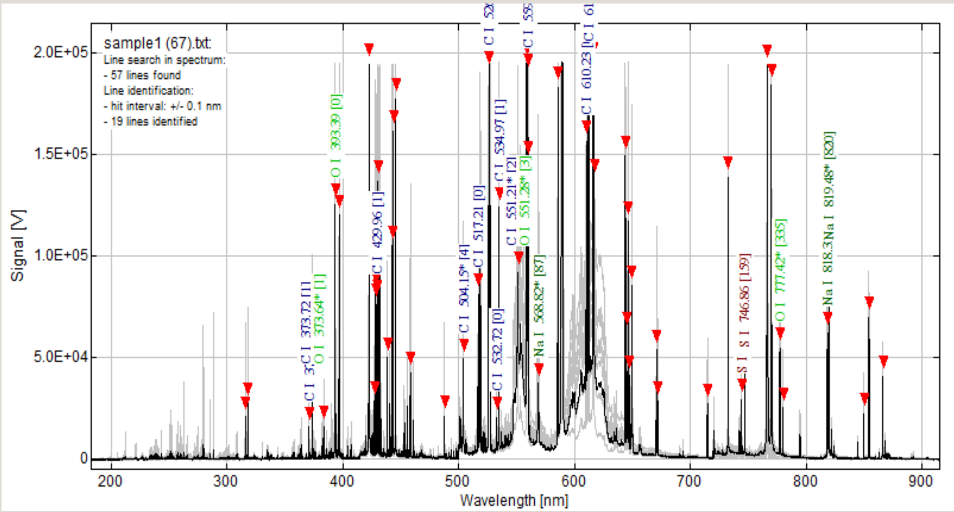
Content

- Background of LIBS System
- Mechanism of LIBS Measurement
- Applicability to concrete materials
- Experimental work on Chloride/Sulfate penetration using LIBS
    - Measurement of chloride penetration in concrete
    - Measurement of Sulfate penetration in concrete
- Calibration of spectral measurement
- Measurement Issues
- Conclusions

Background of LIBS system

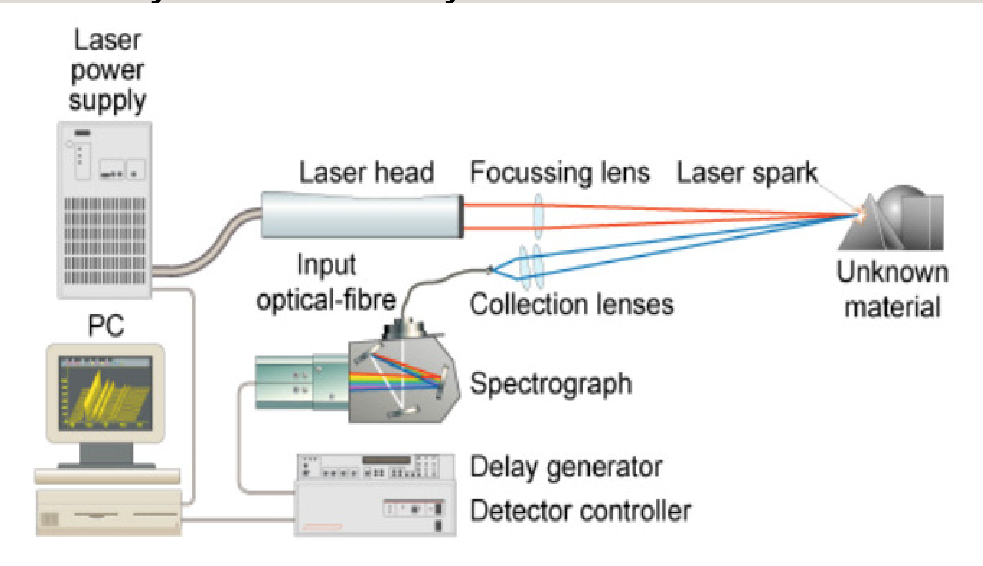
Laser-Induced Breakdown Spectroscopy (LIBS) is an analytical technique that allows elemental compositions of a sample (solid, liquid or gas) to be obtained in a few seconds, without any or with only minimal sample preparation. A LIBS spectrum is obtained within seconds, after delivering several laser shots (typically 1-50) to the sample and collecting light emitted from the resulting sample plasma.

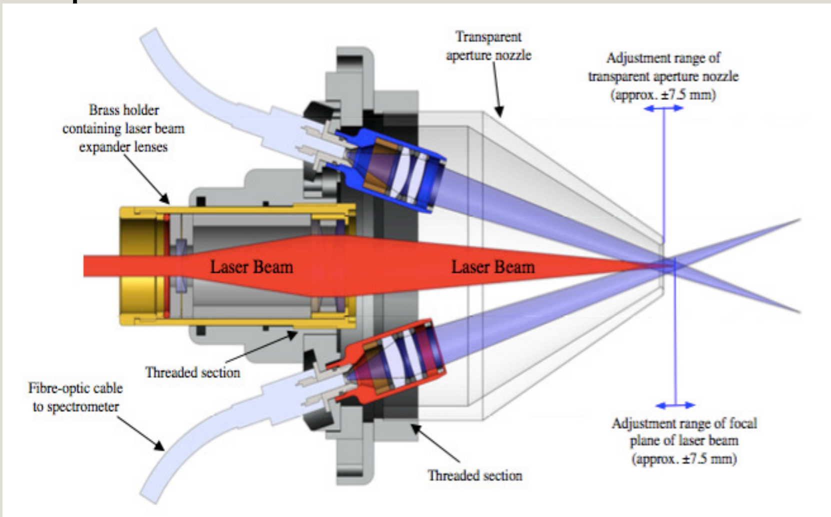
The spectrum acquired contains all the analytical information required for the identification of the analyzed material. A relatively inexperienced users will be able to recognize significant peaks in the spectrum by a peak identification database software.



Background of LIBS system

When conducting a LIBS experiment, the high power laser pulse with a typical pulse duration of a few nanoseconds is focused on surface of the testing sample to be analyzed. The level of power densities can be very high at the surface of material by the effect of pulsed laser, leads to local ionization and generates a plasma radiation. The radiation is guided to a spectrometer and further analyses to identify the elements inside the sample





Laser Beam Focus and Plasma Light Collection Optics

Background of LIBS system

- Sample for LIBS measurement can be placed in the modular chamber in laboratory or directly applied to materials surface on site. Portable instrument operate at a nominal voltage of 12 VDC at a maximum current of approximately 3.0 Amp.

Laboratory use

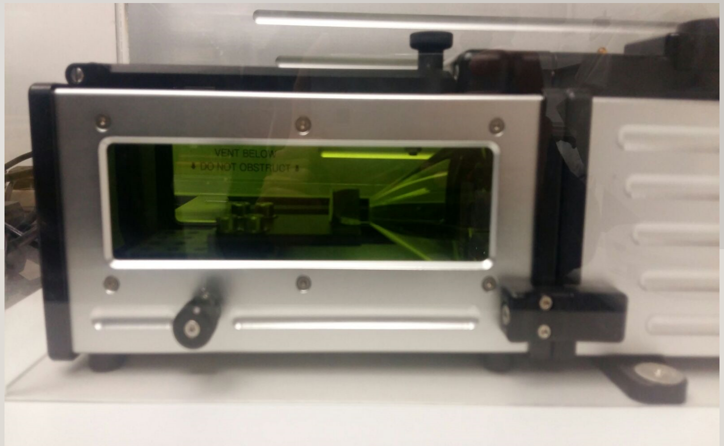
Portable type

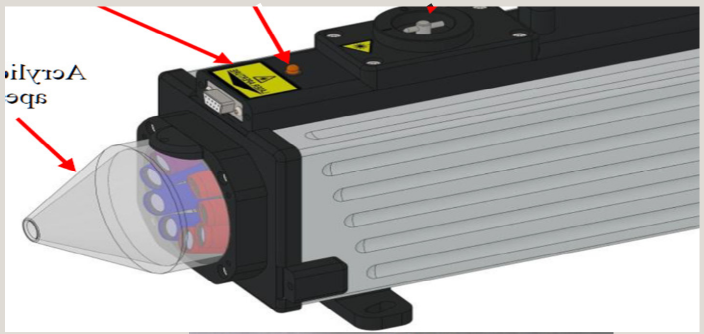
Background of LIBS system

- Laser safety requirements: European standards (BS EN 60825) and USA standards (ANSI Z136.1 – 2007).

- Sample chamber used in laboratory provides adequate containment of the laser radiation to Class 1 Accessible Emission Limits. Laser pulse energies are not excessively high (less than 250mJ @ 1064 nm with a 5-10 ns pulse length)

- User can operate LIBS without the sample chamber (i.e. operation in "open beam" mode for site testing). Becomes Class 4 laser products, wear laser light preventive goggle when use).





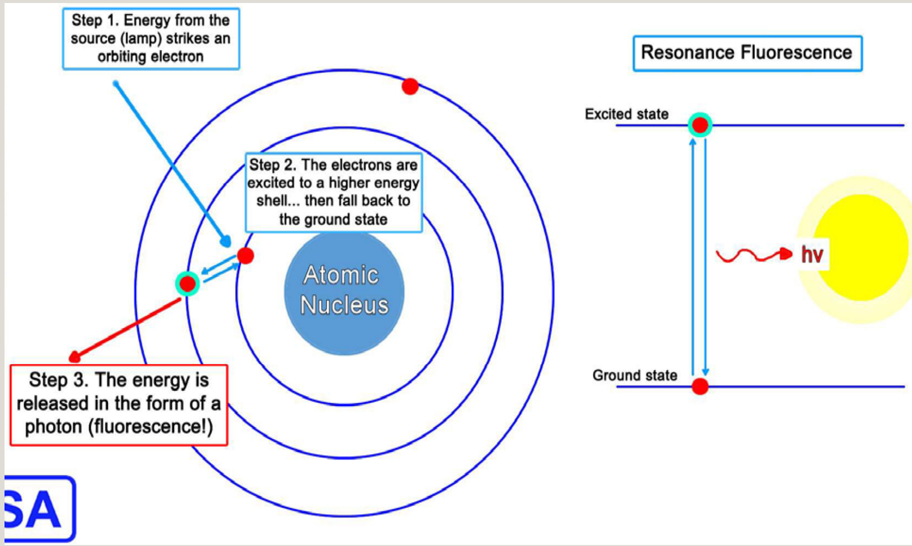
Mechanism of LIBS Measurement

Atomic Fluorescence Spectroscopy

Atomic Fluorescence Spectroscopy (AFS) is a three stages process of excitation and emission

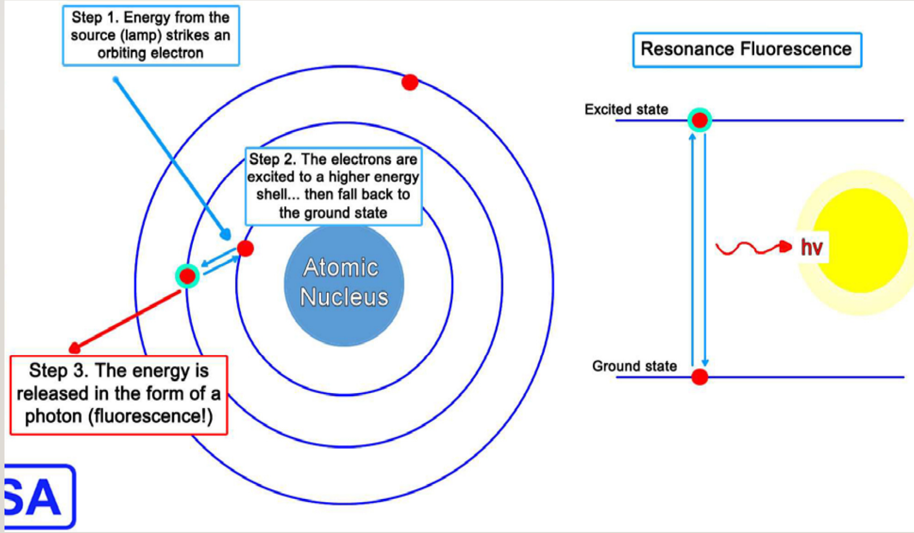
Stage 1: A high intensity monochromatic source (lamp or laser) provides the excitation energy which is focused onto the analyte atoms.

Stage 2: The electrons surrounding the atom absorb the energy (from the laser beam) and are excited to a higher energy level.



Mechanism of LIBS Measurement
Atomic Fluorescence Spectroscopy

Stage 3: In many cases, this excitation is short lived. Electrons which move into higher energy levels is in an unstable state and the electron soon drops back to it's original ground state. In doing so, the election will release the excess energy in the form of emitted light.



Because the energy levels in a particular atom are discrete and precisely defined, the energy is released as photons with characteristic wavelengths, allowing identification of the specific substance under examination. Therefore, atomic fluorescence spectroscopy is ideal for measuring the concentration of an element in a particular sample.

Applicability to Concrete Materials

The major minerals present in the cement are 50–70% tricalcium silicate ($3CaO \cdot SiO_2$), 15–30% dicalcium silicate ($2CaO \cdot SiO_2$), 5–10% tricalcium aluminate ($3CaO \cdot Al_2O_3$), 5–15% tetra-calcium aluminoferrite ($4CaO \cdot Al_2O_3Fe_2O_3$) and 3–8% of other additives like oxides of calcium and magnesium [48].

As far as the LIBS experiment is concerned, the main elemental compositions for concrete sample are **calcium, silicon, aluminum and iron**.

Materials Characterization

Chloride content

Sulfate content

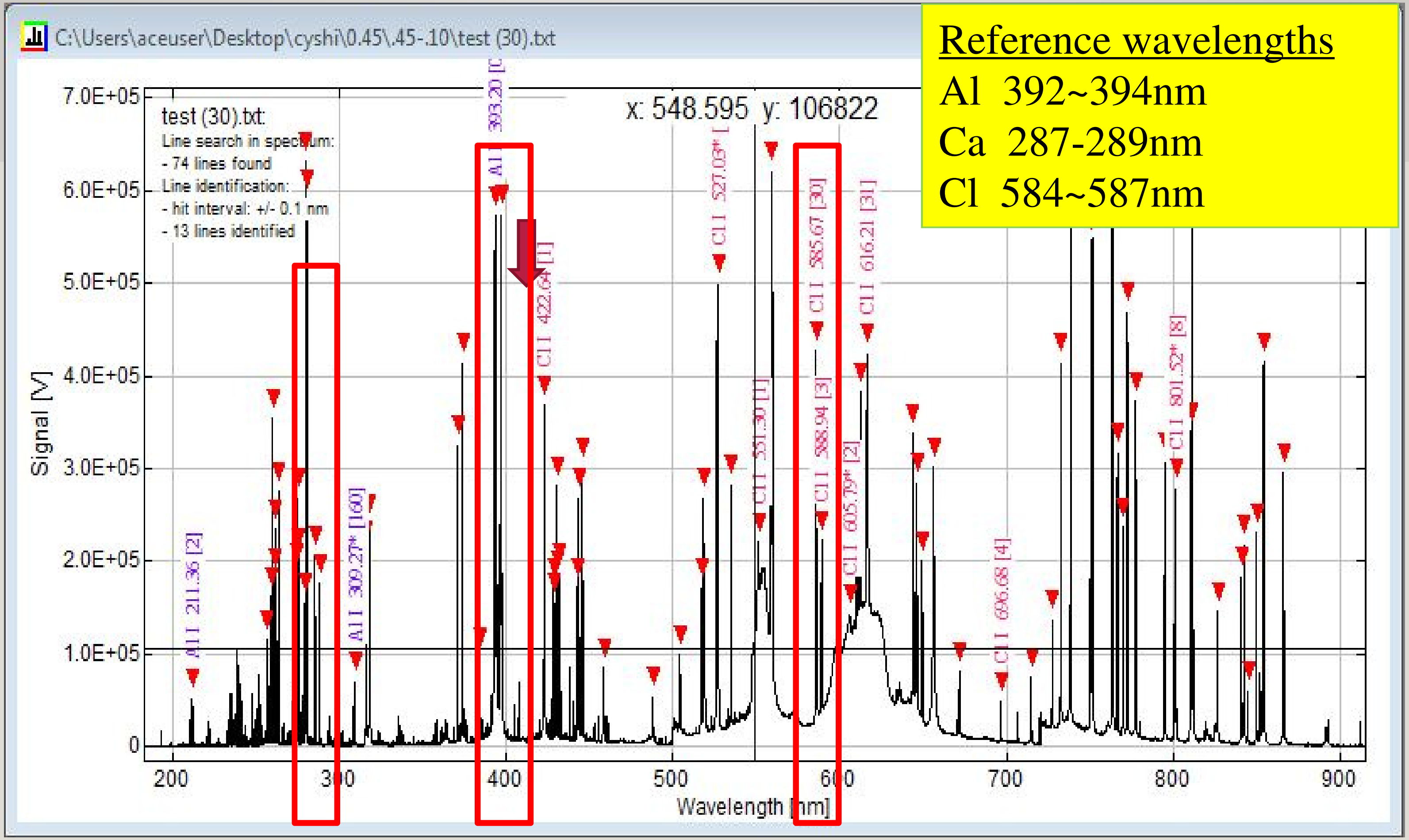
Carbonation

Identification of Contaminations

Classification of construction wastes

Applicability to Concrete Materials

Typical Spectra



Reference wavelengths

Al 392~394nm

Ca 287-289nm

Cl 584~587nm

Typical spectrum obtained from one testing point (3-day, w/c =0.45, Cl%=0.1%)

Objectives of Study

- Measurement of chloride penetration in concrete using LIBS
- Measurement of Sulfate penetration in concrete using LIBS
- Calibration of LIBS - To develop the calibration curves of chloride spectral line of LIBS of cement mortar samples by known chlorine content
- Measurement Issues

Measurement of chloride penetration in concrete using LIBS

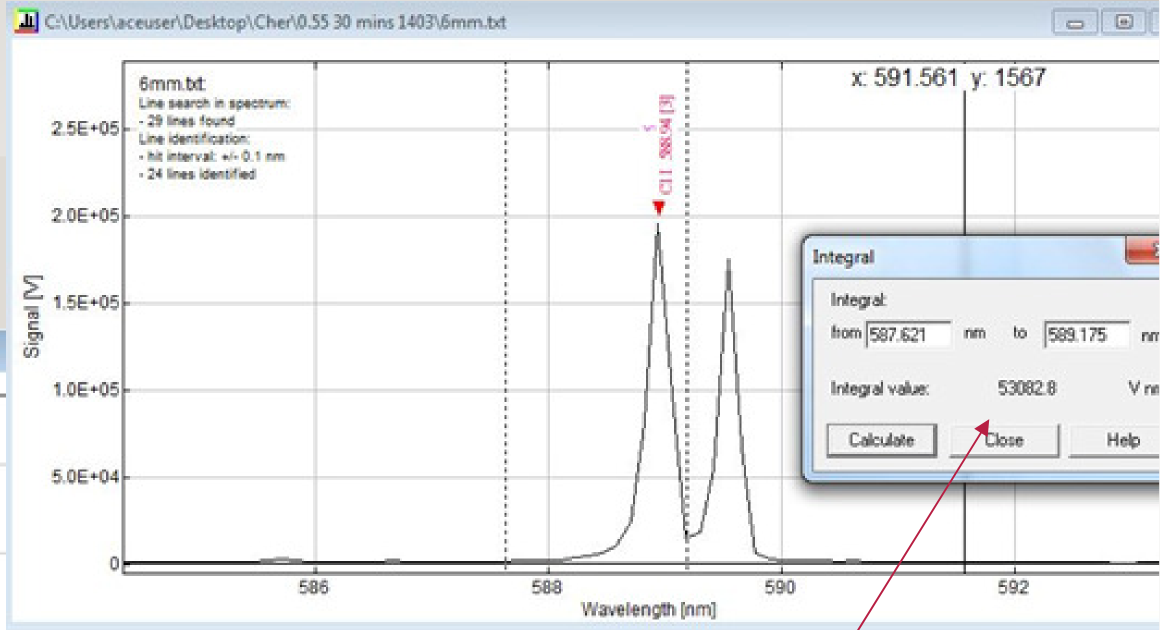
Sample Preparation

- Cylindrical concrete samples
- Allow chloride absorption for seven days
- Oven dry one day before test

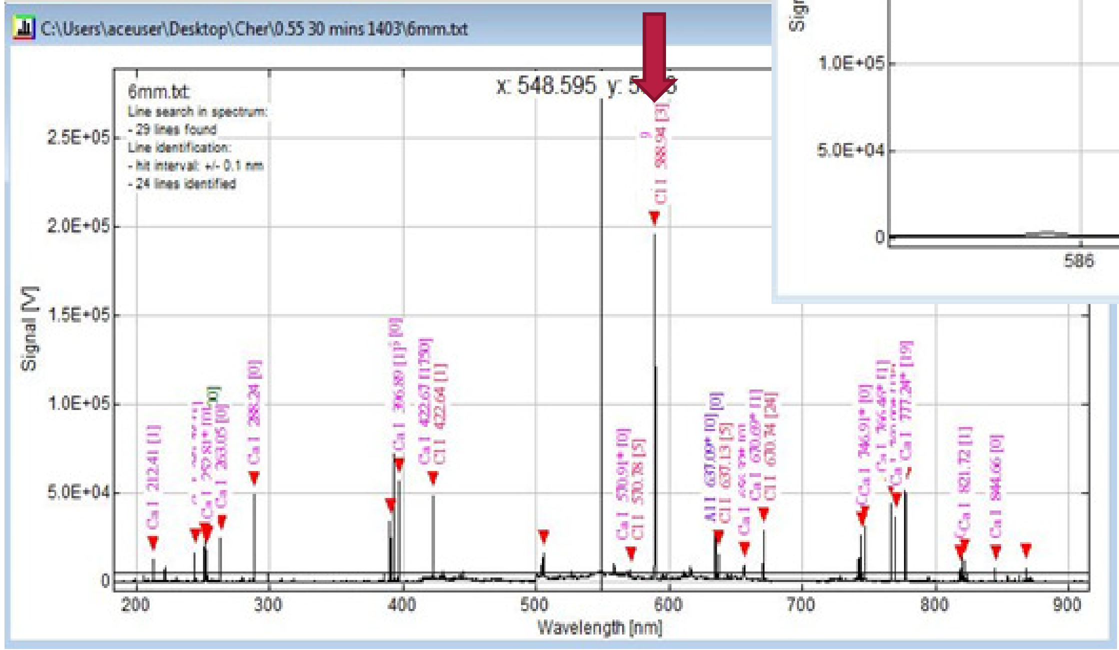
Measurement of chloride penetration in concrete using LIBS

Reference wavelengths

Cl 584~587nm



Peak of Cl



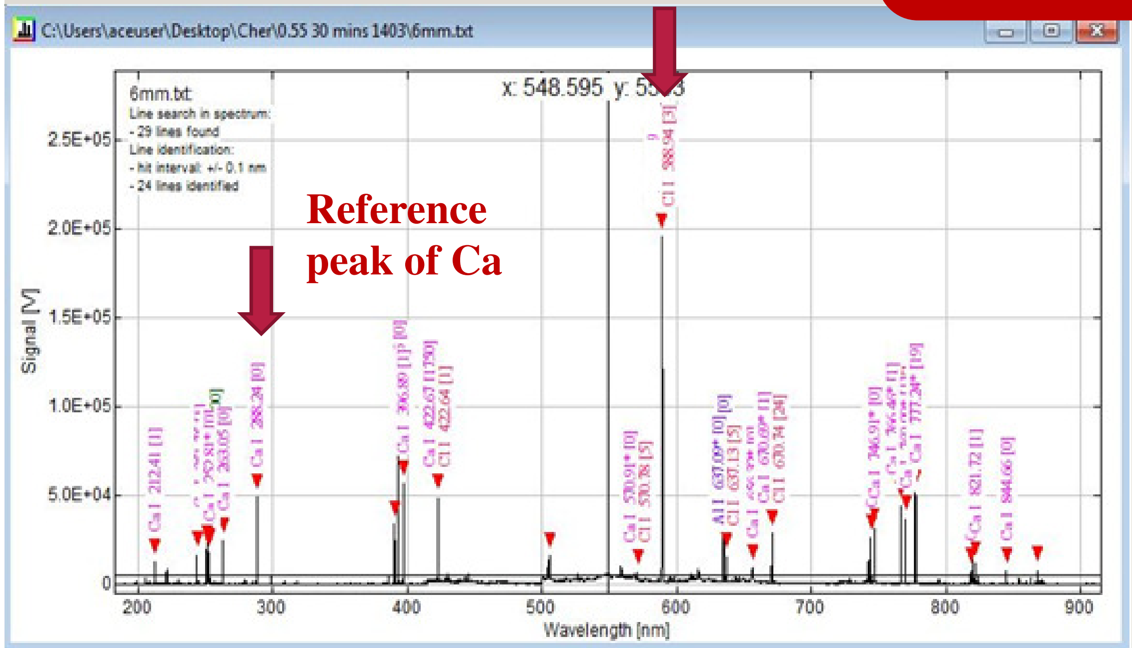
Integral Value $_{Cl}$ = 53082

Measurement of chloride penetration in concrete using LIBS

<u>Reference wavelengths</u>
Ca 287~289nm
Cl 584~587nm

Self-calibration (Qualitative Measurement)
Normalized integral value of chloride to integral value of a reference element

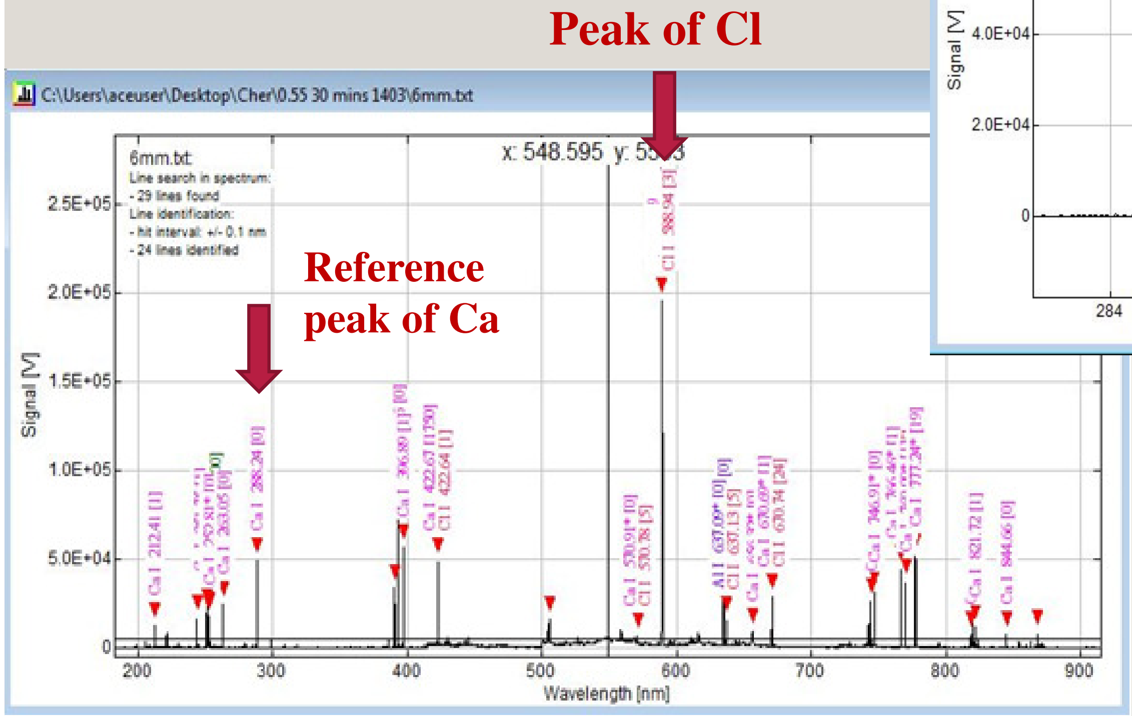
Peak of Cl

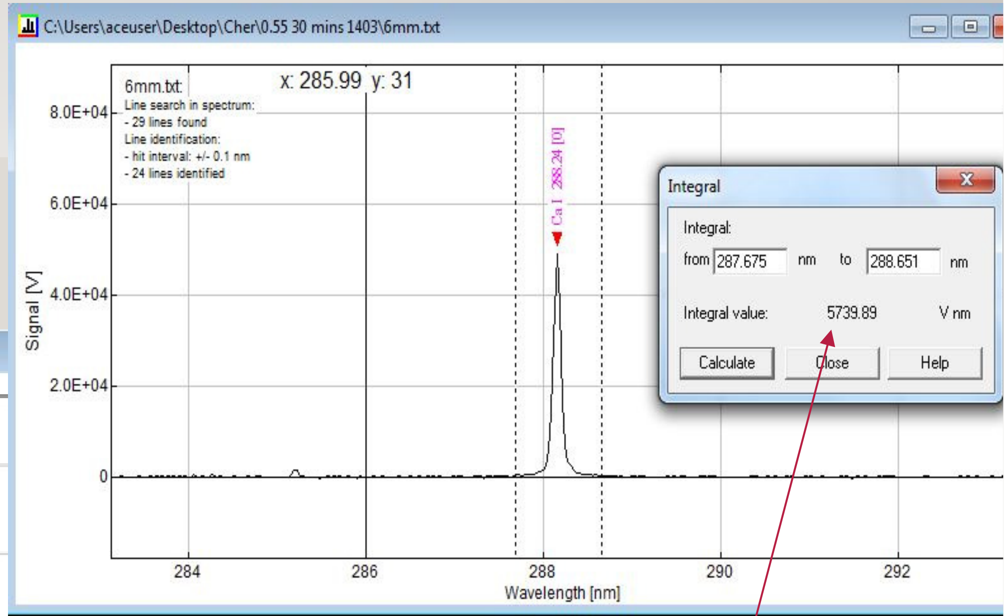


Normalized Integral Value (Cl/Ca; Cl/Al or Cl/Fe)
Arbitrary Unit (a.u.)

Measurement of chloride penetration in concrete using LIBS

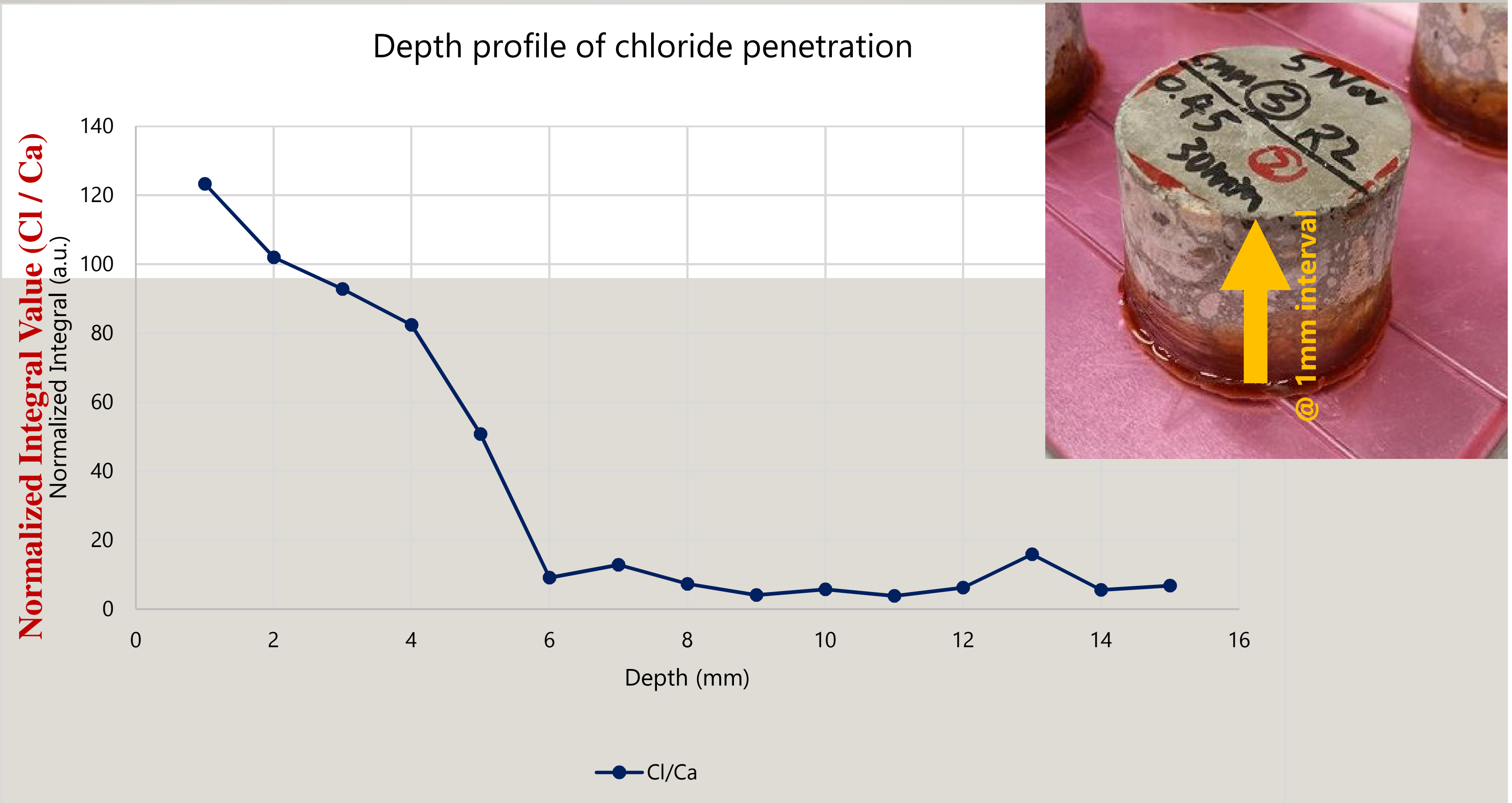
<u>Reference wavelengths</u>
Ca 287~289nm
Cl 584~587nm





Integral Value $_{Ca}$ = 5739

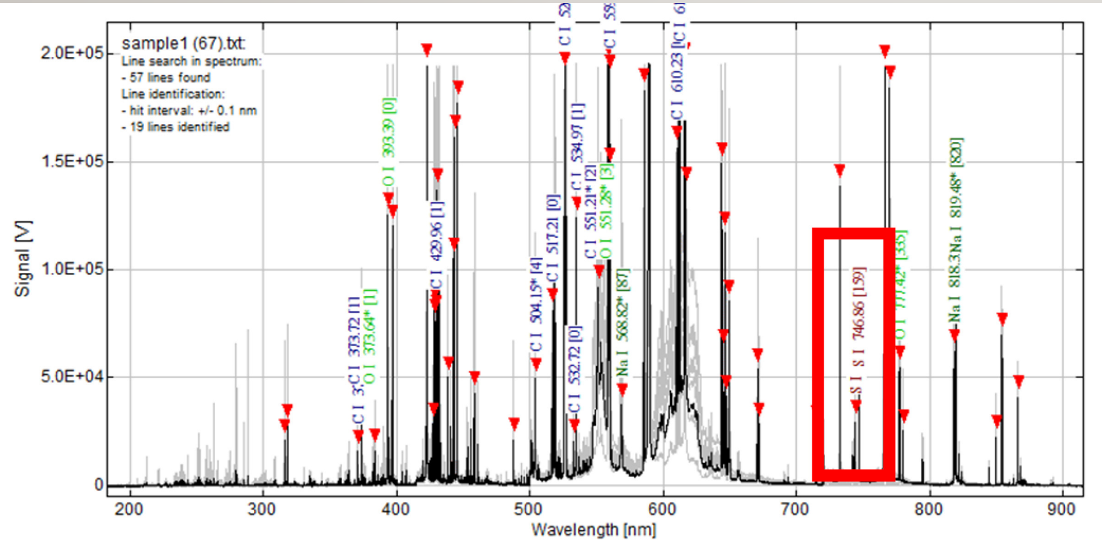
Chloride penetration profile in concrete

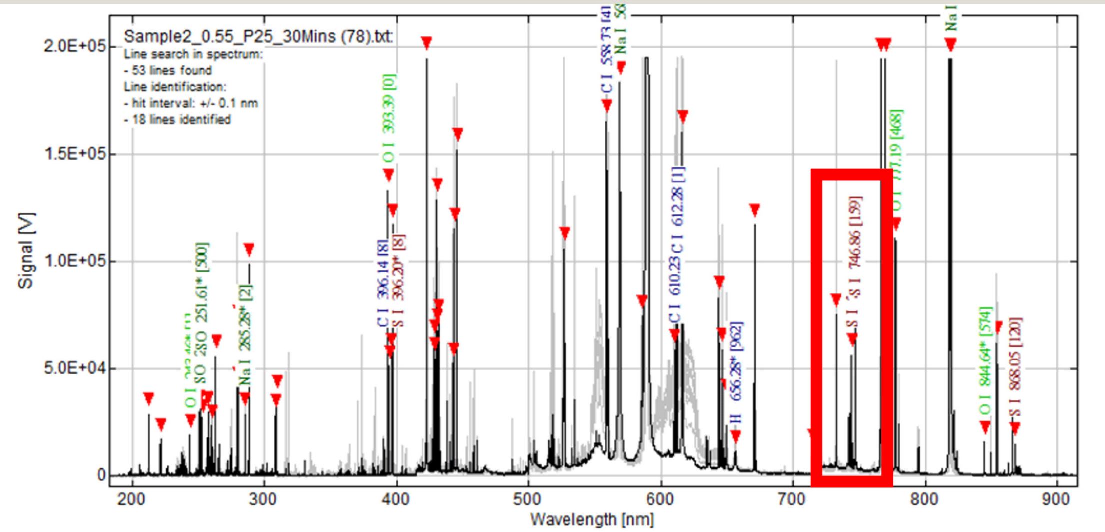


The chloride (content) profile drops with the penetration depth as expected

Normalized integral value of Chloride expressed as arbitrary unit of Cl/Ca
Wavelength peak: Chloride 587-589nm; Calcium 287-289nm

Measurement of Sulfate penetration in concrete

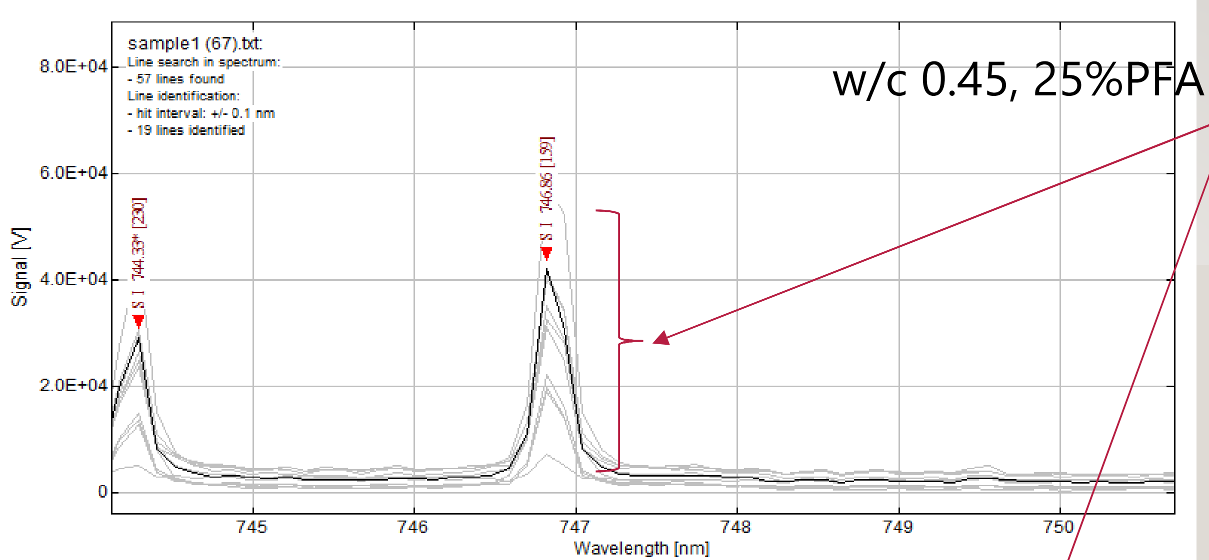


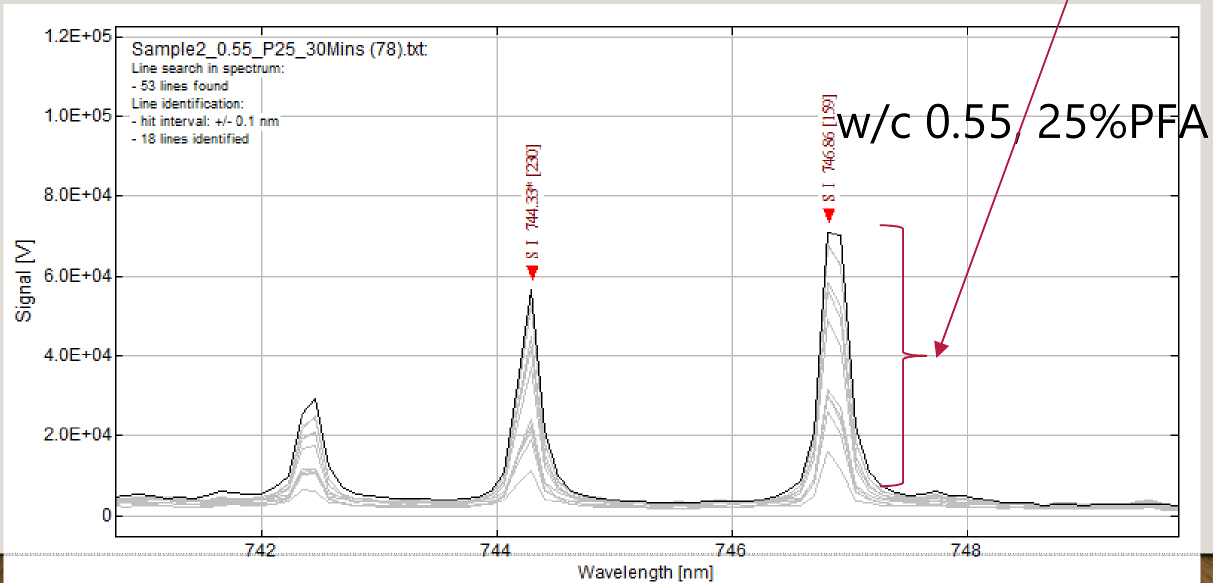


Compared 25% PFA added concrete w/c 0.45 and 0.55, mixed with Na_2SO_4 solution

The presence of sulfate indicated at wavelength 747nm

Measurement of Sulfate penetration in concrete



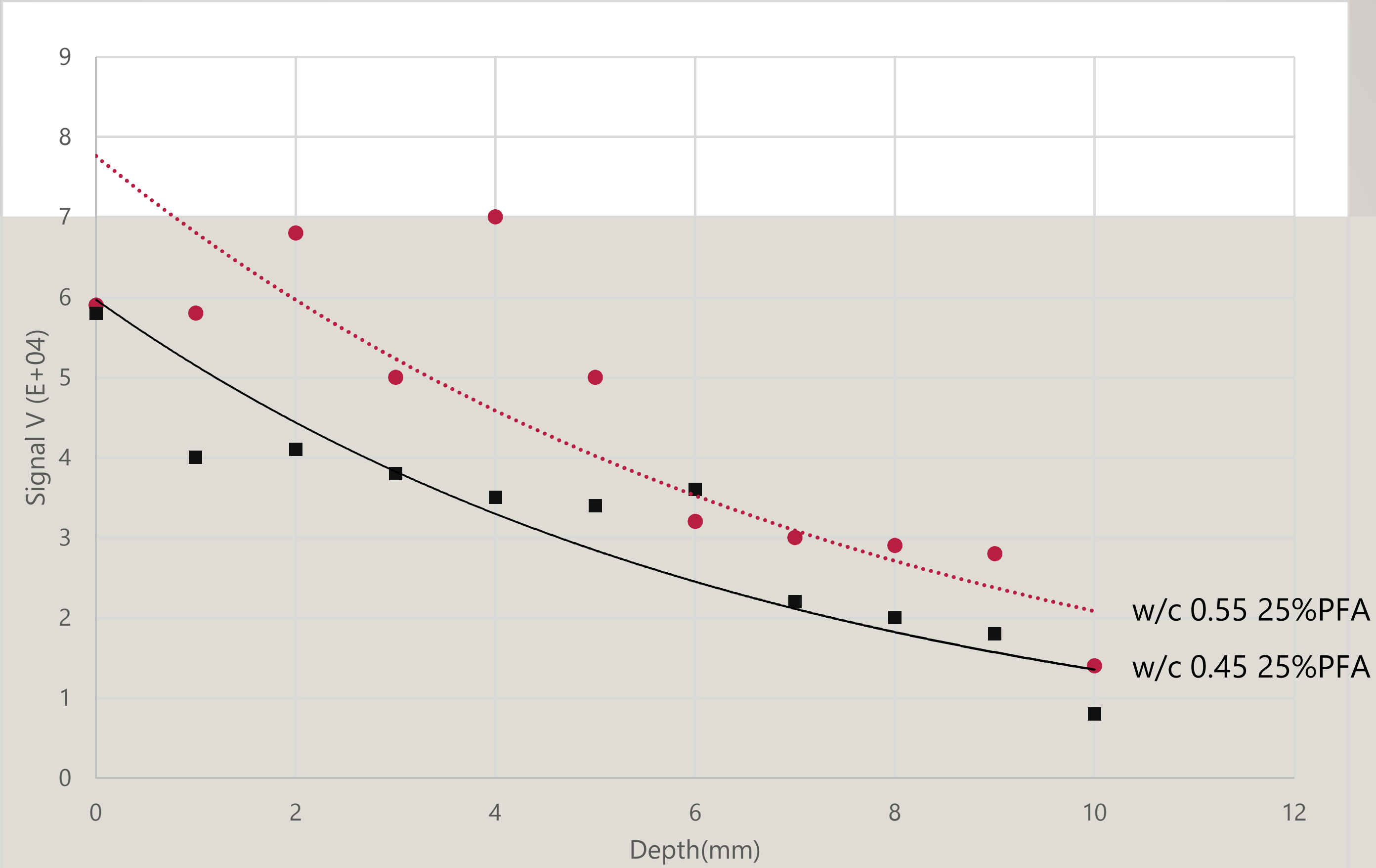


Figures show <u>overlay of 10 spectral lines</u> from one sample, taken at 1mm interval from surfaces of concrete to inner core.

Result indicated that spectral line of sulfate decrease gradually with the depth.

Wavelength of Sulfate = 747

Sulfate Penetration Profile (0.45 and 0.55)



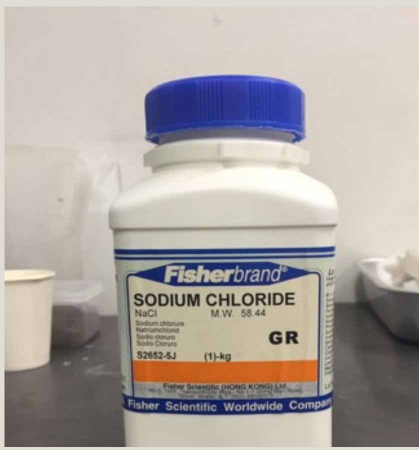
It can be observed that the concrete with a lower water cement ratio will have better resistant to sulfate penetration.

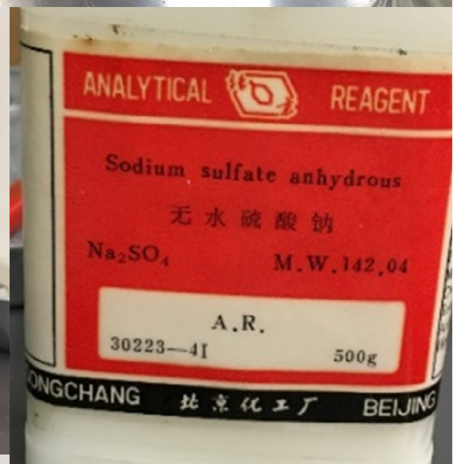
Calibration of spectral measurement

Quantitative Measurement

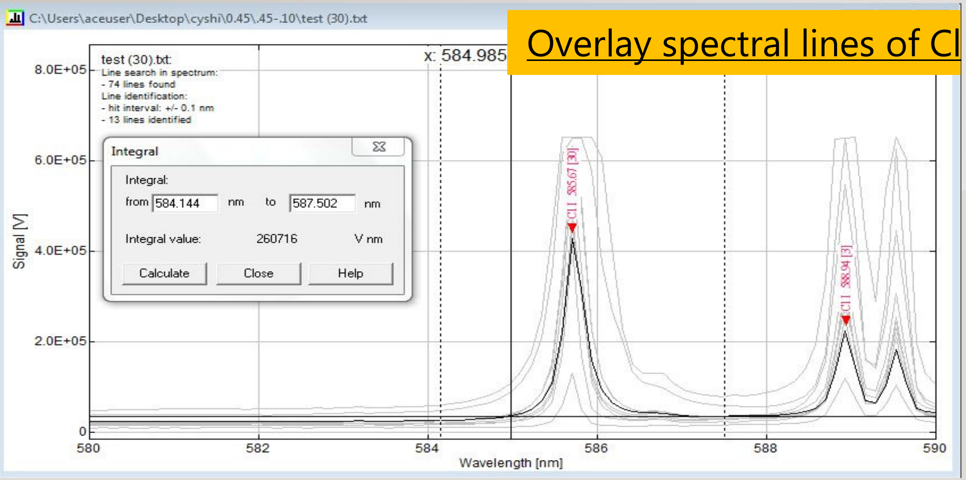
Calibrate normalized element spectral line using samples of known chloride/sulfate content

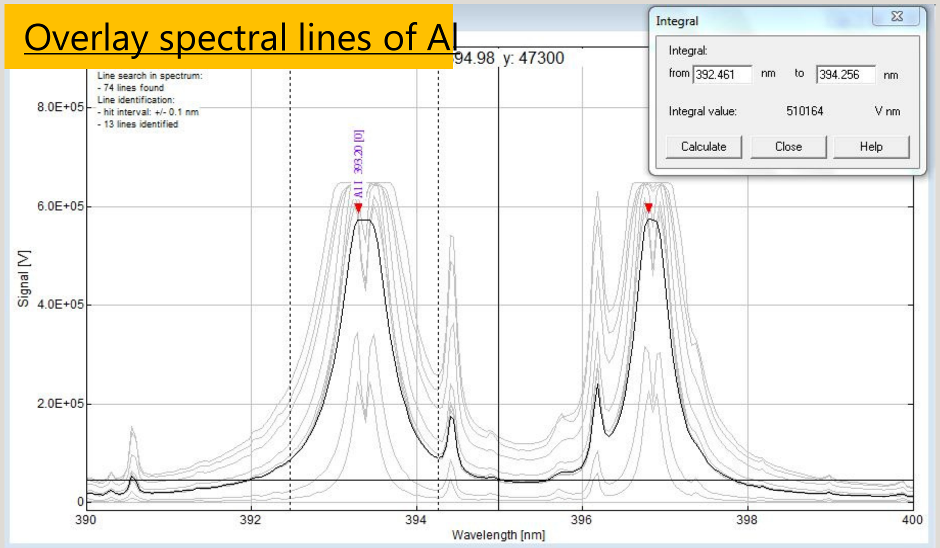
- Use cement/standard sand mortar cube (25x25x25mm size) (w/c at 0.45 and 0.55)
- Mix NaCl solution, Na_2SO_4 solution in concrete mix with percentage of chloride ranges from 0.05% to 0.5%
- Keep samples in drying chamber for 1 day before test
- Measure the Chloride, Sulfate spectral line at age 3D, 7D, 14D and 28Days
- Self-calibration to Al

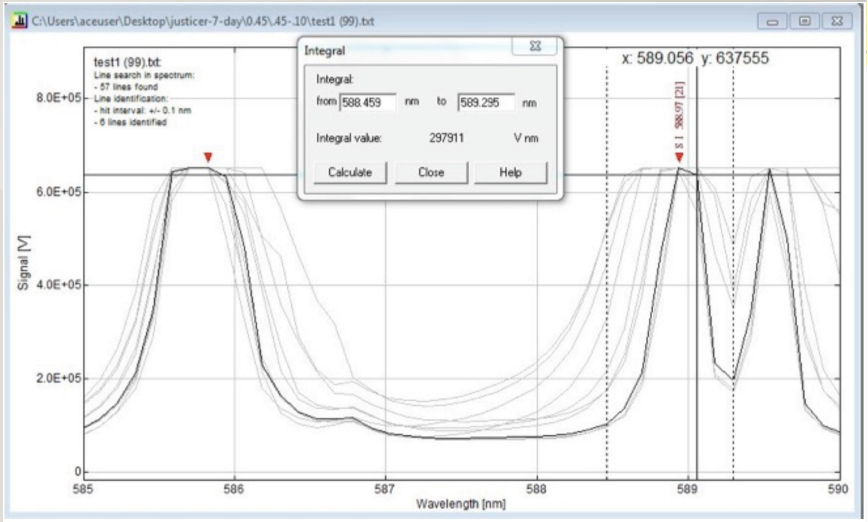




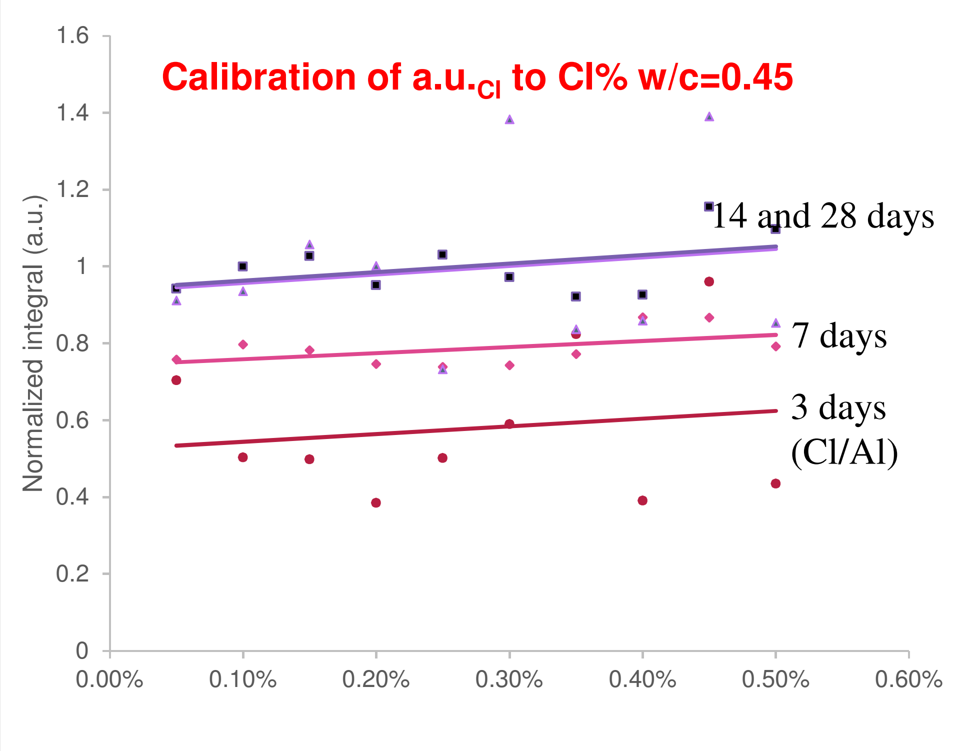
Self-calibration to Al

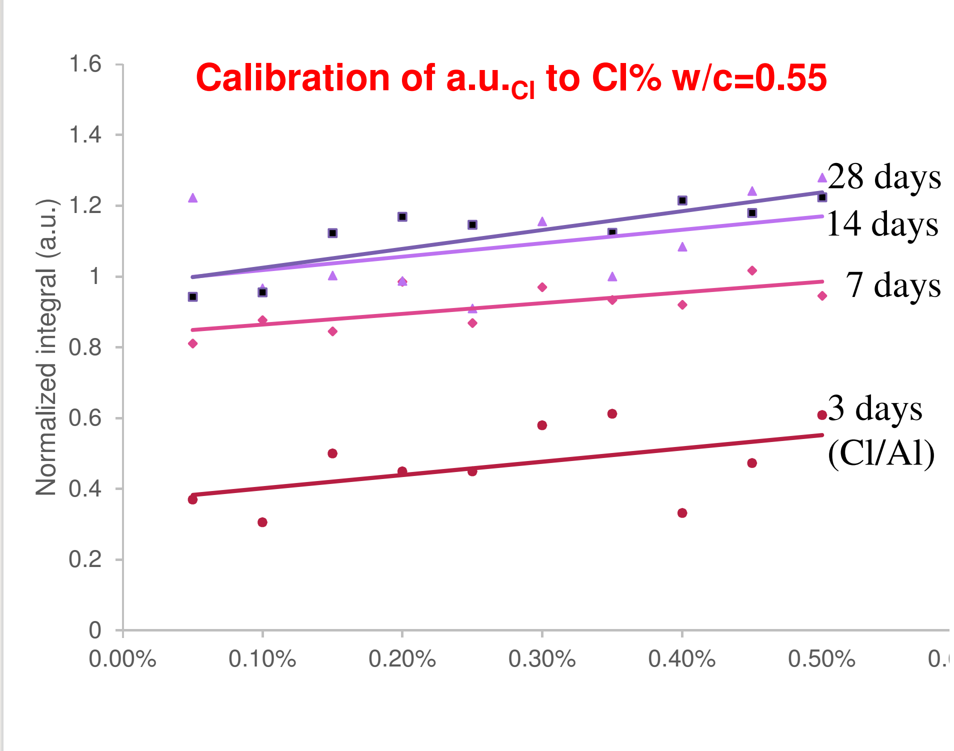






Calibration of Cl Normalized Integral

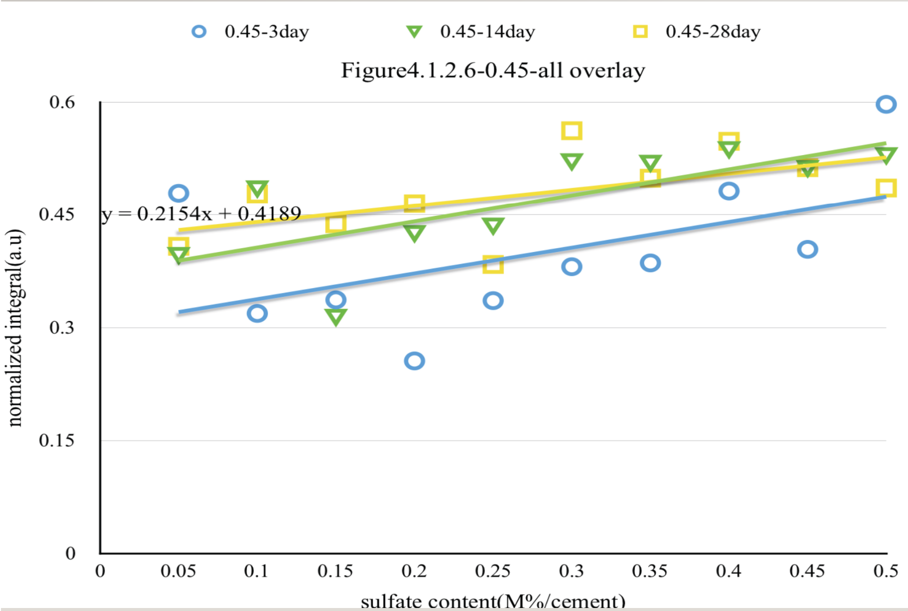


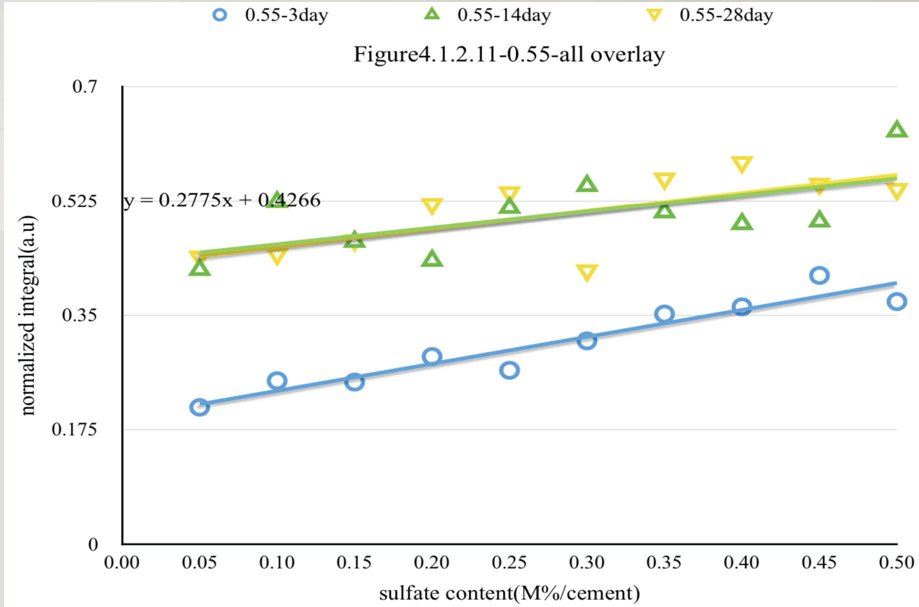


1. Lines are parallel to each other (for all ages)
2. Normalized value goes up with concentration of Chloride content
3. Lines 14 days overlapped with 28 days. i.e. values become stable

Arbitrary Unit (a.u.) Cl/Al

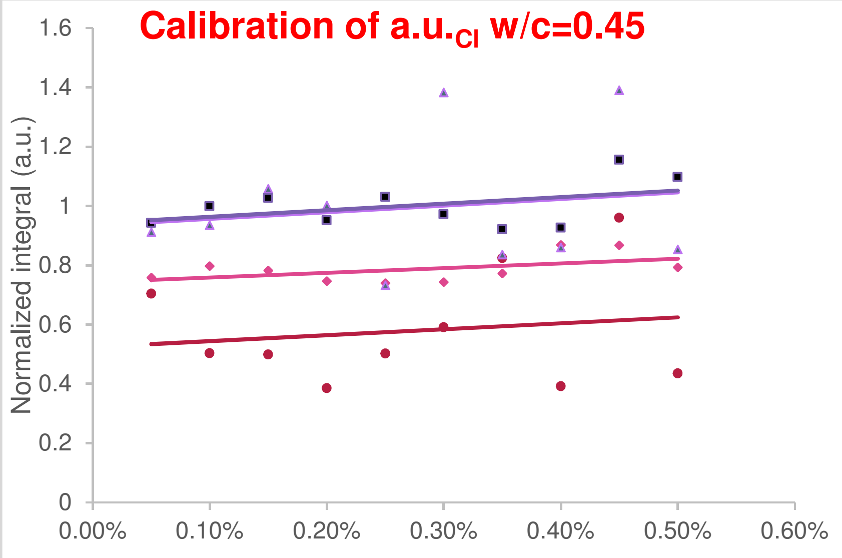
Calibration of Sulfate Normalized Integral

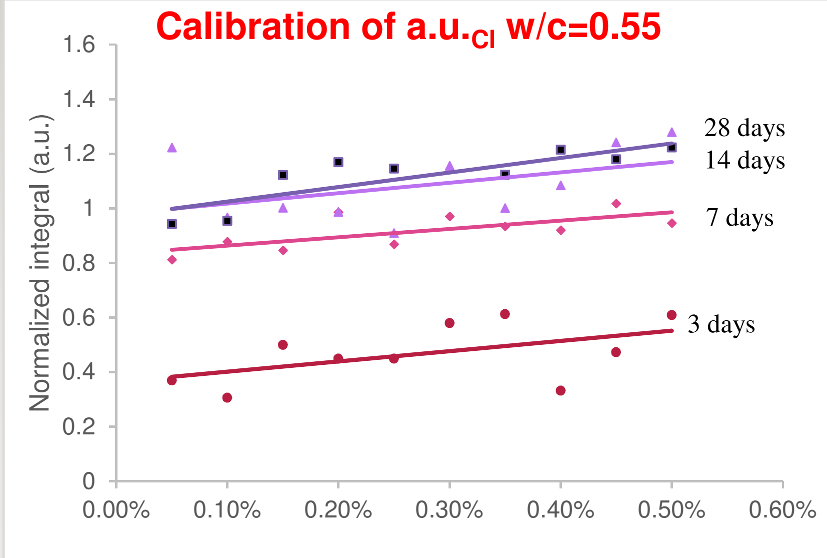




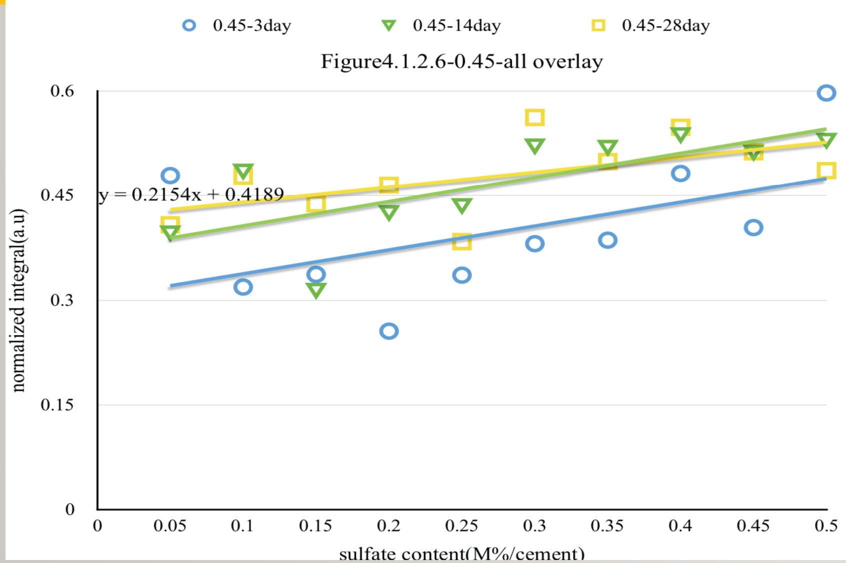
1. Lines are parallel to each other (for all ages)
2. Normalized value goes up with concentration of Sulfate content
3. Lines 14 days overlapped with 28 days. i.e. values become stable

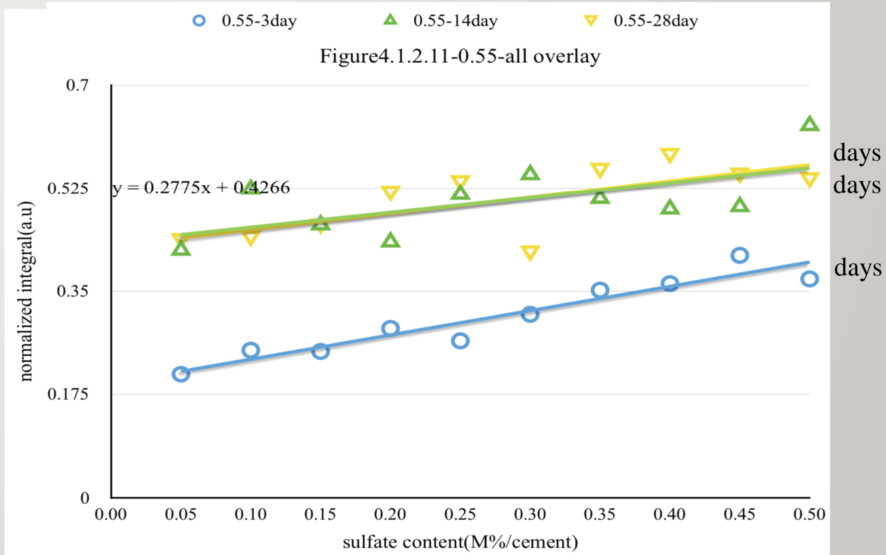
Arbitrary Unit (a.u.) Cl/Al





a.u. of spectral lines become stable after 14 days





Measurement Issues

- **cleaning / conditioning shots** (depends on surface condition)
  - Conditioning laser shots is necessary to clean the contamination surface. Fingerprints spectra of dust and other impurities that existed on the surface of sample will exhibit as experimental result.
  - Number of pre-conditioning shots depends on surface condition, aims of study.

- **Measurement shots**
  (average of a number of shots)

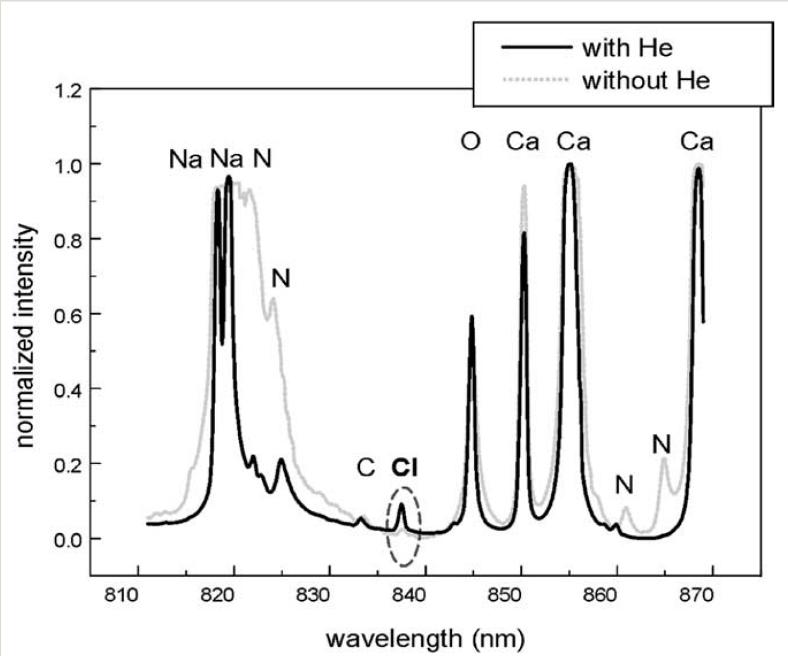
- **Threshold limit of element concentration**
  - Wilsch (2005) suggested there is a threshold limit of 0.15 wt% for detection of chloride content in concrete samples by laser-induced breakdown spectroscopy. In this study, 0.05% Cl still can be measured.

G. Wilsch (2005). Determination of chloride content in concrete structures with laser-induced breakdown spectroscopy. Construction and Building Materials, 724-730

Measurement Issues

purge gas: air or argon gas

- Additional emission lines of O (777nm), N (744nm) and H (656nm) could be detected in the spectrum when the generated plasma interaction with the surrounding atmosphere. Use of Inert gas can elimination measurement noise, increase the sensitivity of element



Comparison of measurements on cement mortar samples accomplished under air and helium atmosphere (Wilsch 2005)

G. Wilsch (2005). Determination of chloride content in concrete structures with laser-induced breakdown spectroscopy. Construction and Building Materials, 724-730

Conclusions

- LIBS is an effective tool allowing for materials characterization and identification, both qualitative and quantitative.
- Profiles of Chloride penetration and Sulphate penetration in concrete can be measured by LIBS.
- Element content in cement samples can be calibrated by reference materials of know element content (such as chloride/sulfate).

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Thank You !

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